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Smail Hamamda · Abdelmalek Zahaf · Yurii Sementsov · Serhii Nedilko · Kateryna Ivanenko *Editors* 

Proceedings of the 2nd International Conference of Nanotechnology for Environmental Protection and Clean Energy Production

ICNEP 2023, 9–10 October, Constantine, Algeria



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# Proceedings of the 2nd International Conference of Nanotechnology for Environmental Protection and Clean Energy Production

ICNEP 2023, 9–10 October, Constantine, Algeria



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## Organization

#### Conference

The International Conference of Nanotechnology for Environmental Protection and Clean Energy Production (ICNEP) provides a forum for specialists and practitioners to present and discuss their research results in the several areas of the conference and also state-of-the-art findings in using the applied nanotechnology and renewable energy to solve national problems that face developing countries. The conference ICNEP publishes papers on experimental studies and applications in the domain of nanoparticles and materials characterization. The objective of the conference is not only the exchange of knowledge and experience, since the conference is an open door to students, but also provides opportunities for researchers to target future collaboration on current issues.

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### Preface

This proceeding book about the Nanotechnology for Environmental Protection and Clean Energy Production conference covers a broad spectrum of topics, the conference focused on nanocomposites and nanomaterials applications, physic-chemical nanomaterials science, nanoscale physics, solids and structures, renewable energy, nanoparticles, metallic and polymer materials, as well as eco-friendly materials and nanocomposites. These diverse topics represent the multidimensional nature of nanotechnology and its profound impact on environmental protection and clean energy production. The main aim of the conference is to create periodical possibility for students, academics, and researchers to exchange their ideas, experimental results, and novel techniques. We try to explore the frontiers of nanotechnology, where cutting-edge research converges with environmental protection and clean energy production. This proceedings book is a testament to the exceptional work showcased at the conference, embodying the spirit of innovation and collaboration that defines our community.

With the support of organizing universities, we ensured that only the most compelling and innovative research was included in this collection. We believe that this conference represents a good standard conference in the domain of Nanotechnology for Environmental Protection and Clean Energy Production. Our sincerest thanks goes to the program committees and reviewers for their meticulous efforts in maintaining the conference's excellence. The contributions of the authors, alongside the dedication of the local organizing committee, have significantly enriched the content and success of the conference. This event is supported by the Constantine 1—Frères Mentouri University, Constantine, Algeria, and mainly financed by Laboratory of Thermodynamic and Treatment of Materials Surface and Directorate General for Scientific Research and Technological Development (DGRSDT).

Constantine, Algeria Constantine, Algeria Kyiv, Ukraine Kyiv, Ukraine Kyiv, Ukraine Smail Hamamda Abdelmalek Zahaf Yurii Sementsov Serhii Nedilko Kateryna Ivanenko

## Contents

Nanocomposites and Nanomaterials Applications	
Multiwall Carbon Nanotubes Effects on the Coefficient of ThermalExpansion of High Density PolyethyleneH. Filali, M. Bouleklab, S. Saadallah, T. Dorbani, N. Barama,and S. Hamamda	3
The Influence of Milling Time and Multiwall CarbonNanotubes Concentrations on the Thermal-Structural Behaviorof Iron–Copper NanocompositesMohamed Cherif Bouleklab, Sorror Saadallah, Hichem Filali,Tahar Dorbani, Serhii Nedilko, and Smail Hamamda	15
The Carbon Nanotubes, Graphene Nanoparticles Their Oxygen Modified Forms and Composites Yuli Shi, Yuliia Hrebelna, Eugeniy Demianenko, Stanislav Makhno, Kateryna Ivanenko, Smail Hamamda, Mariya Terets, Mykola Kartel, and Yurii Sementsov	29
Estimation of Percolation Threshold and Its Influence on the Properties of Epoxy Resin-Based Polymer Composite Materials Filled Carbon Fibers and Carbon Nanotubes Stanislav Makhno, Oksana Lisova, Petro Gorbyk, Yuli Shi, Kateryna Ivanenko, and Yurii Sementsov	39
<b>Preparation, Structure and Luminescence Properties</b> of "Microcrystalline Cellulose—K <sub>3</sub> Tb(PO <sub>4</sub> ) <sub>2</sub> " Composites Vitalii Chornii, Serhii G. Nedilko, Kateryna Terebilenko, Valeria Zozulia, Volodymyr Boyko, Yaroslav Zhydachevskyy, and Andrzej Suchocki	49

Formulation and Optimization of Sustained Release Microparticles	59
Fatima Zohra Badaoui, Souha Meziani, Lina Benmegoura, and Souha Djoumana Hedna	57
Effect of Fe <sub>3</sub> O <sub>4</sub> Nanoparticle on Electronic Cooling: Numerical Investigation of Nanofluid Flow Through a Heat Sink Touba Bouacida and Rachid Bessaih	67
Enhancing Photoluminescence and Crystallinity ThroughAluminum Doping in Sol–Gel Zinc Oxide Thin FilmsIbrahim Yaacoub Bouderbala and Imed-Eddine Bouras	75
Structural Characterization of Chorine Doped Cuprous Oxide Thin Films by X-Ray Diffraction and X-Ray Fluorescence Imed-Eddine Bouras and Ibrahim Yaacoub Bouderbala	85
Experimental Study on the Effect of Drying on the Kinetics of Cubic Beetroot Slices Using an Industrial Electric Food	
<b>Dehydrator</b>	95
Effect of Dip-Coating Seed Layer on the Morphological and Optical Properties of ZnO Nanorods Growth by Hydrothermal Method S. A. Aldhehabi and B. E. Belkerk	105
<b>Elaboration of a Reduced Graphene Oxide–Chitosan Biocomposite</b> Abdallah Cheraitia, Maroua Mezrag, and Roquiya Laghrib	115
<b>Structural and Hydrophobic Properties of Cobalt Doped ZnO</b> <b>Thin Films Prepared by Electrodeposition Method</b> Zehira Belamri	125
Design of a New Photo-Diode Based on (α-PbO)/(α-SnO) Lateral Heterostructure Ali Bakhtatou and Ali Hamidani	133
Numerical Investigation of Laminar Forced Convection HeatTransfer Nanofluids Flow Using Different Base FluidsA. Laichi, A. Bouhezza, H. Köten, and O. Kholai	143
Electronic Properties and Magnetic Stability in Binary Iron Pnictide	157
<b>Structural and Morphology Characterization of an EVA/ZnO</b> <b>Polymer in Thin Film Form for Solar Applications</b> Maifi Lyes, Ayadi Aicha, Hioual Ouided, Mazinz Zaina, Agroui Kamel, and Chari Abdelhamid	167

Contents

Synthesis and Characterization of $Zn_{(1-x)}Ni_{(x=0,01-0,03)}O$ Nanofilms   Under Specific Conditions: Enhancement of Red Emission,   and Photodegradation Retarding Behavior   Abdelhalim Ouhaibi, Bachir Eddine Messaid, Rafik Serhane,   Abdelhalim Zoukel, and Abderezak Zellagui	175
Synthesis and Characterization of Nickel Doped Fe <sub>3</sub> O <sub>4</sub> Nanoparticles Using Solvothermal MethodE. Aliouat, N. Belmokhi, B. Mihoubi, H. Filali, R. Bouhroum,and N. Boukheit	185
Effect of Ni-Doping on ZnO Nanostructures Properties Sonia Attaf, Fouzia Abbas, Chourouk Namoune, and Rabeh Bensaha	197
Synthesis, Characterization and Chemical-Sensor Applications of Zinc Oxide-Graphene Nanocomposite Meriem Boutamine, Leila Grine, Abdelkadir Yessad, Hind Saidani, Hichem Hachemi, Samir Bellal, and Mourad Makhlouf	207
HMDSO/ZnO-Graphene Heterostructure Coated Quartz Crystal     Microbalance Transducer for VOCs Sensing     Leila Grine, Azzedine Bellel, Meriem Boutamine, and Salah Sahli	217
Correlation Between Structural and Optical Properties of CuO Nanoparticule Prepared by Sol–Gel Method: Degradation of Mythylene Blue Fouzia Abbas, Sonia Attaf, Asma Zeibet, and Rabah Bensaha	225
Renewable Energy	
Deposition of Copper Oxide Thin Films by Spray Polarisis Technique with Copper Chloride Solution for Different Spray Number	225
Ketita Nour Elhouda, Daira Radouane, Boudjema Bouzid, and Mohammedi Abdelkader	233
Stability Analysis of Gradient Zone of a Solar PondOuzani Riadh, Alloui Imane, and Alloui Zineddine	245
Heat Transfer Enhancement in a Parabolic Trough Solar Collector Using Inner Wall Fins and Nanofluids Halla Diafi, Sihem Djouimaa, and Djemaa Guerraiche	255
<b>Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn), Promising New Candidate Materials</b> <b>for Electronic and Thermoelectric Applications</b> Djennane Khaoula, Dehbaoui Mourad, Dehimi Nour Elhouda, and Meliani Kawther	265

First-Principles Calculations of Structural, Elastic and Electronic   Properties of Cubic CsBeI <sub>3</sub> Compound   Amel Meziani	273
Impact of High Temperature and Germanium Rate on the Electrical Performance of the SiGe Heterojunction Bipolar Transistor with DPSA-SEG Architecture Chems El Ghizlane Lachkhab, Maya Lakhdara, Abdelaaziz Boulgheb, and Saida Latreche	281
Environmental Protection by the Adsorptive Elimination of Basic Violet 3 Dye from Water K. Saadallah, C. Ad, M. Djedid, M. Benalia, and S. Saadallah	289
The Effect of Increasing the Thickness of an Annular Space Subjected to a Heat Flux Emitted by a Solar Panel on the Dynamic and Thermal Fields Sofiane Touahri, Hassen Haithem, and Toufik Boufendi	297
Control Systems for Renewable Energy Production	
Wind Turbine Energy Production Based on Event-Triggered     Speed Control     Abdelmalek Zahaf, Abdelhamid Bounemeur, and Sofiane Bououden	311
<b>PID Controller for Precise Voltage Output of Solid Oxide Fuel Cell</b> Abdelhamid Bounemeur, Abdelmalek Zahaf, and Mohamed Chemachema	319
Finite-Control-Set Model Predictive Control (FCS-MPC) and Fuzzy Self-Adaptive PI Controller (FSA-PIC) for Wind Turbine System Based on DFIG Amira Aggoune, Farid Berrezzek, and Khaled Khelil	327

## Nanocomposites and Nanomaterials Applications

## Multiwall Carbon Nanotubes Effects on the Coefficient of Thermal Expansion of High Density Polyethylene



H. Filali, M. Bouleklab, S. Saadallah, T. Dorbani, N. Barama, and S. Hamamda

Abstract The aim of this work is studying the influence of multiwall nanotube additions in high-density polyethylene using different complementary techniques. We were able to monitor the degradation of PE + X%MWCNTs using dilatometry, a tool that is highly sensitive to the structural behavior of materials. The small quantities of nanotubes inserted did not reveal any significant changes in the nanocomposites change-of-state temperature. Experimental methods using both calorimetry and thermogravimetry have shown that, overall, degradation temperatures tend to be approximately the same order of magnitude. According to Raman spectroscopy and x-ray diffraction shows that crystallinity elevates with increasing concentration.

**Keywords** Dilatation · Calorimetry · Raman · Nanotube · Carbon · Anisotropy · PE

#### 1 Introduction

Polymer composites are a particularly interesting class of materials in the socioeconomic field. The advantages of using polymers are ease of handling, light weight, and low production costs. However, polymers are less rigid than metals and, above all, non-conductive, which limits their applications in certain technical fields.

The incorporation of nano-objects, and carbon nanotubes in particular, into polymer structures present a possibility to alter their mechanical, thermal and electrical properties, thus broadening their range of applications [1]. Nanofillers have been widely used as reinforcements in the manufacturing of high-performance nanocomposites [2], such properties make them highly regarded in various fields of technology.

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Nanomaterials have also become essential for energy and hydrogen storage, energy conversion, transport and industry [3–5].

In particular, the introduction of CNT into polymers provides not only reinforcement, but also an improvement in other physical and chemical properties, such as electrical and thermal conductivity, thermal, fire and corrosion resistance [6].

High-density polyethylene was chosen as the material. It is a commonly utilized thermoplastic material. With its easy availability, low cost and good processability, polyethylene is also a material of choice as a matrix for composites [1]. All these changing characteristics make polyethylene a much sought-after material, especially since the insertion of carbon nanotubes as a reinforcing element. Polyethylene is used in a variety of fields, including industry, medicine and environmental protection.

The discovery of fullerenes and the subsequent development of carbon nanotubes have revolutionized and contributed to the improvement and replacement of heavy and costly materials with polymer-based nanocomposites containing carbon nanotubes. The major interest in these materials stems from the fact that carbon nanotubes have excellent mechanical properties and good electrical and thermal conductivity [7-10].

They have a very high form factor. They accelerate crystallization by acting as a nucleating agent in a polymer, responsible for increasing the thermal stability of nanomaterials [11]. They have a low and/or negative coefficient of thermal expansion. Their addition to metal or polymer matrices is responsible for the drastic reduction in expansion [12, 13]. Their addition to metal or polymer matrices is responsible for the drastic reduction the drastic reduction in expansion [14, 15].

Today, the search for polymer-based nanocomposites with thermodynamic properties grows considerably owing to its multifunctional uses in advanced engineering and the development of new devices sensitive to thermal expansion.

Several groups have studied polyethylene (PE)-based composites reinforced with CNTs. This combination makes it possible to obtain new combinations of nanocomposites.

Authors in [16] Reported a significant improvement in the mechanical performance of PE containing 1, 3 and 5%MWCNTS. The authors [17] noted a negligible influence on the viscoelastic behavior of PE + X%MWCNTs where (X = 0.2, 0.4, 0.6, 0.8, 1.0%MWCNTs).

References [18, 19] Studied the thermal expansion and diffusion coefficients of PE-CNT and discovered the improvement in the TG, diffusion and thermal expansion coefficients of the system studied.

This work focuses on the dilatometry of the influence of the insertion of multiwall carbon nanotubes in high-density polyethylene.

Thermal expansion behavior is mainly important when PE nanomaterials are used in conjunction with other materials. However, it is preferable to use materials with compatible CTEs. Therefore, understanding the coefficient of thermal expansion (CTE) of PE nanocomposites reinforced with MWCNTs is an important issue. According to the literature, most research has focused on thermomechanical properties. The dilatometric behavior of carbon nanotube-reinforced polyethylene-based nanocomposites has been little studied. This is probably due to the fragility of the material and the difficulty of obtaining samples long enough for accurate dilatation measurements.

#### 2 Methods and Preparations

The high-density polyethylene (HDPE) manufactured by "Ufa OrgSynthesis" (Russia) with 918.5  $\pm$  1.5 kg/m<sup>3</sup> density and multi-walled carbon nanotubes (MWCNTs) were used for the sample preparation. The nanotubes were made by the CVD method in a rotating reactor at the O. Chuiko Institute of Surface Chemistry, NASU (Kyiv, Ukraine). Powder of the Al<sub>2</sub>O<sub>3</sub>–MoO<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub> mixture was applied as a catalyst. Propylene was just used as a carbon source [20], and to avoid the formation of agglomerations of MWCNTs.

During synthesis, highly dispersed silica (VDK brand A 300) was added as a catalyst as well. The average size of the nanotubes was nearly 15 nm, and the average length was between 2 and 5  $\mu$ m. The specific surface area, calculated through argon desorption, was about 300 m<sup>2</sup>/g, while the apparent density was near 30 g/dm<sup>3</sup> [17].

The deagglomeration of MWCNTs was accomplished through the use of an ultrasonic disperser (UZD-N) or a universal rotary hydrodynamic homogenizer in aqueous solutions with varying compositions (Fig. 1).

The samples were prepared via a multistage procedure. First, starting components, the HDPE and MWCNTs powders, were mixed in the revolver-type rotational mixer. The rotation rate and time were 120 rev/min and 4 h, respectively. The isotropic mixtures were being taken after mixing. The sample mixture was loaded into a vacuum extruder cylinder and heated to 120 °C for 40 min at a pressure of 103 Pa. After that, the mixture was pushed through a die. The cylinders of the composites were 3 mm in diameter, and their high was near 5 mm. Different fractions of MWCNTs (0.01, 0.04, 0.07 and 0.1%) were used to prepare the starting mixtures.

Fig. 1 TEM image of MWCNTs by SELMI at an accelerating voltage of 100 kV



For the characterization of the samples, we used the following experimental techniques: X-ray diffraction (XRD), Raman spectroscopy, Infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TG), and dilatometry. The XRD was performed using an XPERTPRO diffractometer, with a CuK $\alpha$  radiation (copper anode,  $\lambda$ CuK $\alpha = 1.541838$  Å) at 45 kV and 40 mA, and a temperature of 25 °C. The samples were scanned over the 2 $\theta$  range of 10–90°. The Raman spectra were recorded using a Bruker Senterra spectrometer (Bruker Optics Inc., Billerica, MA, USA) with an operating wavelength of incident light of 785 nm. The DSC and TG curves were recorded using a Netzsch Jupiter STA 449 F3 calorimeter (Netzsch, Selb, Germany), and the samples were analyzed in an Al<sub>2</sub>O<sub>3</sub>.

sample crucible over the temperature range of 30–145 °C with a heating rate of 5 °C/min. The dilatometry measurements were monitored over the same temperature range. Relative dimensional variations  $\Delta L/L$ , and the thermal expansion coefficient  $\alpha$ (T) (CTE) were measured by using NETZSCH 402C type dilatometer (NETZSCH, Selb, Germany). Each measurement was repeated three times, and the average data was used for further analysis. The precision of the  $\alpha$ (T) measurements was approximately  $10^{-7}$  °C<sup>-1</sup>.

The starting mixtures of the MWCNTs different fractions (0.01, 0.04, 0.07 and 0.1%) were taken, so four types of the samples were prepared for measurements.

Multiwall carbon nanotubes obtained by Chemical vapor deposition method in a rotating reactor [20]. The mean diameter of the carbon nanotubes was 10–20 nm; their specific surface area, which was determined by argon desorption, was 200–400  $m^2/g$ ; and their bulk density varied from 20 to 40 g/dm<sup>3</sup>.

#### **3** Results and Discussion

The dilatometry results for the four samples are shown in Fig. 2. Determination of the expansion  $\alpha$  as a function of temperature in the Z direction for all the samples reveals similar curves.

In the Z direction, the dilatometric curves of the 4 samples have the same shape. They show three domains. In the first, from ambient to 130 °C, they merge. This implies that the effect of the nanotubes is the same. The interaction forces are of the same order of magnitude. The second interval is around 140–145 °C, where each curve contains an anomaly whose intensity changes as a function of concentration. It is probably linked to the degradation phase. The PE + 0.1%MWCNTs interval lags behind the other three. The anomaly is extensive and of very low intensity compared with the others. In the third area, we return to the initial situation where all curves merged.

All in all, the four samples each contained an anomaly whose onset temperatures were a function of concentrations. Its origin is linked to the degradation of the matrix. The temperatures of appearance are a function of the concentrations. So, the greater the quantity of nanotubes, the better the protection of the samples. Their degradation is delayed (Fig. 3).



Fig. 2 The coefficient of thermal expansion measured in the longitudinal direction of PE + X%MWCNTS



Fig. 3 The coefficient of thermal expansion measured in the radial direction of PE + X%MWCNTS

 $\alpha$  of the PE + 0.1%MWCNTs shows a very intense peak, followed by PE + 0.07%MWCNTS. The anomaly disappeared in PE + 0.01MWCNTs and PE + 0.04NT. Beyond the peaks, the curves overlap and behave in a similar way to that observed in the first domain.

In the radial direction, the degradation phenomenon is practically comparable with that in the Z direction.



Fig. 4 Relative variation  $\Delta L/L$  measured in the radial direction of PE + X%MWCNTS

We note that despite the direction of measurement, the dilatometric variations remain unchanged over a wide temperature range. This indicates that, for very low concentrations, thermal expansion coefficients are stable. This may be attributed to the strengthening of interatomic bonds. This behavior is consistent with the increased melting temperature (140 °C) of this type of nanocomposite [21].

Probably, the low concentrations of carbon nanotubes have good dispersion in PE matrices.

We see that the degradation temperatures are all above 140 °C.

Figure 4 shows the relative dimensional variations in the radial direction.

At low temperatures, the four curves are nearly identical and overlap. From 80 °C onwards, the curves separate from each other and the differences become significant as the temperature rises. At around 125 °C, all the curves pass through a maximum and then fall sharply. This behavior is probably linked to the effect of degradation.

Figure 5 shows the relative  $\Delta L/L$  variation in the Z direction.

The four samples are behaved in the same way. The curves are merged over the entire temperature range. They each contain a dilatometric anomaly appearing at the same temperature.

As before, dimensional changes in both directions are relatively stable over the 30-100 °C range, which is not as wide as in the case of expansion.

With regard to differential scanning calorimetry, inserting different concentrations of multiwall carbon nanotubes into the polyethylene did not change the shape of the DSC curves (Fig. 6).



Fig. 5 Relative variation  $\Delta L/L$  measured in the longitudinal direction of PE + X%MWCNTS



Fig. 6 Differential scanning calorimetry of PE + X%MWCNTS samples

They have the same shape. They each feature a calorimetric anomaly appearing at roughly 130–135 °C, already noticed in the dilatometric curves. 130–135 °C However, the anomaly of the sample containing 0.1% carbon nanotubes is larger than that of the others. This anomaly is related to the degradation phenomena. On the calorimetric curves, the temperatures at the start and end of degradation are practically the same for all samples, but they are higher than those for pure PE. This is in accordance with [22].

We note that the calorimetric behavior of all four samples is stable up to a 100  $^{\circ}$ C. This is in line with the dilatometry results.

All this indicates the positive role of MWCNTs in promoting thermal stability across a wide temperature range.

Figure 7 shows the thermogravimetry of the samples studied.

The four thermogravimetric curves have the same appearance. From ambient to 100 °C, the weight loss decreases at a high rate for all 4 materials. This significant drop is probably linked to the evaporation of the organic elements used to make the multiwall carbon nanotubes. Above 120 °C, the curves change slope. They tend towards right-hand segments. This means that the samples stabilize better and mass loss becomes minimal. At high temperatures, thermal agitation is strong. This led to good dispersion of the MWCNTSs, which in turn implies a more stable material.

We are interested in two aspects of the Raman technique. One is related to the D and G bands of carbon and the other is related to the crystallinity of the nanomaterials studied.



Fig. 7 Thermogravimetry of PE + X%MWCNTS samples

In general, the G band reveals highly crystalline graphite layers and the D band reveals the presence of defects in the graphite layer.

The band in the vicinity of  $1420 \text{ cm}^{-1}$  is absent in the PE/0.01%MWCNTs nanocomposite, where the concentration is very low. This implies that concentration plays a significant role. So, the behavior of this new class of nanomaterials depends on the amount of nanoscale carbon inserted.

Figure 8 shows the Raman spectra of all 4 samples containing varying percentages of multi-walled carbon nanotubes. All spectra exhibit the characteristic vibrational modes expected for pure HDPE, notably the intense Raman shift at 1297 cm<sup>-1</sup> associated with CH<sub>2</sub> twisting. Additionally, evident are the orthorhombic crystalline phase vibrations, in particular the peak at 1420 cm<sup>-1</sup> attributed to methylene bending [23]. Tracking the relative intensity of this  $1420 \text{ cm}^{-1}$  peak enables semi-quantitative evaluation of the crystalline fraction within the composite samples. For the HDPE composite containing the lowest 0.01% MWCNTs loading, the 1420 cm<sup>-1</sup> peak is nearly imperceptible even upon background subtraction. This implies an almost entirely amorphous morphology for the HDPE matrix at this MWCNTs concentration. As MWCNT content is increased to 0.04%, a discernible 1420 cm<sup>-1</sup> peak emerges, indicating initial formation of HDPE crystalline domains with the addition of higher MWCNT loadings. The intensity continues to grow for 0.07% MWCNTs, further confirming the nucleating influence of MWCNTs in facilitating crystallization of the HDPE polymer chains. Finally, the composite containing the maximum 10% MWCNTs exhibits both the highest absolute intensity of the  $1420 \text{ cm}^{-1}$  peak and the highest overall degree of crystallinity. Additionally, the characteristic D band Raman shift of MWCNTs becomes slightly visible for the HDPE composite containing 0.07% MWCNTs and continues to increase in intensity with higher MWCNTs loadings due to the greater concentration of nanotubes. In summary, the evolution of the 1420 cm<sup>-1</sup> peak provides evidence that MWCNTs substantially enhance HDPE crystallization in a concentration-dependent manner (Fig. 9).

All four spectra are comparable. They contain virtually the same peaks, but they are very intense compared with those of pure polyethylene. So, nanotubes have an important influence on structural behavior. There are also differences between the intensities of the different X-ray diffraction peaks of the 5 nanocomposites materials studied. This suggests that concentration plays a significant role. The angles of appearance of intense anomalies also depend on concentration. The obtained result can be merged with some techniques in control theory [24–30].

#### 4 Conclusion

Dilatometric measurements enabled us to highlight the degradation phenomenon. The different concentrations did not significantly change the degradation temperatures. The dilatometric measurements in the radial and longitudinal directions were not far apart. Very low concentrations probably lead to relatively weak effects. This



Fig. 8 Raman shift of PE + X%MWCNTS samples



Fig. 9 X-ray diffraction pattern of PE + X%MWCNTS samples

may be due to insignificant anisotropy. Calorimetric and thermogravimetric measurements provide better information on the degradation phenomenon. The Raman shows that crystallinity changes with nanotubes concentration, which is in agreement with the dilatometric results. In conclusion, all the results obtained in this work are of definite importance (improvement of thermostructural characteristics) and testify to the positive role of the introduction of multiwall carbon nanotubes. They have become an essential part of materials science. Their introduction means that heavy, expensive materials can be replaced by polyethylene-based nanocomposites reinforced with multiwall carbon nanotubes. This advantage has led to considerable gains in various areas of industry.

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## The Influence of Milling Time and Multiwall Carbon Nanotubes Concentrations on the Thermal-Structural Behavior of Iron–Copper Nanocomposites



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Abstract In this work we aim to study the effect of incorporating different concentrations of multiwalled carbon nanotubes into Iron–Copper—Fe–Cu with a ratio of 4:1; MWCNTs of 0.5, 1 and 2% in volume—nanocomposites—prepared via high-energy ball milling of different grinding times of 1 and 2 h, respectively— on the thermal and structural properties. The characterization conducted was heat flow, weight change, relative linear expansion ( $\Delta L/L0$ ) and coefficient of thermal expansion (CTE) for the thermal behavior, whereas for the structural changes and assessments, x-ray diffraction, and Raman spectroscopy were applied.

Keywords Carbon nanotube  $\cdot$  Fe–Cu nanocomposite  $\cdot$  Thermal expansion  $\cdot$  Mechanical milling  $\cdot$  Heat flow

#### 1 Introduction

Carbon never ceased to attract the attention of the scientific community, A short time ago, it had been regarded only in three allotropic forms, nowadays their numbers only increased, from graphite foam, fullerenes followed by carbon nanotubes (CNTs) arrival which created a revolution in many fields, especially in materials science, medicine and environmental protection. New types of nanocomposites are obtained by incorporating CNTs into polymers, metals and ceramics. The motivation behind this work is the unique characteristics and exceptional properties of MWCNTs, which

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were revealed only a few decades ago. They possess an advantageous form factor and high specific surface area (up to  $1300 \text{ m}^2 \text{ g}^{-1}$ ) [1]. The strong C–C covalent bonds and the geometry of the MWCNT walls give them outstanding mechanical properties translating into very high Young's modulus (greater than 1 TPa) [2] associated with high resistance to rupture (over 100 GPa) [3]. The space industry is also one of the many fields of application, in particular, the construction of light spacecraft thanks to the use of materials containing these nanofillers. This weight loss is a major asset in the protection of the environment and a significant reduction in greenhouse emissions. Due to the captivating properties of carbon nanotubes, a growing interest in the development of novel metal matrix nanocomposites containing MWCNTs.

Due to their high strength, availability and affordability, iron alloys with carbon reinforcement are among the most commonly used metallic materials in engineering applications and as structural material where mechanical properties are of a key concern. Iron as a transition metal is crucial for electromagnetics and permanent magnets. Because numerous transition metals are used as structural materials in a variety of industries, substantial emphasis has been devoted to the development of techniques for producing novel transition metal-MWCNTs matrix nanocomposites. The transition metals' vacant 3d orbitals enable for 3d–2p hybridization between the metal and graphitic structure MWCNTs [4, 5]. In which result in high interfacial adhesion [6–8].

The Fe–Cu intermetallic nanocomposite systems have been an underlying subject of attention for a long time. despite problems with their manufacturing. This interest was related to the attractiveness of Fe–Cu for many applications as well as their well-known high strength, thermal, and electrical properties [9, 10].

Mechanical alloying (milling) (MA) of the components of the intermetallic system allows for an increase in their solubility compared to equilibrium values and, at the same time, is a rather simple and effective way to produce a large amount of the composite. That is why manufacturing nanocomposite materials by the MA method is today a recognized method of the "cold" treatment of solid powder composites [11, 12]. The materials thus obtained reveal new, interesting properties,

This approach has shown to improve and have favorable impacts on material properties. Nevertheless, the manufacturing of metal matrix-MWCNTs composite has remained problematic due to the difficulty of achieving randomly distribution of CNTs with good interfacial bonding. High-energy ball milling provides high dispersion of CNTs in the matrix. The ball milling procedure, consisting of alternating welding, fracturing, and resoldering of iron powders, can provide iron-based nanocomposites with a homogeneous MWCNTs distribution [13]. It also produces homogeneous and very fine microstructures also it refines the grain size [14–17]. Due to the fascinating properties of carbon nanotubes, there is a growing interest in the development of new metal matrix composites reinforced with multiwall carbon nanotubes.

#### 2 Materials and Methods

#### 2.1 Specimen Preparation

Multiwall carbon nanotubes have been synthesized by chemical vapor deposition (CVD) [18]. Their parameters are:

- Average diameter varies between 10 and 20 nm,
- specific surface (determined by argon desorption) is 200–400 m<sup>2</sup>/g,
- apparent density is between 20 and 40 g/dm<sup>3</sup>.

The matrix comprises of the iron IP-1 and copper PMS-1 powders in a 4:1 weight ratio. The powders were mixed with different multiwall carbon nanotube concentrations of 0, 0.5, 1 and 2%MWCNTs in volume. The Fe–Cu-X%MWCNT nanocomposites obtained via high-energy ball milling. The ball mill (containing 20 hard stainless-steel balls) is of the same alloy as the planetary vial, which sustained an acceleration of 50 g with pressure reaching 5 GPa on a particle.

Three milling times 20, 60 and 120 min were taken. After processing in the ball mill, the nanocomposites were subjected to a 40% compression followed by annealing at 950 °C for 30 min in Argon flow. Then, the powder samples were subjected to cold rolling followed by annealing at 900 °C in Argon flow. The described cycle was repeated three times; thus, the samples were undergone to 80% thinning. Finally, the thickness of the obtained ribbons was near 0.3 mm.

#### 2.2 Characterization Equipment

Different characterization techniques were used to investigate the changes and behaviors in both structural and thermal properties.

A NETZSCH 402C dilatometer (NETZSCH, Selb, Germany) with 3% accuracy was used in the study. The heating rate was near 10 °C/min. The thermal expansion coefficient was measured in the temperature range from 30 to 800 °C.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) tests were conducted using a Jupiter STA 449 F3 calorimeter by NETZSCH (NETZSCH, Selb, Germany). The same heating rate as in the dilatometric measurements was used.

The X-ray diffraction patterns of the nanocomposite under study were obtained using the automated Philips X Pert Pro diffractometer with the filtered cobalt radiation  $K\alpha_1 = 1.7909$  Å under the following scanning parameters: monitoring range [20–80°], with step scan 0.026°.

The Raman spectroscopy was carried out using a Raman Bruker Senterra spectrometer instrument, with a green laser (wavelength  $\lambda = 532$  nm) from an argon ion.

#### **3** Results and Discussion

#### 3.1 Thermal Analysis

The Fe–Cu nanocomposite samples differ by milling time and the amount of multiwalled carbon nanotubes added to the metallic matrix. We proceed with the thermal analysis using dilatometric measurements, The regarded parameter is the coefficient of thermal expansion (CTE or  $\alpha < T$ >).

Figure 1 shows the coefficient of thermal expansion  $\alpha$  <T> of the Fe–Cu-X% MWCNTs nanocomposites ground for 1 and 2 h, respectively. As for the 1 h milling time the CTE variations for the samples of the 60-min milling time, shows that both 1 and 2% MWCNTs additions have the same changes with a slight increase from ambient temperature to around 450 °C followed by slight decrease in the vicinity of 650 °C, both values of CTE intersect at the end of the range near 800 °C. While the CTE for 0.5% sample is increasing steadily over the temperature range.

As for the 1% MWCNTs, it is lower than that of 2% MWCNTs. Perhaps due to the good dispersion of nanofillers in the 1% sample, leading to an amplification of the interatomic bonding between the host matrix and the incorporated CNTs. In the vicinity of 800 °C, the CTE of both 1 and 2% MWCNTs intersect. This situation is due to the strong thermal agitation causing a homogeneous dispersion of the MWCNTs.

The CTE behavior of the 120-min milling time, as for the Fe–Cu-1% MWCNTs nanocomposite is significantly lower than the other two over the entire temperature range. Certainly, this concentration is well-dispersed giving rise to a significant amount of bonding which translates into a force.

On the other hand, for the differential calorimetry accompanied with the weight variation (Thermogravimetry) analysis. Figure 2 shows both heat flow and weight change signals of the 1 h milling time.





At low temperatures, the curves overlap. The signal of all samples has nearly the same shapes. An exothermic peak located around 600 °C and whose intensity is concentration dependent. FeCu1%MWCNT has a high intensity of capacity. At high temperatures, the DSC of the four samples tend to decrease and the differences between the intensities drop. The energy of thermal stirring is probably maximum, which intensely excites MWCNTs and promotes their distribution in all matrices. When the stirring time increases to 120 min, the roles are reversed.

The curves have the same shapes. The TG of FeCu1%MWCNT has the lowest weight loss, compared to that of the other samples, over the entire temperature range. Similarly, oxygen attacks this nanocomposite the least. The highest concentration sample is the less oxidized. Above 700 °C, the TG shows a very strong acceleration leading to intense oxidation. The sample containing the least number of nanotubes has the highest weight gain (oxidation) over almost the whole range. This might be due to the small amount of carbon to wrap the nanomaterial against oxygen (Fig. 3).



The heat flow signal of the 2% becomes very intense. Its intensity is four times higher than that of FeCu1%MWCNT. This confirms that its calorific value is significant. This state is related to a refined structure and a reduced deterioration of MWCNTs. The transition is present and at a high intensity. This anomaly is located around 550 °C. Beyond the transformation, the DSC is approximately equal to 0.90  $\mu$ V/mg and varies linearly. On the other hand, the two other nanocomposites have DSC which have the same appearance, contain very spread-out calorimetric peaks, close intensities and appear late at 50 °C.

The sample with 0.5%MWCNTs, the TG exceeds that of the 1% over the entire temperature range. The 1%MWCNTs concentration is likely diffused homogeneously into the matrix implying little loss of mass. As a result, the effect of oxygen on the sample is less strong. It is better protected against oxidation. On the other hand, the TG of FeCu2%MWCNTs changes little at low temperatures. From 400 °C, it presents an abrupt rise, leading to an abrupt change in mass. Above 550 °C, the thermal agitation is strong. This state leads to a homogeneous distribution of MWCNTs and thus a less accentuated change in the high temperature range. The comparative study of the TG of the three samples shows that 1%MWCNTs is the origin of the small TG. The effect of oxidation is the least strong compared to the other two nanomaterials. This shows that the effect of concentration plays a non-negligible role.

#### 3.2 Structural Analysis

#### X-ray diffraction analysis

The position of the diffraction peaks gives access to the distance  $d_{hkl}$  between crystallographic planes, the structure and lattice parameters.

X-ray diffraction has been applied to study the reaction between metals and carbon components qualitatively. It provides vital information on MMN-CNT composites while also determining phase composition after processing. It delivers quick information on the influence of the processing approach on the changes in the phase existing in the matrix. For instance, in bulk-metallic-glass-CNT composites, it reveals whether the matrix is still crystalline [19]. Qualitative information regarding the alignment of the CNTs can be acquired from the relative intensities of the distinct peaks [20]. In nanocomposites, the mass fraction of CNTs is generally low, and only the (002) peak is discernible. Additionally, to compare the reactivity of different carbon species.

The crystallite size and lattice strain in the powder particles can be determined using the X-ray peak broadening technique. Those peaks are broadened due to (a) instrumental effects, (b) small particle size, and (c) lattice strain in the material. The specific contributions of these effects to the total broadening can be separated using typical approaches and they may be found in some of the textbooks [21] and/or research articles [22–24].

Figure 4 presents XRD diffractogram patterns of Fe–Cu nanocomposite milled for 60 min.

The Influence of Milling Time and Multiwall Carbon Nanotubes ...



A presence of iron oxide only in the samples Fe–Cu without any MWCNTs, while the samples containing different concentrations of CNTs have the same planes corresponding to iron and copper, except for the 1% MWCNTs favoring the plane (200).

The presence of carbide in samples containing CNTs is immanent, but it was recorded only in the samples with 0.5% addition, also a trace of carbon in 1 and 2% and most notably in 0.5% MWCNTs. The average grain size is around 35 nm, the effect of concentrations appeared at a high concentration of 2% (Fig. 5).

A weak appearance for iron carbide presence between lower angles and  $2\theta = 35^{\circ}$  for samples containing 0.5%, 1% and 2% MWCNTs respectively. As for grain size, it averages around 21.5 nm and it doesn't differ from the Fe–Cu without MWCNTs. This grain size is somehow stable, this might be due to, (i) the pining effect, the



formation of carbide on the boundaries between the CNTs and the hosting matrix hindering the grain growth. (ii) Grain refinement.

Table 1 shows the grain size of the different treated samples.

For all grinding times and concentrations, the presence of more or less high background noise suggests the existence of an amorphous phase due to the sample preparation process, as observed by other authors during high-energy grinding [25–27]. The intensity of grinding with very high acceleration, twice as high as that of conventional mills (50 g) gives rise to non-equilibrium supersaturated phases in addition to amorphization. In [28], the authors identified several phases ranging from Fe(95)Cu(5) to Fe(83)Cu(17), such as the Cu supersaturated  $\alpha$ (Fe, Cu) phase and ordered phases.

However, regardless of the grinding time, the XRD spectra do not show a carbide peak. This may be due to the formation of a very small amount of iron carbide in an extremely fine form, which is below the detection limit of the XRD apparatus used.

#### Raman spectroscopy

The influence of the dispersion process on CNTs structure was evaluated by Raman spectroscopy. Through this technique, it is possible to analyses the defect ratio, and thus measure the damage induced by the dispersion technique. The ratio of the intensity of the *D* band  $(I_D)$  to the intensity of the *G* band  $(I_G)$  is used to evaluate the quality of the CNTs [29]. An increase in this ratio indicates a growth in the number of CNTs defects, whereas a decrease indicates a change in the structure of the CNTs.

Each Raman band was analyzed by fitting with Breit–Wigner–Fano lines, and Lorentzian lines.

It is well-known in literature for graphite or composites containing graphitic additions behavior when goes under investigation using Raman spectroscopy, the observation of the presence of two characteristic peaks, D and G in the Fe–Cu nanocomposite with different concentrations of multiwall carbon nanotubes, the above.

The W<sub>G</sub> bandwidth and the I<sub>D</sub>/I<sub>G</sub> intensity ratio have been frequently used to characterize the structures of the graphite like carbons [30–35]. It is widely known that both W<sub>G</sub> and I<sub>D</sub>/I<sub>G</sub> increase with an increasing disorder in the graphite structure [30, 31]. In addition, it has been reported that the I<sub>D</sub>/I<sub>G</sub> intensity ratio is inversely proportional to the size of the finite crystallites constituting the graphite like carbons [31, 36]. Therefore, the W<sub>G</sub> indicates the degree of graphitization, and the I<sub>D</sub>/I<sub>G</sub> concerns not only the degree of graphitization but also the crystallite size (Fig. 6).

Table 2 provides information regarding Raman characterization; peaks, frequencies, bandwidth, and relative intensities related to both D and G bands.

Milling time, min	60			120				
MWCNTs, %	0	0.5	1	2	0	0.5	1	2
Average size, nm	33	30	35	43	19	21	19	23
Strain, %	0.35	0.32	0.27	0.28	0.63	0.42	0.77	0.47

Table 1 The average grain size of the Fe–Cu-x% MWCNTs of different milling times



**Table 2** Peak frequencies, bandwidths, and relative intensities of D And G bands in the Raman spectra of Fe–Cu-X% MWCNTs nanocomposite with different milling times and  $v_D$  and  $v_G$  are the peak frequencies of the D, And G bands, respectively

Milling time, min	MWCNTs, %	$v_D, cm^{-1}$	$W_D, cm^{-1}$	$v_G, cm^{-1}$	$W_G$ , cm <sup>-1</sup>	$I_D/I_G$
60	0.5	1338	1.07	1586	94	0.3
	1	1331	101	1580	119	0.38
	2	1337	113	1587	105	0.29
120	0.5	1346	73.1	1592	77.3	0.41
	1	1334	164.9	1581	153.4	1.11
	2	1364	52.4	1597	76.9	0.47

 $W_d$ , And  $W_g$ , are the widths [Full Widths at Half Maximums (FWHM)] of D And G bands, respectively.  $I_d/I_g$  Is the peak intensity ratio of the D band to the G band. Each band was Analyzed by fitting with a Lorentzian line

The obtained Raman spectra are in the range 1000–2000 cm<sup>-1</sup>, the frequency values of the G band in between 1570 and 1599 cm<sup>-1</sup> due to the  $A_{g1}$ ,  $E_{1g}$  and  $E_{2g}$  vibrational modes, and the frequency of the D band in between 1334 and 1361 cm<sup>-1</sup> arising from the disorder-induced  $A_{g1}$  mode. The width of the G band is related to the CNTs size distribution whereas the intensity of the D band decreases with the degree of graphitization of the tubes. In this work, Raman spectroscopy was mainly used to verify the multiwalled morphological state and the overall homogeneity of the sample. The obtained result can be merged with some techniques in control theory [37–43].
# 4 Conclusion

A classical powder metallurgy route can be used to produce a different aspect ratio of difficult solubility alloys such as iron-copper (4:1) nanocomposites with the volume additions of multiwall carbon nanotubes of 0.5, 1.0, and 2.0% respectively with different grinding times of 1 and 2 h.

This study has evaluated the influence of the dispersion of multiwall carbon nanotubes regarding the presented quantities, and the effect of milling time on both the Fe–Cu nanocomposite thermal behavior as of heat flow, weight variation and linear coefficient of thermal expansion (CTE or  $\alpha$  <T>), the phases presence as well as "grain size", the morphological state of the carbon nanotubes, which plays a very important role in altering grain size, distributing load and transfer heat throughout the matrix.

The heat flow and thermogravimetry show thermal stability and higher calorific capacity for the samples with longer milling time and higher concentrations of CNTs.

As for the coefficient of thermal expansion, improved CTE of the Fe–Cu-1% MWCN milled for two hours while the x-ray diffraction diagrams show a grain refinement for the two hours milling time, also a homogenous distribution of MWCNT (the absence of MWCNT clusters appearing as carbon-graphite). Raman spectroscopy, on the other hand, assessed the CNTs morphology integrity and damage state of the milling time, it revealed a higher defect density with longer milling time, with an exception for the 60 min it shows a lower defect density which indicates the healing and the recovery of CNTs.

However, the results of Raman spectroscopy show that damage to the structure of the MWCNT is higher with a longer milling time, thus compromising the beneficial effect of better dispersion.

The results obtained are of interest and are a certain contribution to the field of nanomaterials. They highlight the important role of multiwall carbon nanotubes in the Fe–Cu metallic matrix. Mechano-synthesis is shown to be a very efficient elaboration technique for the development of nanocomposites.

The use of a high-energy mechano-synthesis allows for the elaboration of Fe–Cubased samples containing different concentrations of multiwall carbon nanotubes that are difficult to obtain by conventional elaboration methods.

The influence of the two parameters, grinding time and CNT concentrations is responsible for significant changes in the behavior of the samples. They are complementary and are responsible for the improvements of the thermal-structural characteristics of the Fe–Cu matrix containing different concentrations and ground for different times. They can be the origin of good performances or deterioration of the physical characteristics of the studied nanomaterials.

The multiple experiments used in this work are complementary and allows us to conclude that the thermo-structural properties of Fe–Cu-based nanocomposites have improved. These results are in agreement with other works. They showed that the mechanical properties of the same nanocomposites were significantly improved because of the high density of dislocations due to the mechanical treatments and whose mobility was blocked by the grain boundaries which became numerous. The dilatometry revealed that the coefficients of thermal expansion of all the samples noticeably decreased.

X-ray diffraction shows that the average crystallite dimensions deduced from the analysis of the Willamson-Hall diffraction line profiles vary between 19 and 43 nm. They change as a function of concentration and grinding time. Longer grinding leads to better refinement compared to the other two cases. As for the micro stresses, their range of variation is between 0.23 and 0.83. Grinding for one hour leads to low values in front of the other two cases. This suggests that the nanocomposites milled for one hour are less constrained and thus allow the MWCNTs to move in the Fe–Cu matrix. Overall, the different anneal after deformation seems to have mitigated the stresses at the crystallites.

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# The Carbon Nanotubes, Graphene Nanoparticles Their Oxygen Modified Forms and Composites



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Abstract Multilayer graphene nanoparticles (GNPs) have unique properties and potential for application. They are more stable compared to single-layer graphene and are suitable for mass production by splitting precursors with a graphite-like structure. The problem is not in the production of GNPs, but in the regulation of its characteristics. The application of GNPs is hindered by their agglomeration due to van der Waals interactions. To avoid this, it is necessary to create a gap between GNPs. Carbon nanotubes (CNTs) are an ideal candidate for this. CNTs can reduce internal electrical resistance and improve overall electrical conductivity. Therefore, the production of GNPs@CNTs hybrids is of interest. In work, a simple and cheap method of GNP synthesis by anodic exfoliation of expanded graphite (EG) foil in a weak alkaline electrolyte is shown. A two-level method of regulating the structure of GNPs by adjusting the nanoscale cluster structure of EG by changing the parameters of its production process and modes of "secondary intercalation", i.e., anodic oxidation of the EG foil, is revealed. The method of synthesis of dispersions of GNPs@CNTs and film materials from them is described. The structural characteristics of GNPs, CNTs and their composites, determined by the methods of X-ray

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diffraction, LCS, Raman spectroscopy, XPS, DTA, TG are presented. The energetic effects of the interaction of partially oxidized graphene-like planes with each other were elucidated by the methods of quantum chemistry. It was found that the reaction between hydroxyl and aldehyde groups of two interacting graphene-like planes is thermodynamically most probable.

**Keywords** Expanded graphite · Carbon nanotubes · Graphene nanoparticles · Anodic and chemical oxidation

# 1 Introduction

Graphene is the only graphitic plane in which sp<sup>2</sup>-hybridized carbon atoms form a hexagonal lattice. It can be represented as a "building block" of graphite, nanotubes, graphite intercalated compounds (GIC), etc. Graphene, with its high specific surface area and unique optical, electronic and mechanical properties, has great potential for applications in many fields, from electronics to medicine. Unique properties are also possessed by multilayer graphene nanoparticles (GNPs), containing up to dozens of layers [1, 2]. They are more stable and suitable for mass production according to the "top-down" scheme that is, by splitting precursors with a graphite-like structure using a wide range of methods [3]. The problem is not in the very fact of obtaining GNPs, but in the possibility of managing their characteristics [3]. The practical application of graphene materials is limited by the agglomeration of graphene sheets due to their strong van der Waals interaction. One of the best approaches to realize the great potential of graphene is to add some space between the folded sheets of graphene. CNTs are an ideal candidate due to their high conductivity, specific surface area and, most importantly, their interaction with graphene sheets due to their similar carbon structure [4]. Therefore, the production of GNPs@CNTs hybrids is of great interest. Electrochemical (anodic) oxidation of graphite materials in electrolytes of various natures is one of the methods that makes it possible to control and regulate the properties of GNPs [5]. We also applied this method, but expanded graphite (EG) was chosen as a precursor. Why did you choose EG? Expanded (exfoliated) graphite [6] is a group of materials with a graphite-like structure, which are obtained by rapid heating at temperatures of 800-1100 °C GIC or their hydrolyzed forms. Decomposition and evaporation of the intercalant leads to a strong expansion along the axis perpendicular to the graphene planes. This effect is most pronounced for graphite salts with mineral acid anions, the molecules of which easily form gaseous products and make it possible to obtain EG powder with a specific surface area of 35–75 m<sup>2</sup>/g (Fig. 1a, b). The positron annihilation method showed that EG samples contain nanopores with an average size of about 0.7 nm [6]. TEM images of EG scales [6] (Fig. 1c, d) showed that the structure contains fragments—folded formations, possibly cylindrical, conical or slotted, convolutions of the graphene plane. The sizes of nanostructured fragments that can be separated range from units to hundreds of nanometers.



Fig. 1 SEM images of EG surface (a, b), TEM images (c, d)

The similarity of the structural elements of EG and SWCNT is confirmed by their Raman spectra [6]. The influence of technological synthesis parameters on the structural characteristics of EG was determined in [6]. The lattice parameter along the C-d<sub>002</sub> axis can vary from 0.335 to 0.344 nm, the sizes of the regions of coherent X-ray scattering in the base plane L<sub>a</sub> from 110 to 21 nm, along the C-L<sub>c</sub> axis—40 to 22 nm. For EG obtained by different methods, the sizes and distribution of pores by size are different, and their values lie in the range from less than 1 to 100 nm.

This brief review shows that EG is a nanoscale cluster system that contains cylindrical, conical, slit-like defects with pore half-widths ranging from less than 1 to  $\sim$  100 nm. The structural characteristics of EG are regulated by changing the technological parameters of the process of its production. Therefore, EG is the most attractive precursor of GNPs for industrial production. It is known that re-intercalation of EG in the classical sense does not occur. Diffusion of the electrolyte (intercalant) occurs along the existing defects. Secondary pseudo-intercalation of the dense EG material allows to "detect" nanoscale defects of the EG structure and to obtain a dispersion of GNPs in an aqueous electrolyte solution.

# 2 Materials and Methods

GNPs was obtained by secondary "intercalation" of electrodes from EG foil (according to TU U 26.8-30969031-002–2002, production of "TMSpetsmash" ltd. Kyiv city, Ukraine) in low-concentration alkaline electrolyte (KOH) with a current density of 6.0–60.0 mA/cm<sup>2</sup>. The scheme of the device is shown in Fig. 2 [7, 8]. Figure 2b shows scheme of a vertical electrochemical reactor for oxidizing dispersed carbon materials. EG foil reinforced with glass fiber of different bulk density is used as a graphite tape. The foil is continuously passed at a speed of 0.5–2.0 cm/h through a solution of potassium hydroxide electrolyte, which moves at a controlled speed through the electrolytic bath, with electric field strength of 2–30 V/cm. The electrolytic bath is divided by a membrane into an anodic and a cathodic space.

The electrochemical reactor (scheme Fig. 2b) consists of a rectangular polypropylene housing 1, in which the cathode 2 and anode 5 are vertically placed, made of a sheet of pure iron (99.4%), the cathode is wrapped with a membrane-separating



**Fig. 2** a Block diagram of the installation for obtaining a suspension of graphene nanoparticles, where: 1—electrolytic bath, 2—cathode, 3—cassette device with a strip of fiberglass-reinforced graphite foil, 4—anode, 5—polypropylene membrane, 6—filter, 7—tank with electrolyte solution of potassium hydroxide, 8—float valve, 9—part of the electrolytic bath for suspension of graphene nanoparticles, 10—photodiode, 11—LED, 12—control unit, 13—control valve drive, 14—control valve, 15—tank for suspension of graphene nanoparticles, 16—tap for removing coarse suspension of EG, 17—container for coarse suspension of expanded graphite. **b** Scheme of a vertical electrochemical reactor: 1—housing, 2—anode, 3—cathode, 4—separator (membrane), 5—CNTs [7]

polypropylene fabric for filters. The space between the anode and the cathode is filled with a mixture of CNTs and sulfuric acid in a mass ratio of approximately 1:2. The gap between the electrodes is ~ 20 mm.

The nanoscale of GNPs was confirmed by studies of Raman spectra (Brucker RFS 100 s spectrometer, the source of radiation was an argon laser,  $\lambda = 514.5$  nm), XRD patterns (powder diffractometer DRON-4 07 CuK $\alpha$  radiation in nickel according to the geometry of Bragg–Brentano surveys), thermogravimetric measurements (Derivatograph Q-1500 D (Hungary) in a static atmosphere, and SEM images (JSM-35, JEOL). The state of the CNTs and EG surface was monitored by the X-ray photoelectron spectroscopy (XPS) (spectrometer Thermo scientific K-Alpha). Aqueous dispersions of the obtained materials were analysed by particle size and mass using laser correlation spectroscopy (LCS) (spectrometer "ZetaSizer 3" Malvern Instrument (UK) with a correlator 7032 and helium–neon laser LG-111 with a power of 25 mW for wavelength  $\lambda = 633$  nm). The autocorrelation function was processed using the program PCS-Size mode v 1.61.

Multiwall CNTs synthesized by the method of catalytic pyrolysis (CCVD), according to [7], conformed to the requirements of the standard TU U 24.1-03291669-009:2009. The average diameter of the CNTs was 10–20 nm, specific surface area determined by argon desorption was 200–400  $m^2/g$ , and bulk density was within 20–40 g/dm<sup>3</sup>. According to TEM, X-ray diffraction, and Raman spectroscopy data, the noticeable amount of amorphous carbon was not detected [7].

### **3** Experimental Results and Discussion

The dependence of the size and shape (the degree of deviation from sphere, reflecting the coefficients of polydispersity) on the parameters of the process of obtaining nanoparticles of graphene material are given in Table 1. There are two groups of particles in the solution that differ in size. Large particles (13  $\mu$ m) were found in the suspensions, which eventually sedimented. The second group of particles sizing up to 450 nm was more stable (Fig. 3). Since the variance is unstable over time, the results should be considered qualitative. The average particle size is ~ 1350 nm. Two fractions: fraction I—size from 10 to 200 nm, quantity—99,9%, weight ~ 26%, the most probable size ~ 40 nm; fraction II—size from 200 to 3200 nm, quantity 0.1%, weight ~ 74%, the most probable size ~ 640 nm; the average polydispersity is ~ 0.6, i.e., the particles have a shape not very far from spherical. Thus, it is possible to adjust the size of graphene particles that are formed during anodic oxidation of EG. A suspension of GNPs diluted 20 times was studied by the SEM method. It was applied to the surface of substrates (films of gold or carbon on glass) and dried.

Two types of particles were detected (Fig. 3). The first type is a lamellar agglomerate with an ordered structure in the form of stacks or a pentagonal hollow prism (Fig. 3a), which may have a disclination origin. The second type of particles is formed into a laminar structure similar to a "flower" and consists of very thin plates (Fig. 3b). The minimum thickness of individual plates of the first type was 25–30 nm (Fig. 3a arrow). Particles of the second type were more often observed on gold substrates

No sample	Average size, nm	Fraction I size, nm		Fraction II size, nm			Poly-dispersity	
		Min	Max	Prob	Min	Max	Prob	
1	2162	8	130	40	130	31,000	7954	1
2	623	12	300	54	300	25,000	4133	1
3	1529	11	200	35	200	68,000	16,500	1
4	3251	11	280	35	280	70,000	16,500	1
5	1264	12	300	55	300	43,000	10,048	1
6	1349	12	200	40	200	3200	642	0.6
7	7049	33	800	42	800	8000	1664	1

Table 1 Particle sizes of GNPs obtained under different conditions of anodic oxidation of EG

**Fig. 3** SEM image of graphite structure on the carbon surface (**a**, **b**)



**Fig. 4** SEM images of GNP samples continuous films; **a** "free" drying; **b** under vacuum ~ 1 atm in a limited volume



(Fig. 3b). The thickness of the plates was determined as 5–7 nm. And taking into account the characteristics of the microscope, we can assume that the thickness of the plates is at least half as much and is 3–4 nm, that is, about ten layers. Dispersions of high concentration form hard films of a complex structure (Fig. 4). In addition, depending on the drying conditions, the surface may be more embossed, with the appearance of individual GNPs and a smoother film.

The Raman scattering spectra of the GNPs synthesized by us are typical for graphene multilayers (Fig. 5). The symmetric, homogeneous 2D band exceeds the G band in intensity (the so-called "graphite" mode of symmetry E<sub>1g</sub> in the G point of the Brillouin zone) at 1581 cm<sup>-1</sup>. In the case of single-layer graphene,  $I_{2D}/I_g$  is ~ 4, and in our case it is 1.12. In addition, a weak band is registered at 2451  $cm^{-1}$ , called D'' [9, 10] which consists of the sum of D and D<sup>1</sup> modes (D<sup>1</sup>-sp<sup>3</sup> at 1060–  $1080 \text{ cm}^{-1}$ ), its appearance is caused by the process of inelastic scattering on the combination D, D" phonons of the edges of the Brillouin zone. On the diffractogram of a GNPs film (Fig. 6a), dried from an aqueous solution, there is an intense peak characteristic of graphite (002) at an angle of 27°, which has a wide influx towards small angles and a less intense, obviously, second order (004), at angle 55.5°. These lines indicate the presence of polycrystalline graphite, and a significant expansion towards small angles corresponds to the presence of an X-ray amorphous phase, i.e. particles of a rather small size—GNPs. Figure 6b presents the dependences of weight loss (TG (1) and differential thermal analysis (DTA (2)) of GNPs films. Temperatures of 450, 620, 660, 690, 1020 K correspond to temperature anomalies in which the mass of the sample decreases during the thermal destruction of individual components: desorption of chemically bound water, destruction of amorphous carbon, melting of KOH, oxidation of polycrystalline graphite, respectively. In the temperature range of 450–620 K, there is a mass loss of about 18%, which indicates the disintegration of oxygen-containing functional groups and is accompanied by the release of water and carbon dioxide. In the range of 670-1020 K, about 50% of the original mass is lost, which is obviously the result of oxidation of graphene nanoparticles. After 1020 K, only polycrystalline graphite remains (loss of mass up to 17% by mass). Thus, gravimetric analysis (Fig. 6b) of annealed films (without volatiles), GNPs is about 75% wt., the rest is graphite particles.

Recently, we developed method of obtaining EG reinforced by CNTs [11] (Fig. 7a). CNTs "mounted" in the EG matrix are indicated by arrows. The use of a nanotube-reinforced EG foil as an anode in the scheme in Fig. 2a made it possible to obtain a suspension of GNPs@CNT. The size distribution of particles according



Fig. 6 GNPs film: a XRD pattern; b dependences of TG (1) and DTA (2) on temperature

to LCS data is shown in Fig. 7b. The dried suspension of GNPs@CNTs gives a continuous film (Fig. 7c).

During industrial production using the CVD method, CNTs are obtained in the of agglomerates with sizes of 20–500  $\mu$ m. Strong acids and oxidizing agents are effective deagglomeration agents for CNT [7]. Multilayered CNTs were treated with a solution of potassium dichromate in sulfuric acid according to the well-known technology of oxidation of natural graphite [6]:

$$C_n + 25H_2SO_4 + K_2Cr_2O_7@6C_{24}^+HSO_4^- \times 2, 5H_2SO_4$$
  
+  $Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O + C_{n-144}$ 



Fig. 7 a TEM image of a foil with EG-CNTs, b the size distribution of GNPs@CNT particles according to LCS data, c SEM images of GNPs@CNT foil

Scheme	Reactions schemes		$\Delta E$ reaction, (kJ/mol)		
		C <sub>16</sub> H <sub>10</sub>	C24H12	C42H16	
1	$\text{GP-OH} + \text{HO-GP} \rightarrow \text{GP-O-GP} + \text{H}_2\text{O}$	+ 22.2	+ 1.3	+ 0.1	
2	$\text{GP-OH} + \text{HOC-GP} \rightarrow \text{GP-OC-GP} + \text{H}_2\text{O}$	- 17.1	+ 0.5	- 0.9	
3	$\text{GP-OH} + \text{HOOC-GP} \rightarrow \text{GP-O-OC-GP} + \text{H}_2\text{O}$	+ 26.0	+ 21.9	+ 19.9	
4	$\text{GP-COOH} + \text{HOOC-GP} \rightarrow \text{GP-CO-O-OC-GP} + \text{H}_2\text{O}$	+ 74.5	+ 70.6	+ 69.3	

 Table 2 Energy effects of the interaction of partially oxidized graphene-like planes

Bold value represents thermodynamically the most probable reaction

The aqueous dispersion of the sample is stable over time: the average particle size  $\sim 50$  nm; two fractions: particle size from 20 to 100 nm, amount 99.9%, mass  $\sim 10\%$  and particle size from 250 to 500 nm, amount 0.1%, mass  $\sim 90\%$ ; high polydispersity ranges from 0.35 to 0.4. Thus, the results of LCS indicate that the chemical treatment of CNTs with powerful oxidants such as potassium dichromate in the presence of concentrated sulfuric acid grinds CNTs to form a stable suspension of particles of almost the same size. We recently found out [12] that ultrasonic treatment of CNTs in GNP suspension gives a compatible suspension of CNTs and GNPs stable for a considerable time period without the use of surfactants. That is, CNTs and GNPs are "surface-active" and stabilizing components in relation to each other, at least when the mass ratio of GNPs to CNTs is 0.1:1.0 and their content is 0.5–0.1% wt. in an aquatic environment. The dried suspension of GNPs@CNTs gives a continuous film in the same way as in Fig. 7c.

In Ref. [13], we used the methods of quantum chemistry to find out the energy effects of the interaction of partially oxidized graphene-like planes with each other and their dependence on the nature of the oxygen-containing functional groups present in them, as well as on the dimensions of the graphene-like planes themselves (Table 2).

The most thermodynamically probable reaction with the formation of a chemical bond is the interaction of two GPs that contain both hydroxyl and aldehyde groups (Table 2, scheme 2).

#### 4 Conclusions

Expanded graphite is a nanoscale cluster-assembled system due to the presence of cylindrical, conical, slit-like defects caused by the convolution of one or more graphene layers. The EG structure is regulated by the technological conditions of its synthesis. The use of rolled EG as an anode during electrochemical oxidation in a weak alkaline electrolyte allows for the implementation of a two-level system of regulating the structure of graphene nanoparticles, which are obtained according to the "top-down" scheme using the secondary "intercalation" mechanism. That is, the first level of management of the structure and composition of EG, the second level—the parameters of the anodic oxidation process.

Oxidation of carbon nanotubes with strong oxidants allows for their deagglomeration and obtaining stable dispersions in aqueous media. Ultrasonic treatment of CNTs in a suspension of GNPs gives a compatible suspension of CNTs and GNPs, which is stable for a considerable time without the use of surfactants. That is, CNTs and GNPs are "surface-active" and stabilizing components in relation to each other. The dried suspension of GNPs as well as GNPs@CNTs gives a continuous (solid) film.

Quantum chemistry methods have shown that the reaction between hydroxyl and aldehyde groups of two interacting graphene-like planes is the most thermodynamically probable, regardless of their size.

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# Estimation of Percolation Threshold and Its Influence on the Properties of Epoxy Resin-Based Polymer Composite Materials Filled Carbon Fibers and Carbon Nanotubes



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Abstract Carbon fillers are widely used in the polymer composite materials to control electrophysical properties, which makes them promising for shielding/ absorbing electromagnetic radiation in various bands, protection against radio interference and antistatic coatings, etc. The study of percolation transitions in such materials is a priority for such tasks. Epoxy resin-carbon fiber (ER-CF) and epoxy resincarbon fiber-carbon nanotubes (ER-CF-CNT) systems with different filler contents were investigated. Electrophysical studies were carried out in the frequency range of 8–12 GHz by the non-contact method, and electrical conductivity at low frequencies of 0.1, 1 and 10 kHz was measured by the two-contact method. The bending strength was tested on a 2167 P-50 tensile tester. It was found that: the electrical conductivity at low frequencies and the complex permittivity at 9 GHz of the composites change significantly (percolation transition) in the range of 0.001-0.005 volume fraction of the combined filler; the values of the real and imaginary components of the complex dielectric constant of the composites are ~ 50, which indicates a significant level of interaction between the components of the system and a uniform distribution of the conductive component in the composite; the maximum values of the relative flexural strength are observed at the content of CF-CNT proportional to the percolation

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threshold in the systems. The composites have a high level of strength at a low content of fillers, which, makes them attractive for use as protective coatings for absorbing or shielding from microwave EMFs.

Keywords Epoxy resin · Carbon fibres and nanotubes · Electrophysical property

# 1 Introduction

Conductive fillers expand the range of applications of polymer composite materials due to their electrical and electromagnetic properties [1]. In particular, polymer composites with carbon fillers [2] are used for electromagnetic radiation shielding in various ranges or absorption [3], protection against radio interference and antistatic coatings [4]. For such systems, it is important that the electrically conductive filler forms a continuous network, that is, it is in a state of a continuous percolation cluster. The study of percolation processes in such composites is a priority for this task [5].

Polymer composites reinforced with carbon fibres (CF) are considered promising structural materials for automotive and aerospace applications due to their excellent mechanical properties, lightweight, and flexible design [6]. When used as a filler CF in the form of continuous threads, products are obtained that have exceptionally high strength characteristics compared to the original polymer. The improvement of the mechanical parameters of the composite depends on the aspect ratio (length/diameter) of the fibres, the ratio of the mechanical properties of the polymer and filler, and the efficiency of interaction at the polymer matrix–fibre interface [6]. Combined and hybrid fibrous fillers with different particles (aluminium oxide, graphene nanoparticles, titanium oxide and silicon carbide, metal nanoparticles, etc.) are often considered in the literature [1, 2, 7–11], synergism of properties is inherent in such fillers [4].

Furthermore, in the work [10], the mechanical properties (tensile and bending) of polyamide polymer composite samples reinforced with long carbon fibers were investigated, and the synergistic effect of incorporating both short and long carbon fibers (combined filler) into the polymer was studied. The tensile strength was higher for samples reinforced with fibers of different lengths compared to polymer composites with only continuous long fibers. In our opinion, in [10], the authors introduce new ideas and approaches to composite creation, as an extremely high fiber content of 20–35% by volume of the polymer is considered.

The results of [11] show that increasing the carbon fibre content in a polymer composite to 2% improves the strength by 20–24%, while further increasing the filler content reduces it.

For the purpose of creating polymer coatings with desired electrophysical and other operational indicators, research was conducted on the epoxy resin–carbon fiber (ER–CF) and epoxy resin–carbon fiber–carbon nanotubes (ER–CF–CNT) systems with varying filler content.

# 2 Materials and Methods

CNTs were used to the requirements of the standard TU U 24.1-03291669-009:2009. The method of their synthesis and the main characteristics are described in [7, 12].

CF was obtained by grinding carbon fabric UVM-24 (TU88-USSR 259-003-89). CF and CNT were dispersed in isopropyl alcohol for 2 min, and the suspension was added to ER LR 285 and mechanically stirred. Then, it was further mixed in a three-roll mixer until the mixture had a uniform color, and a curing agent was added. Final homogenization was performed, and samples of the required size were poured into moulds.

Composite materials with a volumetric content of CF and CNT ranging from 0.0005 to 0.01 volume fractions (vf) were used for the research.

Electrophysical studies were conducted in the frequency range of 8–12 GHz using a non-contact method, and electrical conductivity at low frequencies of 0.1, 1, and 10 kHz was measured using a two-contact method. The relative error of determining  $\epsilon'$ ,  $\epsilon''$ , and  $\sigma$  did not exceed  $\pm 5\%$  [7]. The reflection coefficient R was measured when a 2 mm thick sample was placed on the surface of a metal plate.

Bending testing of layered composites was carried out by the three-point method in accordance with DSTU ISO 7438:2005 on a 2167 P-50 tensile machine with continuous automatic recording of "load-deformation" diagrams on a PC [7], with sample sizes of  $50 \times 20 \times 2$  mm.

## **3** Experimental Results and Discussion

In this work, the dependence of electrophysical characteristics and bending strength on the content of CF and combined filler (CF-CNT) in ES was investigated. Figure 1 shows the dependence of the logarithm of electrical conductivity, and Fig. 2 shows the dependence of the actual  $\varepsilon'$  and imaginary  $\varepsilon''$  components of the complex dielectric constant of the studied systems on the content of the carbon component (CF and CF-CNT). At a filler content of 0.001–0.005 vf in the samples of all systems, a nonlinear dependence of electrical conductivity,  $\varepsilon'$  and  $\varepsilon''$ , is observed, which is associated with the percolation transition. The obtained results were analyzed from the point of view of percolation theory [13] according to equations:

$$\sigma = \sigma_i (\phi - \phi_c)^t, \text{ when } \phi > \phi_c \tag{1}$$

$$\varepsilon' = \varepsilon'_i (\phi_c - \phi)^{-\nu}$$
, when  $0 < \phi < \phi_c$ , (2)

where  $\sigma_i$  and  $\varepsilon'_i$  are the electrical conductivity and permittivity of the composite;  $\phi$ —volume content of the filler;  $\phi_c$  is the volume content value corresponding to the percolation threshold; *t*, *v*—critical indices.



The results of calculations according to (1), (2) are given in Tables 1 and 2. The dependences of electrical conductivity (Fig. 1) and permittivity (Fig. 2) in ER–CF systems on the content of CFs and ER–CF–CNTs with different content of CFs on the content of CNTs have a similar character. The values of the calculated percolation thresholds from the dependences of conductivity and dielectric constant have close values (Tables 1 and 2).

For the ER-CF system, the percolation threshold is ~ 0.003 volume fractions, for the ER-CF-CNT systems, the percolation threshold is lower, and the electrical conductivity around the percolation threshold is higher. For the ER-0.001CF-CNT system, the conductivity at a higher degree of filling than 0.006 vf is lower than that of the ER-CF system. The effect may be associated with a greater number of contacts and a higher overall contact resistance between CNTs agglomerates. If we take into account the total volume content of CFs and CNTs then the percolation threshold for

Parameter	Sample	mple				
	ER–CF	ER-0.001CF-CNT	ER-0.003CF-CNT			
$\phi_c$ , percolation threshold	0.0031	0.002	0.00023			
t, percolation index	1.65	1.81	1.68			
$\sigma_i$ , ( $\Omega$ cm) <sup>-1</sup>	10	14	7			

 Table 1
 Index of the percolation threshold of polymer composites ER–CF and ER–CF–CNT according to electrical conductivity data at a frequency of 1 kHz

 Table 2
 Index of the percolation threshold of polymer composites ER-CF and ER-CF-CNT according to the dielectric constant at a frequency of 9 GHz

Parameter	Sample				
	ER–CF	ER-0.001CF-CNT	ER-0.003CF-CNT		
$\phi_c$ , percolation threshold	0.0026	0.0017	0.00016		
v, percolation index	0.78	1.05	0.91		
$\varepsilon_i'$	1.4	1.2	1.1		

the ER-0.001CF-CNT and ER-0.003CF-CNT systems will be almost the same and equal to  $\phi c = 0.003 \pm 0.0003$ , and the values of the percolation indices  $t = 1.8 \pm 0.2$ ,  $\sigma i = 10 \pm 4$ . Thus, their percolation parameters approach the parameters of the ER-CF system.

Deagglomeration and more uniform distribution of the conductive filler in the polymer matrix contributes to their wetting and increasing the area of the interfacial surface. This increases the degree of polarization of filler particles due to the formation of a double charged layer, as well as the number of polar particles per unit volume of the composite. An increase in the number of dipoles in the volume promotes effective interaction with an electromagnetic wave of the centimetre range. This is also manifested in an increase in the values of the complex permittivity even with a low content of filler in the composite. This approach to the creation of composites allows reducing the content of fillers, but provides high permittivity (~ 50). The parts of the complex permittivity have high values. This indicates a significant level of interaction between the components of the system and a uniform distribution of the conductive component in the composite.

The mechanical properties were investigated, namely the relative limit of bending strength of ER-CF composite systems depending on the content of CFs and ER-CF-CNT depending on the content of CNTs at the content of CFs of 0.001, 0.003 and 0.005 volume fractions (Fig. 3). Bending strength for all systems has maximum values in the range of 0.001–0.007 volume fraction of the filler. For the ER-CF systems, with the content of CF below the percolation threshold, the values of the bending strength limit increase, and with an increase in the CF content approximately above the percolation threshold, the values of the bending strength limit decrease (Fig. 3). Similar dependencies are observed for other systems. That is, there is a certain correlation between mechanical properties and electrical conductivity at low



frequencies in the region of the percolation transition. The maximum limit of the relative bending strength  $P_{max}$  is reached at a somewhat higher content of CFs and CNTs than the percolation threshold. Analyzing the results shown in Figs. 1 and 3, it can be assumed that there is a dependence between the content of CFs and CNTs at the maximum value of the limit of relative strength ( $P_{max}$ ) for bending  $\phi(P_{max})$  and the value of the percolation threshold  $\phi_c$  [14]. This dependence can be expressed as:

$$\phi(P_{\max}) = \kappa_p \cdot \phi_c, \tag{3}$$

where  $\kappa_p$  is the proportionality coefficient, which depends on the aspect ratio (length to diameter ratio) of the filler and the uniformity of its distribution in the polymer volume.

By lowering the percolation threshold in polymer systems with a filler having a high aspect ratio, it is possible to achieve a high level of electrical conductivity and dielectric losses at microwave frequencies at a lower filler content, as well as to obtain higher strength characteristics. One of the methods of reducing the percolation threshold is to reduce the content of CNTs in ER when they are introduced [7, 14], dispersed and stretched fibres and tubes [15] in the polymer volume.

The percolation thresholds determined from the dependences of the logarithm of the electrical conductivity on the volume fraction of the filler are located near the lower bend of the curves (Fig. 1), and the value of  $\phi(\text{Pmax})$  (Fig. 3) is located near the upper bend (Fig. 1). The coefficient  $\kappa_p$  for the considered systems, in the general case, should be a function of the angle of inclination of the curve section between two fractures on the dependences (Fig. 1). With a low content of CFs in the ER-CF system, the addition of CNTs increases the mechanical properties of composite to the content of CNTs  $\phi(P_{max})$ , and then decreases with an increase in the content of CNTs. If the content of CFs exceeds the value of  $\phi(P_{max})$  (Fig. 3), curve 4 (0.005 CF), the introduction of CNTs reduces the mechanical properties of composites.

According to [16], the relationship between the dimensions of the filler (CF or CNT), length *l*, diameter *d* and the percolation threshold  $\phi_c$  can be written as:

$$\phi_c \approx d/l. \tag{4}$$

Accordingly, Eq. (3) will have the form:

$$\phi(P_{\max}) \approx \kappa_p \cdot d/l. \tag{5}$$

Equations (4) and (5) will be fulfilled the better the more uniform will be the distribution of stretched (deagglomerated) filler particles (CFs or CNTs). From calculations according to (4), it was established that with a fibre thickness of approximately 6  $\mu$ m and a percolation threshold of 0.0031 vf (for the ER-CFs system), the length of the fibres should be about 2 mm, which is close to the actual length of the CFs that were introduced into the ER. This indicates a sufficiently uniform distribution of CFs in the binder, and also indirectly indicates the aligned state of the fibres.

Figure 4 shows the dependences of the coefficients of absorption (A) (Fig. 4a) and reflection (R) (Fig. 4b) on the frequency of electromagnetic radiation (EMR) for the ER–CF and ER–CF–0.001CNT systems with a CF vf: 0.003 (1, 1'), 0.005 (2, 2'), 0.008 (3, 3') (Fig. 4).

Composites with a CFs content of 0.005 vf in ER have the maximum values of the absorption coefficient *A* (Fig. 4). When a larger amount of CF is added into the polymer, the value of  $\varepsilon'$  increases, correspondingly, the reflection coefficient *R* also increases, that is, a significant part of the EMR energy will not be absorbed by the sample. According [8]:

$$A = 1 - R - T, (6)$$

where T is the transmission coefficient.

**Fig. 4** The absorption *A* (a) and reflection *R* (b) coefficients on the metal surface on the EMF frequency at the specified experimentally determined values  $\varepsilon'$ ,  $\varepsilon''$  shown in Fig. 1 for a thickness of 2 mm in the systems ER–xCF and ER–xCF–0.001CNT where x(vf) = 0.003 (1, 1'); 0.005(2, 2'); 0.008 (3, 3')



The EMR attenuation coefficient in composite materials will grow according to an exponential law, which for the electric field strength vector E will have the form [17]:

$$E = E_0 \cdot \exp(-k''h),\tag{7}$$

where:  $E_0$  is the electric field intensity vector of the incident electromagnetic wave; k'' is the EMR attenuation coefficient, which depends on the value of  $\varepsilon''$ , h is the thickness of the sample.

Figure 4b shows an increase in the reflectance with an increase in the content of CFs in the composite, since  $\varepsilon'$  also increases. At some frequencies for which the sample thickness satisfies the condition [8]

$$h = \frac{\lambda}{4\sqrt{\varepsilon'}},\tag{8}$$

where  $\lambda$  is the EMV wavelength, which affects a significant decrease in the reflection coefficient, which is associated with the interference attenuation of the wave reflected from the front and back surfaces of the sample.

# 4 Conclusions

The dependence of the electrophysical and mechanical characteristics of the ER-CF and ER-CF-CNT systems on the content of CF and CF-CNT was studied. It was established that the reduction of the percolation threshold to 0.003 volume fraction of fillers in these systems could be achieved by reducing the concentrations of CF and CNT with a more uniform distribution of them in the matrix. This leads to higher electrical conductivity at low frequencies and dielectric loss at microwave frequencies with lower CF and CNT content. It is shown that the maximum strength values correlate with the values of the percolation threshold in the systems and are achieved with a more uniform distribution and alignment of CNTs in the volume of the polymer matrix, with a slightly higher content of CF and CF-CNT than the percolation threshold. The mechanical properties of composites have performance indicators that allow them to be used as a coating. The resulting composites actively interact with EMFs of the centimetres range and are promising for the creation of absorbers and screens.

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# Preparation, Structure and Luminescence Properties of "Microcrystalline Cellulose—K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>" Composites



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Abstract The paper deals with preparation and optical properties of the oxidepolymer composite consisting of the luminescent K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub> polycrystals embedded into microcrystalline cellulose (MCC) matrix. The band gap of the materials under study has been estimated to be 3.76 eV for MCC and 3.15 eV for K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>@MCC, respectively. The photoluminescence spectra of the composite depend on excitation wavelengths: cellulose-related emission dominates under excitation at 405 nm while simultaneous emission from cellulose matrix and Tb<sup>3+</sup> ions observed for case of  $\lambda_{ex} = 300$  nm. At the same time, the composite sample reveals quite intensive green photoluminescence regardless on  $\lambda_{ex}$ . The main band of luminescence excitation undergoes red-shift when moving from MCC to K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>@MCC. These results point out an energy transfer from cellulose to oxide particles. In general, observed peculiarities of the diffuse reflectance and photoluminescence properties reveal interaction between matrix and filler in the composites under study. The specific emission spectra of the composite suggest its possible application at document protection branch.

Keywords Composite · Microcrystalline cellulose · Photoluminescence

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49

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# 1 Introduction

Composites have become an essential issue for a range of modern industrial, clinical, and scientific applications. Mainly, composite materials consist of two or more constituent parts with wide discrepancies in their mechanical, chemical and physical properties. To satisfy the wide range of modern demands the main body of the material is commonly based on polymer with functional particles dispersed inside. In case of nanoparticles used for filling nanocomposites are formed [1]

Nowadays, a huge number of polymer composites are known: some of them are well-known and other ones are just being developed and are promising for application [1]. Polymer composites can be quite flexible, which makes it possible to develop flexible electronic devices based on them: displays, solar batteries, etc. [2, 3]. Unfortunately, most of the polymer composites are products of petroleum processing, and therefore they are harmful to people and the environment. At the contrary, polymer materials based on cellulose are products of plant processing, or the result of the activity of microorganisms (bacteria), and therefore, such polymer materials are environmentally safe. That is why significant attention has been paid to the development of composite materials based on cellulose and its derivatives [4].

In this paper, composites are prepared on the basis of microcrystalline cellulose (MCC), which is widely used in various technological and industrial fields, in particular, in food, pharmaceutical, cosmetic, etc. [5]. Despite the significant area of application, interest in new composite materials containing MCC has been continuously grown up [6]. However, it should be noted there have been developments of composites where MCC fragments are used as reinforcing fillers [7], while developments of composites where MCC is a matrix are few [8]. However, the production of solid composites based on MCC is much simpler than the production of solid composites, for example, based on nanocellulose (NC) [9].

Importantly, the choice of composite filler is determined by considerations regarding the expected properties of the composite, because the purpose of developing of the latter one is to design a material with properties different from those of the matrix. In particular, fillers in the form of particles of oxide compounds are used to modify the optical properties of cellulosic polymers. Namely, oxides containing luminescent ions of rare earth elements (REEs) are of particular interest [10].

Regarding oxide fillers, the cellulose composite acquires new luminescent properties, and therefore can be used for transformation and visualization of light flows, concentration of solar radiation, sensorics, marking, etc. [11]. The use of trivalent terbium ions in oxide compounds—fillers is due to its specific properties, such as wide spectral composition of luminescence (from blue to red light), high radiation intensity and long-lasting afterglow—up to seconds. Micro/nano-sized crystalline powders of K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub> are used in our work as a filler containing luminescent triply charged terbium ions (Tb<sup>3+</sup>). The optical luminescent properties of phosphate compounds containing terbium ions were studied earlier [12]. Comprehensive studies of the luminescent properties of composite materials, where the matrix is microcrystalline cellulose, and the filler is luminescent micro/ nanosized particles of  $K_3$ Tb(PO<sub>4</sub>)<sub>2</sub> oxide, have not been conducted so far.

Therefore, the main tasks of this work are to find out the characteristics of optical absorption (scattering), luminescence and excitation of luminescence of composites "MCC— $K_3Tb(PO_4)_2$ " and to identify manifestations of interaction between the matrix of MCC and  $K_3Tb(PO_4)_2$  filler according to the specified characteristics.

## 2 Experimental

#### 2.1 Samples Preparation

As initial pure microcrystalline cellulose (MCC) in a form of commercial MCC tablets (manufactured by FARMAKOM, Ukraine) have been used in this study. The polycrystalline  $K_3Tb(PO_4)_2$  has been synthesized by solid state method from  $K_2CO_3$ ,  $K_2HPO_4$  and  $Tb_2O_7$  in platinum crucibles at 1300 K. The samples of  $K_3Tb(PO_4)_2$ @MCC have been prepared from MCC and oxide powders those have been simultaneously grinded in a low-speed mill during 7 days. The mass of oxide used is equal to 10% of the total mass of  $K_3Tb(PO_4)_2$ @MCC composite. The UV–Vis spectroscopy has been performed for the samples in a powdered form while PL properties are measured for pressed samples.

#### 2.2 Equipment

The UV–Vis diffuse reflectance spectra as well as photoluminescence properties (emission and its excitation spectra, kinetics, quantum yield) of the studied samples have been obtained using Spectrofluorimeter Fluorolog 3.11, UV/Vis/NIR (JobinYvon-Horiba). The PL kinetics were studied with using of sub-nanosecond ( $\Delta \tau < 0.01$  ns) pulsed light emitting diodes. All the measurements have been performed at room temperature.

### **3** Results and Discussion

### 3.1 Band Gap Determination

The diffuse reflectance spectra have been measured in the 200–800 nm spectral range for powdered MCC, " $K_3Tb(PO_4)_2@MCC$ ", and  $K_3Tb(PO_4)_2$  samples. It has been found that pure MCC demonstrate high diffuse reflection (above 85%) over



**Fig. 1** a The Kubelka–Munk functions and **b** Tauc plots for  $K_3Tb(PO_4)_2$  (1),  $K_3Tb(PO_4)_2$  @MCC (2), MCC (3) powders, and linear combination of curves 1 and 3 (4)

all the visible spectral region. The reflectivity of  $K_3$ Tb(PO<sub>4</sub>)<sub>2</sub> phosphor is near 70% in this region, while the composite sample  $K_3$ Tb(PO<sub>4</sub>)<sub>2</sub>@MCC shows intermediate case of refection intensity between MCC and oxide. The diffuse reflectance spectra have been further analyzed from viewpoint of materials band gap,  $E_g$ . The Tauc plot method is well-known technique for estimation of  $E_g$  for polycrystalline materials [13]. The Kubelka–Munk theory [14] was applied to diffuse reflectance spectra of the samples in order to obtain absorption coefficient:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$
 (1)

where, *R* is diffuse reflectance of a sample normalized to non-absorbing standard, K is proportional to absorption coefficient of the sample, S is an effective scattering coefficient of the sample. The calculated spectra F(R) and Tauc plots are shown in Fig. 1a, b, respectively.

According to literature data [15], the electronic transitions in the  $PO_4^{3-}$  molecular anions take place at photon energies above 7 eV. Thus, the band at 2–5 eV region of K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub> absorption spectrum can be associated with some defects in the crystalline compound. An effective light absorption due to defect-related centers in used oxide takes place for h $\nu > 2.7$  eV (corresponds to wavelength  $\lambda \approx 459$  nm). In case of MCC a light absorption is related with organic chromophores, those are presented in cellulose-based materials: carbonyl, carboxyl, methylol groups, etc. [16]. These chromophores are "regular" moleties of any MCC also, therefore the E<sub>g</sub> obtained value of 3.76 eV can be regarded as band gap of the studied cellulose matrix.

As it follows from Fig. 1, the case of  $K_3$ Tb(PO<sub>4</sub>)<sub>2</sub>@MCC has "intermediate" absorption spectrum between those corresponding to pure MCC and oxide filler. In order to analyze effect of interaction between cellulose and oxide, a curve  $F_4(R)$  in Fig. 1a was fitted as a linear combination of curves for MCC  $F_1(R)$  and oxide  $F_3(R)$ :

Preparation, Structure and Luminescence Properties ...

$$F_4(R) = 0.38297 * F_1(R) + 1.1073 * F_3(R)$$
<sup>(2)</sup>

It can be seen that absorption of composite is not just linear combination of absorption of  $K_3Tb(PO_4)_2$  and MCC powders. So, the  $K_3Tb(PO_4)_2$ @MCC composite is not described by "rule of mixture". The differences between curves 2 and 4 on Fig. 1a can be assumed as evidence of an interaction between cellulose matrix and oxide filler. The calculated band gap value for  $K_3Tb(PO_4)_2$ @MCC sample ( $E_g \approx 3.15 \text{ eV}$ ) is determined by both cellulose-related chromophores and defects of the  $K_3Tb(PO_4)_2$  crystals. Taking into account the results of diffuse reflection, the further PL studies have been performed at excitation wavelengths  $\lambda = 300 \text{ nm}$  (photon energy  $\approx 4.13 \text{ eV}$ ), that is above  $E_g$  for MCC and 405 nm (hv  $\approx 3.06 \text{ eV}$ ) that is close to  $E_g$  for composite.

## 3.2 Photoluminescence Spectroscopy

The room temperature PL spectra of the studied samples are shown in Fig. 2. The photoluminescence of pure MCC is more effectively excited at 405 nm than at 300 nm (Fig. 2a). Such result can be explained by presence of different functional chromophore groups in the MCC, and some of those groups are active in light absorption and they are luminescent groups (fluorophores), too [16]. It is obviously, they reveal very weak emission at 300 nm excitation. This fact indicates a significant role of non-radiation processes which influenced noted luminescence. The PL spectra of MCC under excitation at 300 nm can be fitted by two Gauss components with maxima near 3.09 and 2.55 eV, respectively. The later component has quite large full width at half maximum (FWHM)—0.72 eV that likely due to overlapping of few PL components. Decomposition of PL spectra obtained under excitation at 405 nm has shown two components at 2.50 eV (FWHM = 0.48 eV) and 2.13 eV (FWHM = 0.57 eV). So, the pure MCC has at least three types of luminescence centers.

Only weak wideband luminescence at 520–640 nm range was registered for the PL excitation at 405 nm in the case of the  $K_3$ Tb(PO<sub>4</sub>)<sub>2</sub> powders (Fig. 2c). Similar luminescence of various phosphates compounds was ascribed earlier to defect-related centers of phosphate matrix like ones created at oxygen vacancies sites [17]. The narrow bands of Tb<sup>3+</sup> emission was observed when excitation took place at 300 nm (region of  ${}^7F_6 \rightarrow {}^5H_J$  electronic transitions in terbium ions [12]).

The PL spectra of  $K_3 Tb(PO_4)_2$  @MCC composite consist of narrow bands of  $Tb^{3+}$  ions emission and wide bands of cellulose luminescence. The interactions between MCC matrix and oxide filler are manifested in the PL spectra. Particularly, under excitation at 405 nm narrow band of  $Tb^{3+}$  ions clearly seen at 544 nm (Fig. 2b). In case of PL excitation at 300 nm a redistribution of intensity between  $Tb^{3+}$ —related bands can be noted when moving from "free" oxide to composite. These results can be ascribed to energy transfer from cellulose to filler. It is worth noting, that specific luminescence spectra of  $Tb^{3+}$  ions in composite comparing with "free" oxide when





excitation takes place at 405 nm suggest a possible application of such material in document security.

The PL excitation spectra for pure MCC and  $K_3 Tb(PO_4)_2$ @MCC composite samples are shown in Fig. 3a. A blue luminescence of pure MCC is the most effectively excited at 337 nm (spectrum 1 in Fig. 3a). In case of a composite, a maximum of the blue PL excitation band is shifted to 370 nm. This shift can be explained by assumption that an energy of exciting photons near  $\lambda \sim 300$  nm is absorbed by both cellulose and  $K_3 Tb(PO_4)_2$  filler in the case of composite samples. Consequently, excitation of blue cellulose emission became less effective.

An excitation of red luminescence of cellulose ( $\lambda_{em} = 610$  nm) in MCC and K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>@MCC samples can be done at the region of wide complex band with general maxima near 400 nm. In case of composite this band is modified by light absorption of oxide as intensity drops near 480 nm corresponds to  ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$  electronic transitions in Tb<sup>3+</sup> ions. It is clear from comparison of K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>@MCC luminescence and its excitation spectra that emission from cellulose matrix can be re-absorbed by Tb<sup>3+</sup> ions of the filler.



**Fig. 3** a PL excitation spectra of MCC (1, 3) and  $K_3 Tb(PO_4)_2 @MCC$  (2, 4) samples registered at  $\lambda_{em} = 450$  (1, 2) and 610 nm (3, 4); b PL decay curves for  $K_3 Tb(PO_4)_2 @MCC$  samples.

The  $K_3$ Tb(PO<sub>4</sub>)<sub>2</sub>@MCC sample demonstrate fast luminescence. The decay curves of blue and red luminescence obtained for excitations by nanosecond pulses at ultraviolet and violet regions are shown in Fig. 3b. All the PL decay curves was successfully fitted by double exponential decay functions:

$$I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$
(3)

where A<sub>1</sub> and A<sub>2</sub>—amplitudes,  $\tau_1$  and  $\tau_2$ —PL time constants. The parameters of fitting are collected in Table 1. It is known [18], that the PL time constants  $\tau$  for Tb<sup>3+</sup> emission in K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub> are of ~ 2 ms as corresponding to forbidden *f*-*f* radiation transitions. Thus, observed fast luminescence is related either with cellulose-related centers or with defect-related centers in oxide filler.

The photoluminescence quantum yield (PLQY) of composite was obtained for PL emission in the 450–700 nm spectral range. The chromaticity coordinates for composite sample were calculated for CIE 1931 (x, y) and CIE 1976 (u', v') color space. The results are collected in Table 2.

All the excitation wavelengths in Table 2 correspond to cellulose matrix absorption ( $h\nu < E_g$  for phosphate) but narrow bands of Tb<sup>3+</sup> ions emission was observed in the PL spectra during PLQY measurements. As it follows from analysis of the PL properties, the energy transfer from cellulose matrix to oxide filler takes place in composite at various excitation wavelengths. Such low quantum yields for K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>@MCC

$\lambda_{ex}, nm$	$\lambda_{em}, nm$	A <sub>1</sub> , r.u	$\tau_1$ , ns	A <sub>2</sub> r.u	$\tau_2$ , ns
304	450	$2100 \pm 5$	$0.12 \pm 0.01$	$572 \pm 5$	$0.50\pm0.01$
404	450	$1343 \pm 6$	$0.04\pm0.01$	$456\pm5$	$0.15\pm0.01$
404	600	$1627 \pm 6$	$0.24 \pm 0.01$	$936 \pm 6$	$0.89 \pm 0.01$

Table 1 Parameters of PL decay curves fitting for K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>@MCC sample

$\lambda_{ex}, nm$	PLQY, %	x	у	u′	v′
260	1.04	0.3520	0.5581	0.1566	0.5585
282	0.23	0.2941	0.4939	0.1411	0.5331
370	0.16	0.3867	0.5907	0.1661	0.5707

Table 2 PLQY and color coordinates for K<sub>3</sub>Tb(PO<sub>4</sub>)<sub>2</sub>@MCC sample

can be explained by presence of defects in oxide those create additional ways for dissipation of energy of absorbed photons. The studied composite is a green light emitting material which color of emission can be tuned by changing of the PL excitation wavelength. While  $K_3 Tb(PO_4)_2$  is perfect host for Eu<sup>3+</sup> ions [19], the studied composite can be also the base for elaboration of multicolor luminescence covers.

# 4 Conclusions

The samples of the  $K_3Tb(PO_4)_2@MCC$  composite have been obtained by simple method of simultaneous low speed grinding of its component with subsequent pressing. The analysis of the optical properties has showed that studied  $K_3Tb(PO_4)_2@MCC$  samples are not a simple mechanical mixture of its constituents. The interaction between cellulose matrix and oxide filler manifested in diffuse reflectance spectra as well as in photoluminescence properties. Particularly, the energy transfer from cellulose to oxide-related emission centers take place in composite under study. The specific emission spectra of the composite suggest its possible application at document protection branch.

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# Formulation and Optimization of Sustained Release Microparticles of Ketoprofen



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Abstract Microparticles are one of the drug delivery systems used to sustain the release of drugs. The purpose of this work was to forumlate sustained-release microparticles of ketoprofen (KTP) for ocular delivery. The microparticles were prepared by the method of quasi emulsion-solvent diffusion using the design of experiments, the MINITAB 16 was used to analyze the results. EC:KTP mass ratio (%), PVA concentration (m/v %) and stirring speed (rpm) were selected as factors. Encapsulation efficiency rate (EE%) and in vitro release after 6h (REL6%) were selected as responses. The central composite design (CCD) was used for the formulation optimization. The results indicated that the optimal microparticles formulated has an EE = 78.89%, REL6% = 39.98% for a EC:KTP mass ratio = 80.59%, PVA concentration = 0.52% and stirring speed = 477.11 rpm. The optical microscope was used to determine the morphology of the optimized microparticles, they were of spherical shape. The in vitro dissolution at 35 °C in a medium with pH = 7.4 gave a sustained release in which 36.98% of ketoprofen was released after 6 h. According to the results obtained, the microparticles of ketoprofen can be used for the ocular sustained release.

Keywords Microparticles  $\cdot$  Ketoprofen  $\cdot$  Sustained release  $\cdot$  Design of experiment  $\cdot$  Ocular delivery

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59

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# 1 Introduction

Microencapsulation is a technique for preserving the quality of sensitive substances by enclosing liquids or solids in a membrane. It is a method to produce materials with interesting new properties, consisting of a coating material containing an active substance. The product obtained by this process is called "microparticles", which are differentiated by their morphology and structure [1].

Microparticles (MP) are known for offering prolonged or controlled release of the entrapped active ingredient through the use of the polymeric matrix. In addition, the active ingredient is also protected from direct contact with various physiological fluids and/or enzymes, thus preventing its immediate degradation. MP are generally prepared using biodegradable or erodible polymers that modify the release mode of the drug [2].

Ketoprofen (KTP) is a non-steroidal anti-inflammatory derived from aryl carboxylic acid, a member of the propionic group. It has several properties as peripheral and central analgesic, antipyretic, anti-inflammatory and enables short-term inhibition of platelet functions, it has a short half-life, therfore it requires several administrations in the same day [3].

In order to enhance efficacy and avoid adverse effects of ketoprofen, it has been formulated in polymeric microparticles for prolonged ophthalmic release.

# 2 Materials and Methods

#### 2.1 Materials

Ketoprofen was a gift from LNCPP-Constantine. Dialysis bags (cut-off 12 kDa), Polyvinylalcohol (87–90% hydrolyzed, average mol wt. 30.000–70.000) and Ethylcellulose (viscosity 22cP, 48% ethoxyl) were purchased from Sigma Aldrich USA. All other ingredients and solvents were of analytical grade.

# 2.2 Methods

#### **Preparation of Microparticles**

The quasi-emulsion solvent diffusion (ESD) was the method used for the preparation of KTP microparticles [4]. To 5 mL of a mixture of ethanol and dichloromethane (v:v; 1:1), ethylcellulose (EC) and KTP were added under vigorous magnetic stirring. To obtain an emulsion O/W, the solution obtained was emulsified with a mechanical propeller stirrer in 50 mL of the aqueous solution of PVA. Under mechanical stirring at room temperature, the organic solvents were left to evaporate for 2 h in order to

obtain the microparticles suspension. The microparticles were separated by vacuum filtration, washed and dried. The filtrate was used for non encapsulated KTP analysis.

#### **Characterization of Microparticles**

#### Entrapment Efficiency (EE)

The indirect method was used to determine the KTP entrapment efficiency and was calculated as mentioned below. The amount of non-encapsulated KTP present in the filtrate was analyzed by UV–visible spectroscopy (Shimadzu, UV 1800, Japan) at 255 nm.

$$EE = \frac{\text{Initial weight of feeding drug} - \text{Weight of not encapsulated drug in filtrate}}{\text{Initial weight of feeding drug}}$$
(1)

#### In Vitro Dissolution

The invitro dissolution test was realized in conditions representing the ocular medium (50 rpm, 35 °C  $\pm$  0.5). The dry powder of the microparticles formulated which contain a predetermined quantity of KTP was dissolved with Phosphate Buffered Saline (PBS, pH = 7.4) and placed into cellulose dialysis bags. The dialysis bags were submerged in 100 ml of the dissolution medium PBS (pH = 7.4). At each time interval, 3 mL of the dissolution medium were withdrawn, filtered, diluted and tested by UV–visible spectrophotometry to determine the quantity of the KTP released.

#### Morphology

An optical microscope was used to observe the morphology of the optimized microparticles. To observe the morphology of MP, the dry powder of the microparticles was placed on a glass slide and overlaid by a lamella.

#### **Experimental Design**

A Central Composite Design was used for the KTP-loaded microparticles preparation. Minitab<sup>®</sup> was the software used for data analysis.

The mass ratio of EC:KTP (X<sub>1</sub>:  $\frac{mEC}{mKTP+mEC} \times 100$ ), the PVA concentration (X<sub>2</sub>: w/v %) and the speed of agitation (X<sub>3</sub>: rpm) were the factors evaluated. Table 1 describe the levels used for each factor studied. Two responses were chosen: were the entrapment efficiency (Y1) and the release of KTP after 6 h (Y2).

Table 2 summarizes the results of CCD with factors levels. The model generated by the design was quadratic non-linear and presented as follow:

$$Y = A_0 + A_1 X_1 + A_2 X_2 + A_3 X_3 + A_{12} X_1 X_2 + A_{13} X_1 X_3 + A_{23} X_2 X_3 + A_{11} X_1^2 + A_{22} X_2^2 + A_{33} X_3^2$$
(2)

where

Factors: independent variables	Coded and real values				
	Low (- 1)	Intermediate (0)	High (+ 1)		
X <sub>1</sub> : mass ratio of EC:KTP (%)	71.42	75.71	80		
X <sub>2</sub> : PVA concentration (%)	0.4	0.5	0.6		
X <sub>3</sub> : speed of agitation	400	600	800		
Responses: dependent variables	Constraints				
Y1: entrapment efficiency (EE %)	Maximize (30–90)				
Y2: release of KTP after 6 h (REL6%)	Minimize (40–60)				

 Table 1
 Dependent and independent variables in CCD

Table 2 Data and factors levels of CCD							
EXP	X1 (%)	X2 (%)	X3 (rpm)	Y1 (%)	Y2 (%)		
1	71.42	0.4	400	39.157	48.448		
2	80	0.4	400	61.741	41.207		
3	71.42	0.6	400	69.540	61.169		
4	80	0.6	400	79.038	54.968		
5	71.42	0.4	800	50.320	76.938		
6	80	0.4	800	55.445	68.634		
7	71.42	0.6	800	51.978	77.257		
8	80	0.6	800	67.253	74.724		
9	68.495	0.5	600	33.874	44.896		
10	82.924	0.5	600	84.340	45.654		
11	75.71	0.305	600	46.087	49.076		
12	7571	0.66	600	70.447	50.868		
13	75.71	0.5	263.64	65.532	34.465		
14	75.71	0.5	939.35	69.256	75.910		
15	75.71	0.5	600	61.373	40.505		
16	75.71	0.5	600	72.080	23.472		
17	75.71	0.5	600	78.387	31.609		
18	75.71	0.5	600	63.981	49.530		
19	75.71	0.5	600	60.367	53.938		
20	75.71	0.5	600	81.456	35.288		

 Table 2
 Data and factors levels of CCD

- Y: the obtained response
- A<sub>0:</sub> an intercept
- A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>: the coefficients of linear regression
- A<sub>12</sub>, A<sub>13</sub>, A<sub>23</sub>: the coefficients of interactive regression
- $A_{11}, A_{22}, A_{33}$ : the coefficients of quadratic regression

Formulation and Optimization of Sustained Release Microparticles ...

- X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>: the studied factors
- $X_1^2, X_2^2, X_3^2$ : the quadratic effects
- $X_1X_2, X_1X_3, X_2X_3$ : the interaction between the variables [5].

To select the desirable optimum region, the method named desirability function was used. Table 1 shows the constraints used in order to choose an optimum formulation.

First, the individual desirability function d1 and d2 were calculated by transformation of responses Y1 and Y2 as follow:

$$d1, d2 = \left(\frac{Y1 - L}{T - L}\right) \tag{3}$$

U, L are the upper and lower acceptable values of response, T is the target value desired. The individual desirability functions vary over the range  $0 \le (d1, d2) \le 1$ .

The following equation was used for calculation of the overall desirability value (D):

$$D = \sqrt{d1 \times d2} \tag{4}$$

# **3** Results and Discussion

### 3.1 Experimental Design

The R<sup>2</sup>, adjusted R<sup>2</sup>, and p-values of the model were the quality indicators for the obtained model. The highest R<sup>2</sup> values, insignificant lack of fit p-value (p > 0.05) and significant model *p*-value (p < 0.05) for Y1 and Y2 were observed with the quadratic model without interactions as mentioned in Table 3.

The regression equations of the fitted models that describe the experimental responses are presented as follow:

$$Y = 69.66 + 10.05X1 + 7.47X2 - 1.33X3 - 4.09X12 - 4.38X22 - 1.16 X32 - 4.27X2X3$$
(5)

	Adjusted R <sup>2</sup>	R <sup>2</sup>	<i>p</i> -value	
			Lack of fit	Model
Y1	0.77	0.64	0.689	0.004
Y2	0.74	0.62	0.760	0.003

 Table 3
 Results of the regression analysis


Fig. 1 Factors and responses of optimized KTP microparticles

$$Y2 = 38.66 - 1.68X1 + 2.62X2 + 11.82X3 + 4.75X12 + 6.41X22 + 8.25 X32$$
(6)

The optimum MP formulation shows an EE (Y1) of 78.89% and a release of KTP after 6 h (Y2) of 39.98%, at levels of factors: EC:KTP ratio X1 = 80.52%, PVA concentration X2 = 0.52% and stirring speed X3 = 447.10 rpm. According to Fig. 1, the overall desirability value D = 0.90 with d1 = 0.81 and d2 = 1.

### 3.2 Morphology

The microscopic observation of the optimized KTP microparticles shows a spherical shape (Fig. 2).

### 3.3 In Vitro Release Test

Over 6 h, only 36.98% of the KTP was released from the optimized microparticles (Fig. 3). The release of KTP from the optimized microparticles demonstrate a biphasic behavior, where 31.04% of KTP were released after one hour, and then the appereance of a plateau. This behavior can be explained by the release of the encapsulated KTP



Fig. 2 Microscopic observation of the optimized Ketoprofen microparticles  $\mathbf{a} \times 10$  (b)  $\times 40$ 



inside the microparticles after the discharge of the adsorbed KTP on the MP surface [6, 7].

## 4 Conclusion

The optimized microparticles obtained have an EE of 78.89% and a sustained release over 6 h REL6% of 39.98% with a spherical shape. Ketoprofen loaded Ethylcellulose microparticles showed an interesting ocular anti-inflammatory sustained effect.

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# Effect of Fe<sub>3</sub>O<sub>4</sub> Nanoparticle on Electronic Cooling: Numerical Investigation of Nanofluid Flow Through a Heat Sink

Touba Bouacida and Rachid Bessaih

Abstract Nanotechnology is a branch of science and engineering concerned with the design, production and use of structures, and systems through manipulating of atoms and molecules on the nanoscale, which has become necessary in electronics to follow rapid development in this sector, where precision and high performance are required. To learn about how adding nanoparticles affects heat transfer, flow of water and nanofluid inside heat sink filled with copper foam at a constant porosity is compared numerically in this paper. Fe<sub>3</sub>O<sub>4</sub>–H<sub>2</sub>O nanofluid is selected as a coolant with constant concentration and diameter of nanoparticles. To enhance simulation accuracy, Eulerian two-phase modeling is used to predict the behavior of nanofluid. The simulation results were validated by comparing them with experimental data found in the literature, and good agreement was reached. Results clearly confirmed that nanofluid improved heat transfer by 50% and surface temperature reduced by 14 °C compared with water as a coolant. Opposite position of copper foam inside heat sink leads to an enhancement of Nusselt number, thus improving cooling efficiency.

Keywords Electronic cooling · Heat sink · Nanoparticles

## 1 Introduction

Adding nanoparticles to base liquids is a technology that is attracting the interest of scientists due to its effective results in numerous studies, particularly in heat transfer domain [1] and renewable energies [2]. On the other hand, electronics is one of the fields that have followed this technology to solve the problem of heat dissipation of electronic components, which is one of several causes of damage and short lifespan. Researchers have confirmed that increasing the temperature of these components by 10 °C reduces their reliability and efficiency by 50% [3]. In order to remove above

67

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problems and improve thermal management capacity, Faraji et al. [4] proposed a heat sink in the presence of a variable-phase material using 4 types of single and hybrid nanoparticles. They found that hybrid nanoparticles boosted the melting period of variable-phase material and reduced the temperature to 11 °C. For the same purpose, Zhao et al. [5] experimentally studied the effect of TiO<sub>2</sub> nanoparticle concentration ratio (0–0.5%) and Re number (472–1198) on CPU cooling. They demonstrated that nanoparticle concentration between 0.3 and 0.4% produced best results in terms of cooling efficiency. Nanoparticles were not limited to electronics, but were also applied to storage [6] and solar heat exchangers [7, 8]. According to a research study conducted by Khan et al. [9], biosynthetic nanoparticles can significantly boost solar panel efficiency. It can also be used in various medical and biological fields.

Based on the aforementioned research studies, its content is focused on how to improve performance and efficiency of devices using nanoparticle technology. Similarly, this study aims to enhance cooling efficiency of electronic components by employing nanoparticles and porous media. The flow of water and nanofluid inside copper foam-filled heat sink was numerically compared in this paper.

### 2 Modeling and Mathematical Equations

This study aims to simulate the 3D flow of water and Fe<sub>3</sub>O<sub>4</sub>–H<sub>2</sub>O nanofluid in a heat sink used to cool electronic components as a CPU. The dimensions of the area study is H × L × W (12mm × 45mm × 36mm) respectively, heat sink is equipped with copper foam at a constant porosity ( $\epsilon = 0.8$ ) whose dimensions are h × 1 × w (6mm × 22.5mm × 2.5mm). Fe<sub>3</sub>O<sub>4</sub>-H<sub>2</sub>O nf was used as a coolant with a constant concentration and diameter of nanoparticles ( $\phi = 0.3\%$  and dn = 20 nm, respectively), its characteristics are illustrated in Table 1. Laminar flow (400 ≤ Re ≤ 1100) of water and nf are applied to the heat sink to dissipate heat from the bottom surface of CPU subjected to a heat flux of 220 kW/m<sup>2</sup>. Eulerian two-phase modeling is used to predict the behavior of nf in the studied domain.

To simplify the study, the following assumptions were adopted: nanofluid flow is 3D, laminar, incompressible and stationary, the effect of gravity is negligible, and thermo-physical properties of solid are considered constant. The continuity equation, the equations of motion, and the energy equation are [11]:

$$\frac{\partial \mathbf{u}}{\partial \mathbf{x}} + \frac{\partial \mathbf{v}}{\partial \mathbf{y}} + \frac{\partial \mathbf{w}}{\partial \mathbf{z}} = 0 \tag{1}$$

Physical properties	$\rho$ (kg/m <sup>3</sup> )	Cp (J/kg K)	k (W/m K)	μ (Pa s)
Water	998.1	4179	0.613	0.0013004
Fe <sub>3</sub> O <sub>4</sub> nanoparticle	5180	670	80	-

 Table 1 Physical properties of Fe<sub>3</sub>O<sub>4</sub>-H<sub>2</sub>O nanofluid [10]

$$\frac{1}{\varepsilon^{2}} \left( u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right) = -\frac{1}{\rho} \frac{\partial P}{\partial x} + \frac{\upsilon}{\varepsilon} \left( \frac{\partial^{2} u}{\partial x^{2}} + \frac{\partial^{2} u}{\partial y^{2}} + \frac{\partial^{2} u}{\partial z^{2}} \right) - \left( \frac{\upsilon}{K} + \frac{C}{\sqrt{K}} \sqrt{u^{2} + v^{2} + w^{2}} \right) u$$
(2)

$$\frac{1}{\varepsilon^{2}} \left( u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} \right) = -\frac{1}{\rho} \frac{\partial P}{\partial y} + \frac{\upsilon}{\varepsilon} \left( \frac{\partial^{2} v}{\partial x^{2}} + \frac{\partial^{2} v}{\partial y^{2}} + \frac{\partial^{2} v}{\partial z^{2}} \right) - \left( \frac{\upsilon}{K} + \frac{C}{\sqrt{K}} \sqrt{u^{2} + v^{2} + w^{2}} \right) v$$
(3)

$$\frac{1}{\varepsilon^{2}} \left( u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} \right) = -\frac{1}{\rho} \frac{\partial P}{\partial z} + \frac{\upsilon}{\varepsilon} \left( \frac{\partial^{2} w}{\partial x^{2}} + \frac{\partial^{2} w}{\partial y^{2}} + \frac{\partial^{2} w}{\partial z^{2}} \right) - \left( \frac{\upsilon}{K} + \frac{C}{\sqrt{K}} \sqrt{u^{2} + v^{2} + w^{2}} \right) w$$
(4)

C is the coefficient of inertia which is expressed as [11]:  $C = \frac{1.75}{\sqrt{150\epsilon^3}}$ .

$$u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} + w\frac{\partial T}{\partial z} = \frac{K_{eff}}{\rho C p} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right)$$
(5)

$$k_{\rm eff} = \varepsilon k_{\rm nf} + (1 - \varepsilon) k_{\rm s} \tag{6}$$

Nusselt number can be computed by:

$$Nu = \frac{k_{nf}}{k_{bf}} \cdot \left(\frac{\partial T}{\partial x} \cdot \frac{D_h}{T - T_{in}}\right)$$
(7)

Average Nusselt number:

$$\overline{\mathrm{Nu}} = \frac{1}{\mathrm{A}} \int \mathrm{Nu} \, \mathrm{dA} \tag{8}$$

ANSYS 14.0 [12] software has been used for this numerical study. Coupled algorithm based on finite volume method was used to discretize the partial differential Eqs. (1-5). Constant velocity inlet, constant heat flux, and atmospheric pressure

#### Fig. 1 Mesh domain



outlet boundary conditions were applied to the computational domain. A mesh of 432,000 elements was adopted in this simulation (see Fig. 1).

### **3** Validation

To verify the reliability of this domain, results were compared with experimental results of Chen et al. [13], for copper foam of porosity 0.9 and laminar flow of TiO<sub>2</sub>– H<sub>2</sub>O nanofluid (Re: 414–1179) at constant nanoparticle concentration ( $\phi = 0.3\%$ ) as illustrated in Fig. 2. Numerical results are in good agreement with the experimental ones, showing a maximum relative error of less than 4%.





### 4 Results and Discussion

Laminar forced convection of Fe<sub>3</sub>O<sub>4</sub>–H<sub>2</sub>O is simulated for Reynolds number range  $400 \le \text{Re} \le 1100$ , nanoparticle concentration  $\phi = 0.3\%$  and diameter of nanoparticle dn = 20 nm. Results are presented in terms of Nusselt number, temperature, temperature and velocity counters detailed in this section.

Figure 3 shows a comparison of surface temperature exposed to heat flux cooled by water and nanofluid. Temperature decreases as flow accelerates, but cooling is efficient with nanofluid as surface temperature drops to 304.8 °C, versus using water where temperature is 318 °C at Re = 1100. That is due to penetration of nanofluid into pores of copper foam loaded with oxidized iron nanoparticles, which transmit heat rapidly on account of their high conductivity compared to pure water molecules.

The variation of average Nussult number in term of Re is presented in Fig. 4. In accordance with the majority of previous research [10],  $Nu_{avg}$  increases with flow velocity. This is due largely to a rise in heat exchange coefficient h as a result of forced convection of nf into copper foam, which creates a large surface area for heat exchange, leading to a lower convection/conduction ratio. The use of nanofluid enhances heat transfer by 50% compared to water at Re = 600.

Understanding the thermal cooling of heat sink, Fig. 5 plots temperature contours at Re = 900 for both cooling fluids (a) nanofluid, (b) water). Isotherms are denser around heated surfaces, explaining heat transfer between a heat sink and CPU. In porous regions, temperatures are more steady, indicating that copper foam has been able to remove excess energy internally from the CPU through greater conductive heat transfer. Isotherm length in Fig. 5a is less than in Fig. b where water flows into heat sink. When nanoparticles are added, the thickness of thermal boundary layer on bottom surface of heat sink decreases due to collisions between particles and porous medium. All this improves the efficiency of heat exchange, so temperature drops significantly.







Fig. 5 Heat sink temperature contours at Re = 900

Figure 6 present velocity contour of water inside heat sink at Re = 900. It is clear that velocity is highest in areas without metal foam. This can be explained by foam pores acting as a barrier to water passage, in addition to the collisions occurring between water and porous medium.



### 5 Conclusion

Addition of nanoparticles to base fluids is an attractive technique that has been used in many fields and proven effective in a numerous investigations. This numerical study aims to improve cooling efficiency of electronic components using nanoparticles and porous media. The flow of water and nanofluid ( $\phi = 0.3\%$ ) inside a heat sink filled with copper foam ( $\varepsilon = 0.8$ ) was compared. Main results obtained can be summarized as follows:

- The addition of Fe<sub>3</sub>O<sub>4</sub> nanoparticles to the base fluid at constant concentration improves heat transfer by up to 50% compared with water.
- Using copper foam leads to an enhancement of Nusselt number at constant porosity.
- The presence of nanoparticles reduced heat sink temperature to 14 °C, thus improving cooling efficiency.

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# **Enhancing Photoluminescence and Crystallinity Through Aluminum Doping in Sol–Gel Zinc Oxide Thin Films**



Ibrahim Yaacoub Bouderbala D and Imed-Eddine Bouras

**Abstract** This study investigates to see how aluminum (Al) doping affects the optical and photoluminescent properties of sol–gel zinc oxide (ZnO) thin films. The sol–gel method was used to produce Al-doped ZnO films, which were further investigated using X-ray diffraction, UV–VIS spectrophotometry, and photoluminescence studies. According to the findings, increased Al doping concentrations resulted in reduced crystallinity and a blue shift in the UV emission peak, which was ascribed to the Moss-Burstein effect. Al doping prohibited the visible emission band, but higher annealing temperatures enhanced film quality and the UV-to-visible emission ratio. This research looks at the link between Al doping, crystallinity, and photoluminescence in Al-doped ZnO thin films.

Keywords Aluminum doping · Zinc oxide thin films · Photoluminescence

### 1 Introduction

Zinc oxide (ZnO) has attracted considerable attention for its multifunctional utility in a wide range of applications, including antireflection coatings, transparent solar cell electrodes [1, 2], thin film gas sensors [3, 4], spintronic devices [5, 6], and lightemitting diodes [7, 8]. This attractiveness comes from its large band gap, exceptional chemical and thermal stability, and exceptional electrical and optoelectronic properties as an II-VI semiconductor with a high exciton binding energy. ZnO shows

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tetrahedral coordination of Zn atoms with O atoms in its usual hexagonal configuration with values a = 3.25 and c = 5.12, resulting in hybridization of Zn d-electrons with O p-electrons [9].

Chemical doping has a significant impact on the electrical and optical properties of ZnO, making the control of defects essential to practical ZnO applications. Doped ZnO thin films have a wide range of applications, including transparent conducting electrodes [10], insulating or dielectric layers [11], and spintronic devices [4]. Notably, Al-doped ZnO (AZO) films have drawn interest as transparent conducting electrodes due to their excellent conductivity and optical transparency [10]. Intrinsic defects present in undoped ZnO, such as Zn vacancies, interstitial Zn, O vacancies, interstitial O, and antisite O ( $O_{Zn}$ ) [12], contribute to acceptor or donor levels inside the band gap, altering ZnO's luminescence properties considerably [13]. When external dopants, such as Al, are introduced, the defect structure changes because Al atoms either replace for Zn atoms or occupy interstitial positions. As a result, understanding the effect of Al doping on the characteristics of AZO is essential.

The sol-gel method is used in this work because of its precise compositional control, molecular-level uniformity, and lower crystallization temperatures. Nacib et al. [14] and Sharmin et al. [15] have recently investigated the electrical and optical properties of c-axis-oriented sol-gel AZO films. We expand the investigation in this paper to investigate the optical and photoluminescent behavior of sol-gel ZnO films, taking into consideration the impacts of aluminum doping and subsequent annealing.

### **2** Experimental Details

## 2.1 Deposition of Thin Films by Sol–Gel Process

The basic starting material for the current investigation was zinc acetate 2-hydrate (99.5% purity,  $Zn(CH_3COO)_2H_2O$ ). The solvent was absolute ethanol, and the sol stabilizer was diethanolamine (HN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, DEA). Aluminum was used as a dopant, using Al(NO<sub>3</sub>)<sub>3</sub>9H<sub>2</sub>O with 0.0025 and 0.0050 M. In a 100 mL conical flask, dissolve 0.5 M of zinc acetate 2-hydrate in 0.1 L of 100% ethanol. DEA was steadily added drop by drop during 30 min of vigorous stirring, keeping a constant DEA/Zn<sup>2+</sup> molar ratio of 1. The solution became clear after about 20 min of stirring. Before being used for thin film coating, it was constantly swirled overnight.

The dip coating process was used to create thin AZO films around 300 nm thick on supporting substrates. Prior to deposition, rigorous cleaning was performed using distilled water, ethanol, and acetone, followed by distilled water washing, and finished with drying using a nitrogen gas gun. After immersing the cleaned substrates in the sol, they were removed at a rate of 1.12 mm/s, yielding homogeneous films. After every dip coating, the films were direct dried at 200 °C for 10 min. This method was done six times followed by an hour of annealing at 400 and 600 °C in an air environment.

### 2.2 Characterization of Thin Films

X-ray diffraction (XRD) was used to identify crystal phases. A Philips PW3710 diffractometer with CuK1 radiation at 40 kV and 45 mA was used to obtain XRD patterns. The optical properties of films were examined using a UV–VIS spectrophotometer (HP 8453) and normal incident transmittance measurements. A SPEX 750 M PL spectrometer was used to perform photoluminescence (PL) measurements. A 325 nm He-Cd laser with a power output of 4 mW at room temperature was used to excite the samples.

### **3** Results and Discussion

Figure 1 depicts the X-ray diffraction (XRD) patterns of AZO thin films after 1 h of annealing at 400 °C in an air environment. All samples are polycrystalline, having a hexagonal structure (JCPDS 36-1451), and distinct peaks observed within the reported range. The XRD investigation revealed no further crystalline phases. Figure 1 shows that when doping concentrations increase, the intensity of the diffraction peaks decreases but the Full Width at Half Maximum (FWHM) of these peaks increases. This pattern indicates a decrease in film crystallinity. Because of the fast diffusion of Zn interstitials, grain formation in ZnO is often enhanced at temperatures over 327 °C [16]. However, in the case of trivalent cation doping, the concentration of zinc interstitials is reduced for charge balance, resulting in slowed ZnO grain development and a concomitant drop in crystallinity [17]. This reduction in crystallinity indicates that Al has been integrated into the ZnO structure.

Figure 2 shows the optical transmission spectra of AZO films after 1 h of annealing at 400 °C in an air environment. Within the visible range, all films exhibit an average optical transparency of more than 80%. The oscillations seen in the spectra are caused mostly by interference between the thin film layers. These interferences fringes patterns are seen in the spectra of all samples, highlighting the film's excellence and homogeneity. They are caused by the flat surface of the films and the interaction with the FTO substrate. This implies that the film surfaces reflect with little scattering or absorption inside the film [18, 19]. Multiple reflections between the lower substrate-contacting surface and the layer's free surface cause interference fringes to form across all wavelengths. As a result, the transmission spectrum peaks and minima vary as a function of wavelength. The envelope approach makes it easier to determine the optical thickness and refractive index of a semiconductor by utilizing its characteristic transmission spectrum profile. The refractive index and thickness of substrate must be determined for this approach. A refractometer was used to measure the glass's



Fig. 1 XRD patterns of AZO films annealed at 400 °C with diffrent doping concentrations

refractive index, which was 1.52. With these characteristics determined, the indices and thicknesses of the ZnO nanostructures may be calculated.

The envelope approach is to trace envelop curves around the transmission curve, which connects the maxima  $(T_M)$  and minima  $(T_m)$  as continuous functions of wavelength. This method, based on the Swanepoel method, makes use of  $T_M$  and  $T_m$  arising from the interference fringes. The approach is particularly successful in calculating the refractive index and thickness in the low-absorption and transparent portion of





the transmission spectrum. The thickness is determined from the following equation [20]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \tag{1}$$

 $n_1$  and  $n_2$  are the refractive indices of the layer for the wavelengths  $\lambda_1$ ,  $\lambda_2$  and are taken from the relationship:

$$n = \left[N + \left(N^2 - n_S\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$
(2)

In addition, N can be calculated by the relation:

$$N = \frac{2n_S(T_M - T_m)}{T_M T_m} + \frac{n_S^2 + 1}{2}$$
(3)

With  $n_s$  is the index of the substrate and  $T_M$  and  $T_m$  are the transmission values for the upper and lower envelope respectively for a chosen wavelength. The basic equation for interference fringes is given by [20]:

$$2d = m\lambda \tag{4}$$

where, the order numbers *m* is integer for maxima and half integer for minima.

The results shown in Table 1 show that there is a notable tendency of increased thickness with increasing Al atom concentrations. This increase in the thickness correlates to a decrease in transmission, as shown in Fig. 2. The increase of Aldoped ZnO thin films can be attributed to the formation of atoms' clusters as the aluminum is incorporated in the ZnO lattice during the sol–gel formation [21–23].

From UV spectra, there is a visible blue shift in the UV absorption edge as the Al doping concentration increases, as shown in the inset of Fig. 2. This alteration indicates that the optical band gap (Eg) is increasing. ZnO has a direct band gap in its wurtzite structure, and the absorption edge associated with a direct interband transition is described by the Tauc's formula [24].

Figure 3 shows the  $(hv)^2$  plotted versus photon energy  $(\alpha hv)$  for all samples. The linear relationship found at higher photon energy implies that the AZO films are fundamentally direct-transition-type semiconductors. The optical band gap is obtained by extrapolating the linear component of the curve to zero. Figure 3 shows

and thickness of the ZnO		Refraction index	Thickness (nm)	
estimated by the envelope method	Undoped	1.852	275.14	
	Doped with 0.0025 M	1.873	281.38	
	Doped with 0.0050 M	1.906	289.47	

Fig. 3 Tauc's plot of AZO with different Al concentration



that  $E_g$  is 3.27, 3.31, and 3.34 eV for AZO thin films with Al doping concentrations of 0, 0.0025, and 0.0050 M.

The Moss-Burstein shift [25] refers to the increasing of the band gap. According to the Moss-Burstein hypothesis, donor electrons occupy states near the bottom of the conduction band in strongly doped zinc oxide films. Valence electrons require greater energy to move to higher energy levels inside the conduction band due to the Pauli exclusion principle and the vertical character of optical transitions. As a result, the optical band gap of doped zinc oxide films is larger than that of undoped zinc oxide films.

Figure 4 displays the Photoluminescence (PL) spectra of AZO films annealed at temperatures ranging of 400 and 600 °C. Two emission bands exist: a strong and narrow UV luminescence about 382 nm and a wide visible emission ranging from 450 to 640 nm, resulting in the green-yellow region [26]. Temperature and Al doping concentration have an effect on these emission bands. Notably, when Al doping increases, the UV emission almost blue-shifts and deteriorates, whereas the visible emission is inhibited. Elevating the annealing temperature improves UV emission and raises the UV-to-visible emission ratio, resulting in improved film quality.

Free exciton emission is responsible for the UV emission peak at 382 nm. The blue shift in the UV peak with increased Al doping corresponds to the trends found in the transmittance spectra, which are caused by the Moss-Burstein shift, which increases the band gap. The prior XRD data indicate that the attenuation of UV emission is potentially connected to poor film crystallinity produced by the addition of Al. The reduction in structural flaws is responsible for the increase in the UV-to-visible emission ratio.

This result clearly suggests that the integration of Al as dopant with different concentration caused a compromise in the crystalline structure of the all the films,



which is consistent with the observed XRD. As a result, our results present a complete view of the effect of Al doping on the photoluminescent behavior of Al-doped ZnO thin films, revealing a link between variations in crystallinity, PL intensity, and Al concentration [27].

### 4 Conclusion

Finally, our study gives information on the complex relationship of aluminum doping, crystallinity, and photoluminescence characteristics in sol–gel zinc oxide thin films. The results of the study highlight the impact of Al doping concentrations on film quality, with greater doping resulting in impaired crystallinity and changed emission characteristics. The connection between doping and optoelectronic behavior is demonstrated by the blue shift in the UV emission peak, which is connected to the Moss-Burstein shift owing to increased band gap. Furthermore, increasing UV emission and the UV-to-visible emission ratio through higher annealing temperatures reveals an approach to better film quality. These findings add to our understanding of doped semiconductor materials and their prospective uses in optoelectronic devices.

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# Structural Characterization of Chorine Doped Cuprous Oxide Thin Films by X-Ray Diffraction and X-Ray Fluorescence



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Abstract This study investigates the structural changes in Cl-doped Cu<sub>2</sub>O thin films through X-ray diffraction (XRD). The incorporation of Cl<sup>-</sup> ions into the Cu<sub>2</sub>O lattice is analyzed at varying concentrations. XRD patterns reveal shifts in the (111) peak due to Cl<sup>-</sup> ion interaction, indicative of interstitial and substitutional incorporation. The lattice parameter and interatomic distance are compared between theoretical and experimental values, reflecting volume changes caused by Cl<sup>-</sup> ion presence. At lower concentrations, interstitial incorporation contracts the lattice, while higher concentrations lead to lattice expansion through substitutional incorporation. These findings provide insights into the structural modifications induced by Cl<sup>-</sup> doping, crucial for understanding the conductive properties of the thin films.

Keywords  $Cu_2O$  thin films  $\cdot Cl^-$  doping  $\cdot$  Structural modification

## 1 Introduction

Extensive study into the creation and manipulation of nanostructures with special electronic properties has been stimulated by the quest for effective and adaptable semiconductor materials [1, 2]. Cuprous oxide (Cu<sub>2</sub>O) nanostructures, one of these, have drawn a lot of interest because of their fascinating properties and prospective uses in optoelectronics, catalysis, and energy storage devices [3, 4]. A possible way to modify Cu<sub>2</sub>O nanostructures' characteristics for particular purposes is by controlled electrodeposition [5]. In order to understand the role of doping and their impact on

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85

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the final properties, this research explores the complex interplay of electrochemical processes and crystal lattice alterations during the electrodeposition of  $Cu_2O$  films.

Due to their abundance, nontoxicity, and low cost, cuprous oxide (Cu<sub>2</sub>O) thin films with high oriented crystalline structure along (111) plane are extensively researched for practical applications [6, 7]. Because of the work of Kennard et al., [8] Cu<sub>2</sub>O is the first known material to exhibit p-type semiconductor behavior since 1917. Cu<sub>2</sub>O is one of the most promising metal oxides for the production of optoelectronic devices like solar cells because of its straight band gap of 2 eV [9]. Sol–gel approach [10], chemical vapor deposition (CVD) [11, 12], oxidation of metallic copper [13], chemical bath deposition [14], and electrochemical deposition [15–19] are a few techniques that have been utilized to synthesize Cu<sub>2</sub>O nanostructures.

The incorporation of doping agents, specifically chloride ions (Cl<sup>-</sup>), into the Cu<sub>2</sub>O lattice, is a significant aspect of this work. Dopants can significantly change a material's electronic structure, resulting in changes to the conductivity type and structural characteristics [20]. This study attempts to elucidate the mechanisms underlying the change from p-type to n-type conductivity in Cu<sub>2</sub>O thin films by closely examining the impact of Cl<sup>-</sup> ions on the crystal lattice [20].

To customize semiconductor structures' characteristics for particular applications, dopant ions are crucially important.  $Cu_2O$  has drawn attention for doping investigations because of its potential for optoelectronic and energy applications. In this situation, X-ray diffraction (XRD) appears as an effective method to explain the structural alterations brought on by dopants. Particularly, the influence of  $Cl^-$  ions on conductivity and optoelectronic behavior has drawn attention to the inclusion of  $Cu_2O$  thin films with  $Cl^-$  ions. By examining the crystalline lattice and locating shifts in diffraction peaks, XRD enables us to learn more about the locations and interactions of the dopant ions.

This study uses XRD analysis to look at the microstructural development of Cl<sup>-</sup> doped Cu<sub>2</sub>O thin films. Cl<sup>-</sup> ion concentration-dependent variations in the (111) peak provide information about the incorporation processes, including whether substitutional or interstitial sites are involved. To measure the structural changes brought on by Cl<sup>-</sup> doping, theoretical values for the lattice parameter and interatomic distances will be compared with experimental data. Optimizing the characteristics of Cu<sub>2</sub>O thin films for varied purposes requires a thorough understanding of these structural alterations.

### **2** Experimental Details

Cu<sub>2</sub>O films were prepared using electrochemical cell with three electrodes. A platinum electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. A fluorine tin oxide (FTO)-coated conducting glass substrate was used as working electrode. The substrates were cleaned ultrasonically in acetone and methanol for 20 min, then rinsed in distilled water and dried naturally. Different concentrations of sodium chloride (NaCl) varying from 0.002 to 0.010 M were dissolved in distilled water with 0.1 M of copper nitrate (CuNO<sub>3</sub>), after that, 1 M of lactic acid (C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>) was added to all electrolytes as a complexing agent to prevent the precipitation of copper when adding NaOH to the solution to adjust the pH to 9.5. The temperature and time deposition were maintained at 70 °C and 25 min respectively.

Using a Rigaku Ultima IV and JEOL JDX 3530 diffractometer (40 mA, 45 kV) with CuK1 radiation ( $\lambda = 0.15406$  nm) in a Bragg–Brentano geometry (2 $\theta$ ) between 27° and 75°, the structures of Cu<sub>2</sub>O thin films were examined. It has become imperative to investigate how Cl<sup>-</sup> ions are incorporated into the Cu<sub>2</sub>O crystal lattice. X-ray fluorescence (XRF) investigations were carried out for this purpose utilizing a JEOL—JSX-3201 M spectrometer (150 kV, 1 mm diameter collimator).

### **3** Results and Discussion

A voltametric investigation is required to determine the potentials of the current oxidation–reduction reactions in the electrolyte and to select the proper potential to deposit  $Cu_2O$  by chronoamperometry in order to explore the  $Cu_2O$  nanostructures electrodeposition process. By supplying a constant voltage between the FTO and the counter electrode referred to a SCE,  $Cu_2O$  nanostructures are electrodeposited.

Several publications [21-23] have anticipated electrochemical reaction to produce CuCl in the presence of Cl<sup>-</sup> ions in the deposition bath. Assuming that Cl<sup>-</sup> doped Cu<sub>2</sub>O was formed by the insertion of Cl<sup>-</sup> into the Cu<sub>2</sub>O lattice, the low solubility of CuCl suggests that even small concentrations of Cu<sup>+</sup> and Cl<sup>-</sup> in the solution will react and precipitate. Since chlorine atoms have a radius greater than the oxygen, chlorine atoms positioned in an interstitial position act as donors. In the case that chlorine is positioned in substitutional site, they will act as acceptors. It is well known that the copper and oxygen sites in cause doping, which results in p and n doping, respectively [24].

We used photocurrent measurements to identify the different semiconductors' conductivity types. Only a system made up of a light source, a lighting switch, a threeelectrode cell containing 0.8 M Na<sub>2</sub>SO<sub>4</sub>, and a potentiostat may be used to perform this approach. We see cathodic current generated by some films, one of which is undoped and the others two doped with 0.002 and 0.004 M of chloride ions as shown on Fig. 1a, indicating that the depletion zone is negatively charged. As a result, in the presence of light, the holes flow in the direction of the semiconductor layer and the electrons in the direction of the electrolyte. This demonstrates clearly that these semi-conductors exhibit p-type conductivities. The depletion zone of the other films, on the other hand, produces an anodic current as we can see on Fig. 1b, which is positively charged. In this case, n-type conduction is clearly obtained with increasing the Cl<sup>-</sup> concentration because holes go toward the electrolyte while electrons move toward the layer.

Figure 2a demonstrates how the Cu/O atomic ratio changes depending on the amount of dopant present as well as the proportion of Cl<sup>-</sup> ions included in the



Fig. 1 Photocurrent measurements for undoped and doped Cu<sub>2</sub>O nanostructures with different Cl<sup>-</sup> concentration **a** Cu<sub>2</sub>O-**p**, **b** Cu<sub>2</sub>O-**n** 

crystalline lattice. These findings show that copper and oxygen atoms are abundant in all thin layers of  $Cu_2O$  and that the concentration of  $Cl^-$  ions in the deposition bath affects how quickly  $Cl^-$  ions are incorporated into the crystal structure.

Additionally, according to the JCPDS Sheet No. 00-005-0667, XRF investigation showed that the Cu/O atomic ratio of the two type-p thin layers is less than the theoretical ratio of Cu<sub>2</sub>O, which is equal to 2. This suggests that there are copper vacancies (VCu) in the crystal lattice, which explains why the conduction is p-type. However, compared to the predicted ratio, the atomic ratio of the other thin layers



Fig. 2 a Copper/oxygen atomic ratio and rate of incorporated chloride ions in the crystal lattice of  $Cu_2O$ , b XRD diffraction patterns of thin  $Cu_2O$  layers prepared at different chloride ions concentrations

is higher. This explains why there is a change in conduction when  $Cl^-$  ions are incorporated into substitutional sites ( $O^{2-}$ ).

X-ray diffraction (XRD) investigations were carried out to identify existing phases and analyze the microstructural development of the thin Cu<sub>2</sub>O layers. Figure 2b displays the X-ray diffraction patterns of doped and undoped Cu<sub>2</sub>O thin layers produced by electrodeposition at E = -0.3 V/ECS. The tetragonal phase of the FTO substrate is indicated by the peaks denoted by stars.

The (111) orientation crystallizing in the cubic phase is indicated by the existence of a Cu<sub>2</sub>O peak at  $36.5^{\circ}$  (JCPDS No. 00-005-0667), according to XRD studies. Cu<sub>2</sub>O thin layers grow perpendicular to the (111) plane since all the other peaks show a small intensity comparing to the (111), and no other peaks representing other phases or impurities were found, which mean that our film are pure Cu<sub>2</sub>O. Han et al. [25] discovered the same outcome when they placed thin layers of Cl-doped Cu<sub>2</sub>O on a gold (Au) substrate; they only got one Cu<sub>2</sub>O peak that corresponded to the (111) orientation. The crystalline planes' surface energies, which control crystal development along these planes, are the cause for that.

Calculating the texture coefficient  $T_C(hkl)$  given by the following calculation [16] is necessary to confirm the Cu<sub>2</sub>O thin films' preferred orientation:

$$T_{C}(hkl) = n \frac{I_{m}(hkl)/I_{0}(hkl)}{\sum_{1}^{n} I_{m}(hkl)/I_{0}(hkl)}$$
(1)

where n is the total number of diffraction peaks taken into account in the evaluation (5 in our case),  $I_m$  is the measured relative intensity of the peak corresponding to the hkl diffraction,  $I_0$  is the relative intensity from the identical diffraction in the standard powder sample. Figure 3 illustrates how the concentration of chloride ions changes the textural coefficient of Cu<sub>2</sub>O thin films along different crystallographic planes. While the texture coefficient along the other planes nearly stabilizes, it increases with an increase in Cl<sup>-</sup> concentration for the major peak orientation of (111), which is higher than that for the other planes. The (111) peak intensifies as Cl<sup>-</sup> increases, which is related to an increase in the number of grains along that plane and suggests improved crystallinity.

A decrease in full width at half maximum (FWHM) is seen when comparing the deposited samples, which causes an increase in crystallite size and the creation of microstructural changes in  $Cu_2O$  nanostructures. By applying the traditional Scherrer's relation [20, 26] to the (111) peaks, the average crystallite size was determined:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where  $\theta$  is the diffraction angle,  $\beta$  is the full width at half maximum (FWHM) given in radians, and  $\lambda$  is the X-ray beam's wavelength ( $\lambda = 1.5406$ ). For the undoped Cu<sub>2</sub>O films and doped with 0.002, 0.004, 0.006, 0.008, and 0.01 M of Cl<sup>-</sup> concentrations, the crystallite size (D) was determined to be 70.14, 73.42, 77.89, 84.57, 89.15, and





90.11 nm, respectively. The crystallite size increase with the chloride ions indication the successful of incorporation of chloride ions in the structure of cuprous oxide by changing the structural properties.

The relative surface energies for a cubic structure like  $Cu_2O$  are 111, 100, and 110. Bravais' law [27] and the Gibbs-Wulff growth theory indicate that faces with greater surface energies will crystallize more quickly, reducing their surface area. Lower surface energy faces will develop more slowly, increasing their surface area.  $Cu_2O$  thin layers will grow perpendicular to the (111) face in our situation because it has a lower surface energy due to the intensity of the (111) peak compared to other orientations. The (110) and (100) faces will disappear progressively due of the quickest crystal development, while the (111) will gradually appear because of the slower growth rate.

Depending on the deposition conditions, thin layers of Cu<sub>2</sub>O with the (111) orientation will be easier to create than layers with other orientations (or crystalline planes). The (111) peak becomes more intense for a concentration of 0.008 M compared to other depositions, showing good crystallinity. As the concentration of Cl<sup>-</sup> ions rises, it can be seen from the diffraction patterns that the FWHM of the (111) peaks decreases, suggesting an increase in the average size of the crystallites and creating microstructural changes in the crystalline lattice. Dislocations and/or stresses, which are present in these alterations, are reduced as the average size of the crystallites rises.

 $Cu^+$  ions will combine with  $Cl^-$  ions to create CuCl during the deposition of thin layers of  $Cu_2O$  at varied  $Cl^-$  ion concentrations, shifting the (111) peak for the various  $Cl^-$  doped  $Cu_2O$  layers. The non-dimensionalized curves of the (111) peak





are shown in Fig. 4. Because most  $Cl^-$  ions are in interstitial sites, a level of acceptor is produced above the valence band, as shown by the peak shift of the  $Cu_2O$  doped with 0.002 and 0.004 M towards higher angles. This explains p-type conductivity [28] quite effectively.

The peak shift is seen when the Cl ions in the deposition bath is increased; this time, the peak shift is towards lower angles, suggesting that the majority of  $Cl^-$  are incorporated in substitutional oxygen sites, resulting in a switch from p-type to n-type conductivity. As a result, a donor level below the conduction band is created [29].

When comparing the theoretical values of the lattice parameter (a = 4.269 Å) and the interatomic distance (d<sub>hkl</sub>) with the experimental values of Cu<sub>2</sub>O (a<sub>undoped</sub> = 4.2574 Å, a<sub>0.002</sub> = 4.2562 Å, a<sub>0.004</sub> = 4.2557 Å, a<sub>0.006</sub> = 4.2596 Å, a<sub>0.008</sub> = 4.2599 Å, a<sub>0.010</sub> = 4.261 Å), we notice a slight difference, which is attributed to the constraints associated with the deposition method. The incorporation of Cl<sup>-</sup> ions into the Cu<sub>2</sub>O lattice doped with 0.002 and 0.004 M chlorine ions led to a decrease in the lattice parameter, resulting in a contraction of the volume of the Cu<sub>2</sub>O lattice. This strongly indicates the insertion of Cl<sup>-</sup> ions into the deposition bath increases, we observe an increase in the lattice parameter, leading to lattice expansion and an increase in the volume of the Cu<sub>2</sub>O lattice. This confirms the incorporation of Cl<sup>-</sup> ions into the substitutional oxygen sites.

## 4 Conclusion

In conclusion, XRD has provided valuable insights into the structural changes induced by Cl<sup>-</sup> doping in Cu<sub>2</sub>O thin films. The shifts in the (111) peak position as a function of Cl<sup>-</sup> ion concentration clearly demonstrate the different incorporation mechanisms. The lattice parameter variations and interatomic distances further confirm these structural modifications. At low concentrations, interstitial incorporation contracts the lattice, while substitutional incorporation at higher concentrations leads to lattice expansion. These findings highlight the role of Cl<sup>-</sup> in altering the crystalline structure of Cu<sub>2</sub>O thin films, which in turn impacts their electrical and optical properties. This study contributes to the fundamental understanding of dopant-induced structural changes and their implications for Cu<sub>2</sub>O's potential applications in optoelectronics and energy devices.

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# Experimental Study on the Effect of Drying on the Kinetics of Cubic Beetroot Slices Using an Industrial Electric Food Dehydrator



### Soufounizia Boultif, Noureddine Belghar, and Foued Chabane

**Abstract** Fresh beetroots need appropriate storage methods due to their high moisture content, since failure to do so would result in their decay and subsequent disposal. Drying is often regarded as one of the most effective methods of preservation. This study investigates the impact of using an industrial electric food dehydrator on beetroot slices of varying thicknesses, namely 3, 4, and 5 mm. When subjected to an airflow at a temperature of 50 °C for 225 min, the initial weights of the objects were 30 grammes, 31 grammes, and 45 grammes, respectively. The final results indicated a significant reduction in the importance of the beets, with measurements of 0.5 g, 0.1 g, and 0.6 g, respectively, which suggests that the water removal rate was fast. Furthermore, the beetroot transformed its physical structure, adopting a chip-like shape while retaining its original colour. The electric food dehydrator is efficacious in addressing all three aspects mentioned.

Keywords Drying · Beetroot · Kinetics

## 1 Introduction

Red beetroots are essential vegetables due to their nutritional and physiological benefits. Its high magnesium and potassium content and low sodium concentrations improve human ionic equilibrium. Betacyanins reduce oxidative stress and free

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95

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radical damage. They combat viruses and germs, prevent cancer, and prevent heart disease [1].

Besides its many active components, beetroot is a superfood with many health advantages. Antioxidants in beetroots inhibit tumour growth and kill malignant cells. Evidence suggests it is most beneficial for prostate, colon, and breast cancer, but it also promotes pancreatic cancer recovery [2].

Due to its high fibre and saponin content, beetroot cleanses the intestines and blood and aids in natural detoxification. Optimising nutrition absorption requires improved digestion and regular, full waste evacuation. Beets help reduce deficiencies-related illnesses. It optimises liver function and treats cirrhosis, hepatitis, and other liver diseases. Beetroot reduces digestive tract inflammation and relieves discomfort [3]. Drying reduces water activity to preserve this superfood, preserve its nutritious worth, and prevent bacterial and fungal contamination: Drying involves evaporating water to transfer bulk. In recent years, it has been used to preserve food by eliminating water. As health-conscious people learn more about natural products, beets (Beta vulgaris) have gained popularity as a functional food. Numerous research have examined this topic, including Shekhar Pandharipande and Bhushan Bele's artificial neural network study on sodium chloride content, time, and temperature's effects on beetroot slice drying and weight loss. The findings show that salt solution osmotic dehydration can dewater beetroot slices [4].

In their paper, Kulwinder Kaur and A. K. Singh explain their beetroot drying and quality trials with air temperature and microwave power. Osmotically prepared materials were dehydrated using a convection Tray. High air temperature (75 °C) and microwave power (1080 W) increased drying rates and lowered drying time [5].

Whereas Adam Figiel et al. made 18-mm-diameter beetroot slices with variable thicknesses in 40Bx chokeberry juice at 50 °C for two hours before vacuummicrowave (VM) drying at various microwave power levels. This increased its bioactivity. Increased sample specific surface area led to shorter drying periods, lower material temperatures, and better dried product quality [6].

Bhupinder Singh and Bahadur Singh Hathan's work aimed to enhance the beetroot juice spray drying procedure. Using the response surface method, many parameters were checked. The models were shown to be correct when the experimental data matched the expected values [7].

Recently, some new methods have been looked into. For example, Vallespir et al. studied how freezing before drying and ultrasonic waves affected beetroot microstructure, drying curves, and bioactive compounds. Results showed that both methods improved drying mass transfer [8].

A cutting-edge hybrid dryer was employed for drying trials. However, Dominik Mierzwa et al. used high-power airborne ultrasound, microwaves, and hot air to study how drying red beets in short bursts affected process kinetics and quality indicators. Hybrid drying periodically improves drying speed and output quality while lowering drying duration and power usage, the result being a more porous, pleasant-colored, and crispy vegetable product [9]. In another work by Atul Dhiman et al., Besides freeze-drying and spray-drying, they discuss various beetroot treatments. It showed beetroot can form stable microcapsules. By making beetroot more tasty,

consumers can get more nutrition from these products [10]. SantanuMalakar et al. also tested an evacuated tube sun dryer (ETSD) with and without beetroot slices. ETSD and sun drying were used to compare beetroot slice drying kinetics, mass transfer phenomena, colour changes, and bioactive component preservation. ETSD dried many food commodities quickly and retained quality attributes [11]. The goal of the study by Yan Liu et al. was to evaluate the effects of hot air drying beetroot slices at 50–100 °C on their physicochemical and drying properties. Raising temperatures may cut drying time from 12.5 to 4.5 h. Beetroot slices dried at 60 °C showed the last colour variation [12].

To determine the features of beetroot dried in a cabinet Tray dryer at 600 °C with pretreatment, Vipul Chaudhary and Vivek Kumar conducted an experimental investigation. The findings showed that the pretreatments T3 (bleaching) and T4 (steam blanching) were determined to be of higher quality than other pretreatments. It also demonstrated that, compared to other powders, these two pretreatments offer the highest functional qualities for beetroot powder [13].

Nikola Tomic et al. aimed to compare the sensory properties and acceptance of dried, ready-to-eat beetroot snacks due to various drying methods: CO<sub>2</sub>-drying, freeze-drying, and frying. Direct scCO<sub>2</sub>-drying without a pre-cooking step emerged from the sensory evaluation as a promising alternative drying process in making dried beetroot snacks. The main drawbacks of freeze-drying were look and flavour [14]. Finally, Manhal Gobara Hamid and Abdel Azim Ahmed Mohamed Nour's papers examine how drying methods affect beetroot slice quality. The chemical arrangement, total energy, mineral content, and nitrate content of dried slices were substantially higher than fresh slices [15].

### 2 Materials and Methods

### 2.1 Raw Materials

The experiment employed a local variety of fresh beetroot from the Biskra neighbourhood market. To remove soil and other accumulated material, they were carefully cleaned with water, then peeled and weighed. Finally divided into  $4 \times 3$  by 3, 4, and 5 mm-thick cubic slices.

#### 2.2 Method

A sealed stainless steel Nabertherm drying oven was used for the studies. Ventilated ovens improve room thermal homogeneity. The ventilation may be adjusted to suit the tank. Horizontal air circulation and a continuous back wall exhaust with a front adjustment control maintain temperature homogeneity within 5 °C. Self-diagnostic

#### S. Boultif et al.

#### Fig. 1 3 mm cubic slices



PID microprocessors control drying parameters. Max operational temperature is 3000 °C, range is + 30 °C above ambient to 3000 °C. Multi-level loading. After setting the drier to the right temperature, the samples were weighed and placed on three trays on the two tiers of the 50 °C electric food dehydrator. Slices of 3, 4, and 5 mm thickness weighed 30, 31, and 45 g in dry-ing trials. Each drying trial measured the product's mass by removing it from the drying chamber for 40 s until a steady weight was attained. These steps occurred every 15 min. Figures 1, 2 and 3 show the finished result after 225 min.

Fig. 2 4 mm cubic slices

Fig. 3 5 mm cubic slices





### **3** Nutritional Properties Before Drying

### 3.1 Before Drying

As shown in various studies, betta vulgaris, or beets, have several health-enhancing properties. They are rich in iron, vitamin C, and numerous vitamins and minerals. They also have the most incredible sugar content of any vegetable. They notably contain magnesium, potassium, betaine, and boron.

### 3.2 After Drying

According to Manthal Gobara Hamid's study, the chemical composition, total energy, minerals, and nitrate of the Tray-dried beet slices can be increased more than those of fresh beet slices [15]. Tray drying ensures a high content of it all due to the moderate drying temperature of 50 °C, which guarantees that all nutrients are conserved after drying.

### 4 Results and Discussion

The mass of water vapour is depicted in Fig. 4. As a time function, and we can see that  $m_{v1}$  begins at 7 g before changing until it reaches 0 g at 170 min.  $m_{v2}$  begins at 8.8 g and fluctuates until it reaches 0 g at 175 min. Finally,  $m_{v3}$  begins at 9 g before varying till it reaches 0 g at 230 min (Fig. 5).





The water enthalpy of the 3 mm-thick product begins at 2 w and fluctuates until 110 min, at which point it turns null. Then, at 120 min, 4 mm thickness begins at 2.4 W and fluctuates until it reaches zero. Finally, the thickness of 5 mm begins at 3.7 W and varies until 130 min, when it is null. These variations reflect the heat generated during drying within the chamber.

A bar graph of the mass of water vapour in time is revealed in Fig. 6. Where we observe that the first product has a minimum value of 1 W at three different times and 7.1 W at 75 min. The second product has a maximum weight of 9 W at the beginning and a minimum of 1 W six times. The third product has a minimum value of 1 W at four distinct points and a maximum weight of 9 W at the beginning.

In the line graph of the product mass in time function that appears in Fig. 7. We can see that Product One's mass starts at 30 g and decreases to 5 g after 195 min. Product Two's mass begins at 31 g and is reduced to 1 g after 210 min. The third product's mass begins at 45 g and shrinks to 6 g after 225 min. 13%. These values



**Fig. 5** A line graph that shows the water enthalpy in time function

give us the percentage of the product's weight loss: Tray 1, Tray 2, and Tray 3 were 13%, 3%, and 13%, respectively.

The temperature of the product is depicted in Fig. 8. As a function of time, and we can see that the first product has a maximum value of 57 °C at 160 min and a low value of 26 °C at the beginning. The second product, meantime, has the same minimum value as the first product and a maximum value of 53 °C at 190 min. The third product has a minimum value of 26.5 °C at the beginning and a maximum value of 54 °C at 225 min.

The temperature in time function is displayed in Fig. 9. And it is evident that the ambient temperature is almost constant between 28 and 29 °C. The temperature within the chamber fluctuates between 49.5 and 62.3 °C which is the highest temperature achieved during the drying. The overall temperature ranges from 38 to 42 °C.






## 5 Conclusion

In light of the results displayed in the curves, we came to the conclusion that this method is adequate for drying cubic beetroot slices because:

- There was a large loss in the mass of water vapor throughout the entire experiment.
- The product's mass shrank significantly during a brief period of roughly 4 h.
- The moisture extraction rate was fast and effective considering the loss in weight of the product Tray1, Tray2 and Tray3 respectively 13%, 3% and 13%.
- This method dried the samples in a time of 3–4 h to completely dry which is considered short.
- The highest temperature of the heated air was 63 °C obtained after almost an hour of drying.
- The maximum degree of heat of the product Tray 1, Tray 2 and Tray 3 was obtained at 57 °C, 53 °C and 54 °C, respectively at 160 min, 190 min and 225 min respectively.
- The total water enthalpy was decreased significantly to almost zero which means the evolved heat during drying was strong enough to release all of the product water.

Because of its ease of use, low operating costs, and practical design, this approach has been shown to be effective when compared to other vegetable drying techniques.

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## Effect of Dip-Coating Seed Layer on the Morphological and Optical Properties of ZnO Nanorods Growth by Hydrothermal Method



S. A. Aldhehabi and B. E. Belkerk

Abstract This paper presents the fabrication and characteristic analysis of ZnO nanorods grown on glass substrates using a two-step approach involving dip-coating for the seed layer and hydrothermal growth for ZnO nanorods. The study systematically investigates the effects of different dip-coating cycles using advanced characterization techniques to investigate the impact on the morphology, crystal structure, and properties of the nanorods, Incorporating field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) examination, and UV-VIS doublebeam spectrometry. The ZnO nanorods exhibit a hexagonal morphology, with average diameters ranging from 60 to 450 nm through control of the dip-coating cycles. X-ray diffraction analysis reveals improved crystallinity with increasing dip-coating cycles. The UV transmittance spectra show characteristic absorption peaks in the UV range (360-380 nm) for all samples, with a decreasing band gap observed as the number of dip-coating cycles increases. These findings provide valuable insights into tailored ZnO nanorod synthesis and their potential applications in areas such as photocatalysis and optoelectronics. The study contributes to the fundamental understanding of nanomaterial properties, offering pathways for optimizing ZnO nanorod-based devices and technologies.

Keywords Dip-coating · Hydrothermal · ZnO · Nanorods

105

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#### **1** Introduction

Zinc oxide (ZnO) has garnered significant attention in scientific and technological circles owing to its remarkable properties as a semiconductor material [1]. These attributes have stimulated extensive research, elevating ZnO's importance in nanotechnology [2], optoelectronics [3], and catalysis [4], among other disciplines. The crystalline structure of ZnO, predominantly wurtzite [5], bestows a multitude of advantageous traits upon the material. Notably, ZnO's direct bandgap endows it with exceptional light absorption and emission capabilities [6], rendering it an exemplary candidate for optoelectronic applications [7]. With an approximate bandgap energy of 3.37 eV, ZnO exhibits pronounced sensitivity to ultraviolet (UV) light [8], amplifying its value in UV photodetectors, sensors, and related devices. Additionally, ZnO displays a significant exciton binding energy of approximately 60 meV [9], greatly influencing its optical emission and charge carrier dynamics. The multifaceted attributes of ZnO offer boundless prospects for pioneering advancements in diverse technological applications.

The crystalline quality of ZnO films obtained through chemical and physical deposition processes exhibits significant variability, contingent upon the employed synthesis conditions and growth mechanisms [10]. Typically, these synthesized ZnO materials manifest polycrystalline structures, characterized by a diverse range of nanostructures with distinct optical and electrical properties [11].

In recent times, A variety of ZnO nanostructure forms have demonstrated promising optical and electrical characteristics, ZnO nanostructures have garnered remarkable prominence in the realm of miniaturized and high-performance semiconductor devices, primarily owing to their exceptional optical performance. Moreover, the utilization of diverse thin film deposition methods has facilitated the fabrication of these ZnO nanostructures, unlocking a plethora of applications encompassing light-emitting diodes [12], lasers [13], gas sensors [14], and UV photodetector [15].

In this study, we present a comprehensive investigation of ZnO nanorods fabricated on seed layers using varying dip-coating cycles (from 3 to 10) followed by hydrothermal growth. The morphological, structural, and optical characteristics of the produced ZnO nanorods will be systematically analyzed to gain deeper insights into the influence of deposition cycles on both the development and properties of the nanorods. The outcomes of this research hold great potential for advancing the understanding and application of ZnO nanorods in cutting-edge technologies.

#### 2 Experimental

#### 2.1 Sample Preparation and Deposition of ZnO Seed Layer

The ZnO thin seed layers were cultivated on the glass slides through a precise dipcoating process. For this purpose, a solution was prepared using Zinc acetate dehydrate  $Zn(CH_3COO)_22H_2O$  as the precursor and ethanol  $C_2H_6O$  as the solvent. A 0.025 M zinc acetate dehydrate solution was meticulously prepared by magnetic stirring in 90 ml of ethanol at room temperature for 2 h, followed by additional stirring for 60 min at 60 °C. Once a transparent solution was obtained, the dip-coating process was conducted under experimentally optimized growth conditions, Involving factors such as the concentration of the chemical precursor solution, withdrawal speed, and dipping speed.

Multiple deposition cycles were carried out to produce four distinct samples, denoted as 3 dip, 5 dip, 7 dip, and 10 dip, each possessing ZnO seed layers. To promote crystallization and structural integrity, all samples (3 dip, 5 dip, 7 dip, and 10 dip) underwent annealing in a furnace at 300 °C for a duration of 30 min. this precisely regulated thermal treatment guaranteed the development of sturdy and precisely delineated ZnO seed layers on the glass substrates.

#### 2.2 Growth of ZnO Nanorods

ZnO nanorods were meticulously cultivated via a hydrothermal process, building upon a well-established ZnO seed layer. The solution of the chemical precursor, an amalgamation of zinc acetate dihydrate  $(Zn(CH_3COO)_22H_2O)$  and hexamethylenetetramine [(CH)<sub>2</sub>6N<sub>4</sub>, HMT], was dissolved in distilled water at a precise equimolar ratio of 0.025 M.

To foster homogeneity and reactivity, the solution underwent meticulous magnetic stirring at ambient temperature for a duration of 2 h, followed by an additional hour within the reactor at 60 °C. The pursuit of a transparent and harmonious solution was relentlessly pursued, marking a pivotal milestone in the process.

The ZnO seed layer, previously germinated, became the foundation for the subsequent hydrothermal process. Submerging the samples into the hydrothermal reactor at precisely 80 °C for an extended duration of 20 h initiated the controlled growth of ZnO nanorods. This carefully tailored hydrothermal environment nurtured the nanorods, promoting their desired morphology and crystalline structure.

To culminate this intricate synthesis, the samples were cautiously retrieved from the reactor and subjected to annealing at a precisely maintained temperature of 400 °C for a crucial duration of 4 h. This thermal treatment, meticulously administered, ushered in the pinnacle of quality, furnishing high-quality ZnO nanorods with exceptional properties and structural integrity.

#### **3** Results and Discussion

#### 3.1 Morphology and Structural Analysis

Scanning electron microscopy (SEM) images of ZnO nanorods fabricated on glass substrates at different cycle dip-coating times are depicted in Fig. 1a. The nanorods exhibit a uniform distribution and a homogenous, hexagonal structure (inset of Fig. 1), with vertical alignment on the glass substrate. Top-view images (Fig. 1a.1–a.4) reveal an average diameter ranging from 60 to 450 nm for the ZnO nanorods.

Notably, the cycle dip-coating process induces significant alterations in the surface morphology of the ZnO nanorods, particularly in terms of their diameter. Remarkably dense ZnO nanorod arrays, consistent with previous studies [16], are observed.

Figure 1b demonstrates the approximate diameter scanned within a 1  $\mu$ m area for each sample. With an increase in the number of dip-coating cycles, a prominent growth in the diameter of ZnO nanorods is evident. This observation can be attributed to an increase in the number of seeds available on the substrate, facilitating the formation of nanorods with larger diameters.

Intriguingly, the sample subjected to 5 dip-coating cycles exhibits the largest diameter of 450 nm, while those subjected to 3, 7, and 10 cycles display diameters of 90 nm, 100 nm, and 60 nm, respectively.

The X-ray diffraction (XRD) profiles of ZnO nanorods, produced using a hydrothermal method with different cycle dip-coating, are depicted in Fig. 3. These patterns exhibit a polycrystalline nature, demonstrating the characteristic hexagonal wurtzite structure for all four ZnO nanorod samples [17].

Notably, Fig. 2a illustrates the absence of any peaks corresponding to other elements in the XRD patterns which denotes that there are no impurities present in the sample, confirming the purity and exclusive presence of ZnO in the samples.

Table 1 provides a visual representation of the influence of cycle dip-coating on the intensity of the 002 peak, along with the corresponding tabulated results, which



**Fig. 1** a MEB images of the ZnO nanorods (a.1) 3 dip, (a.2) 5 dip, (a.3) 7 dip and (a.4) ZnO nanorods 10 dip respectively, **b** diameters of the ZnO nanorods for different dip-coating cycle



Fig. 2 The X-ray diffraction analyses with, **a** pattern of ZnO nanorods at different times of cycle dipcoating and **b** variation of microstrain and crystallite size with different times of cycle dip-coating calculated using Debye Scherrer's equations

are presented in Table 1. The observed trend reveals The intensity of the 002 peak demonstrates a gradual increase with the escalation in cycle dip-coating [18].

Specifically, the XRD peak associated with the seven dip-coating cycle demonstrates the highest intensity, suggesting an enhanced degree of crystallinity at this particular coating stage. However, as the number of coating cycles is further increased to ten, a significant reduction in peak intensity is observed, indicating a diminishing level of crystallinity. The crystallite size (D) was determined using the Debye–Scherrer formula (1) [19] and is presented in Table 1:

$$D = \frac{\kappa \lambda}{\beta \text{COS}\theta} \tag{1}$$

D denotes the crystallite size,  $\lambda$  (1.5418 nm) represents the wavelength of the incident X-ray beam (CuKa),  $\beta$  signifies the full width at half-maximum (FWHM), and  $\theta$  corresponds to the Bragg diffraction angle.

The crystallite sizes of ZnO exhibited a range from 23.4 to 26.8 Å, and their variation was influenced by the cycle dip-coating process. With an increase in the number of cycle dip-coating, the crystallite sizes demonstrated an initial increase followed by a subsequent decrease. Figure 2b visually depicts this trend, notably, the Full Width at Half Maximum (FWHM) values showed only slight variations,

<b>i</b>				1 ( )
Sample	2θ <sub>(002)</sub>	I (a. u.)	d (Å)	FWMH
ZnO-3 dip	34.49022	2030	2.60105	0.31654
ZnO-5 dip	34.47203	2102	2.60255	0.27597
ZnO-7 dip	34.51252	5900	2.5996	0.29
ZnO-10 dip	34.49022	1845	2.60105	0.31651

 Table 1
 Structural parameters of ZnO nanorods as determined from the diffraction peak (002)

which signifies the production of high-quality ZnO nanorods. The minimal changes in FWHM indicate that the structural integrity and crystalline quality of the ZnO nanorods were well-maintained throughout the cycle dip-coating process.

The Lattice strain broadening in ZnO nanorods due to crystal imperfection and distortion was calculated using the formula (2) [20]:

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{2}$$

The observed higher microstrain in the 3 and 10 dip-coating cycles signifies a more significant lattice distortion in these particular samples when compared to the others. Moreover, as the number of cycle dip-coating increased, there was a consistent and progressive increase in the lattice strain values, furthermore, the systematic rise in lattice strain values with an increasing number of cycle dip-coating suggests a cumulative effect of the coating process on the lattice arrangement and integrity of the ZnO nanorods.

#### 3.2 Optical Properties

Figure 3a illustrates the transmission spectra of ZnO nanorods at various cycle dipcoating times. Evidently, the transmittance of ZnO thin films diminishes with the progressive increase in cycle dip-coating [21], and a shift towards lower UV wavelengths is observed [22]. Furthermore, the absorption peak at 375 nm, 376 nm, 382 nm, and 383 nm for 3, 5, 7, and 10 cycle dip-coating, respectively, indicates ZnO nanoparticle absorption. Notably, all ZnO nanorod samples exhibit a pronounced intensity drop starting from 360 nm, corresponding to a sharp peak attributed to the free exciton. The observed light absorption within the spectral range of 360– 380 nm suggests the excitation potential of ZnO nanorods by blue light, indicative of excellent optical quality. These findings are consistent with the existing literature [23].

The band gap is measured by extrapolating the linear portion curve of  $(\alpha h\nu)^2$  against the photon energy  $(h\nu)$ , using Tauc's plot [24] for direct transition semiconductor on the following Eq. (3):

$$(\alpha h\nu)^2 = A(h\nu - E_g)^n \tag{3}$$

In this context,  $\alpha$ ,  $h\nu$ , A, E\_g, and n symbolize the absorption coefficient, photon energy, a constant, the optical band-gap energy, and a factor dependent on the transmission type (equivalent to 1/2 for allowed straight transmission), respectively. The absorption coefficient ( $\alpha$ ) is ascertainable from the transmittance through the application of the following Eq. (4):



Fig. 3 a UV–VIS transmittance spectra for ZnO at different cycle dip-coating, **b** the plots of f  $(\alpha h\nu)2$  as a function of photon energy with values of the band-gap for ZnO at different cycle dip-coating

$$\alpha = \frac{\ln(T)}{d} \tag{4}$$

where T is the transmittance, and d is the average length of ZnO nanorods.

The plot of  $(\alpha h\nu)^2$  against hv was utilized to determine the energy bandgap  $(E_g)$  of ZnO nanorods (refer to Fig. 3b). Two distinct absorption edges were observed, indicating the presence of two electronic transitions. The energy values for the first and second transitions are denoted as  $E_{gh}$  and  $E_{gL}$ , respectively (where  $E_{gh} > E_{gL}$ ) [25].

The first gap,  $E_{gh}$ , is referred to as the fundamental bandgap, responsible for the direct electron transition when ZnO nanorods are excited by blue light. This corresponds to the peak of absorption observed in the transmittance spectrum within the range of (360–380) nm (as shown in Fig. 3a). The second gap,  $E_{gL}$  is termed the optical bandgap or deep-level emission, arising from the recombination of electrons with deeply trapped holes in oxygen vacancies or can be linked to zinc ions in ZnO nanomaterials [26].

The values of  $E_{gh}$  were determined as 3.50, 3.38, 3.32, and 3.57 eV for 3, 5, 7, and 10 cycle dip-coating, respectively, and were obtained at higher photon energy. In contrast, the values of  $E_{gL}$  were found to be 1.60, 1.90, 2.76, and 2.50 eV for the respective cycle dip-coating conditions and were obtained at lower photon energy, notably, an inverse relationship was observed between the cycle dip-coating and the band gap. As the cycle dip-coating increased, the band gap decreased, approaching the ZnO band gap value of 3.37 eV.

## 4 Conclusion

In summary, we successfully fabricated ZnO nanorods using a dip-coating method for the seed layer and a hydrothermal growth technique. The nanorods exhibited a hexagonal morphology, and their average diameter increased from 60 to 450 nm with an increasing number of dip-coating cycles. The X-ray diffraction analysis indicated improved crystallinity in the sample with a higher number of dip-coating cycles. UV transmittance spectra revealed characteristic absorption peaks in the UV range around 360–380 nm for all samples, with the band gap decreasing as the number of dip-coating cycles increased. Our findings provide valuable insights for tailored synthesis and applications of ZnO nanorods in various fields such as photocatalysis and optoelectronics.

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# Elaboration of a Reduced Graphene Oxide–Chitosan Biocomposite



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**Abstract** In this work, to develop a reduced graphene oxide-chitosan (rGO-Cs) biocomposite by solution intercalation and cyclic voltammetry, we used reduced graphene oxide (rGO) and chitosan. We have synthesized reduced graphene oxide (rGO), from recycled, processed and activated graphite extracted from batteries or carbon from electric motors, by electrochemical process using KOH as electrolyte. We have extracted Chitosan from shrimp shells chemically in two steps: Extraction of chitin by demineralization, deproteinization and discoloration of shrimp shells. Then by deacetylation we obtain chitosan of off-white color, soluble in acetic acid and non-conductive and with a viscosity of 3.267 Pa s with a good yield and a DDA of 72%, which indicates the good quality of the chitosan produced; Using elaborated chitosan and commercial chitosan, reduced graphene oxide-chitosan (rGO-Cs) composites were synthesized; We characterized the produced samples by FTIR and UV–Vis spectroscopy, by cyclic voltammetry and by rheology in addition to conductivity and solubility tests.

Keywords Biocomposite · Reduced graphene oxide · Chitosan · Exfoliation

## 1 Introduction

Chitosan is a natural polymer derived from chitin, which is the main component of the exoskeleton of crustaceans such as shrimp, crabs, and lobsters. It was used in traditional medicine for its wound-healing properties [1]. Chitosan has a variety of

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<sup>115</sup> 

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properties that make it a versatile material with a wide range of potential applications. It is biodegradable, biocompatible, and non-toxic, and it has antimicrobial and antioxidant properties.

Pure chitosan is not a good conductor of electricity; we can modified chemically it by introducing functional groups that can interact with electrons witch increase the electrical conductivity of chitosan [2, 3].

Graphene-chitosan composites are emerging materials that combine the properties of graphene and chitosan. The graphene is a very strong and conductive material [4, 5], with chitosan, a natural polymer with safe biocompatible and biodegradable properties [6]. This combination of properties makes graphene-chitosan composites highly promising for a variety of applications [7], including electronics (sensors and displays...etc.), biomedical devices (implants, wound dressings, and drug delivery systems), and environmental remediation to remove pollutants from water and air [8–10].

## 2 Experimental Procedure

#### 2.1 Electrochemical Exfoliation of Graphite

We have synthesized black powder of reduced graphene oxide (rGO) by electrochemical exfoliation of graphite in an electrolytic KOH solution by applying a voltage (10 V) between the graphite electrodes (Fig. 1).

The proposed mechanism for electrochemical exfoliation [6] is based on the polarization of graphene layers by OH<sup>-</sup> ions. The reactions that occur at the electrodes are as follows:

- At the cathode:  $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$
- At the anode:  $4OH^- \rightarrow O_2(g) + 2H_2O + 4e^-$



Fig. 1 Electrochemical exfoliation steps of graphite to rGO in KOH solution

The intercalation of graphitic layers is caused by the presence of  $OH^-$  ions, the formation during the electrochemical process of  $O_2$  leads to the exfoliation of graphite by expansion of space between layers of graphite and partial oxidation of graphene.

#### 2.2 Extraction of Chitosan

We have extracted chitosan from shrimp shells in four main steps (Fig. 2).

First, we wash, dry, and grind shrimp shells into a fine powder. Next, we dissolve minerals such as CaCO<sub>3</sub>, the main mineral compound in the shell, in an HCl acid solution.

Finally, we remove proteins by an alkaline treatment using concentrated NaOH solution at a high temperature of 90-100 °C (Fig. 3).

After bleaching with an oxidant such as  $H_2O_2$ , we obtain white chitin. The next step is to extract chitosan by deacetylating chitin. This is a delicate step that involves



Fig. 2 Chitosan extraction steps from shrimp shells



Fig. 3 Mechanism of deproteinization



Fig. 4 Deacetylation of chitin reaction

substituting a maximum and sufficient number of acetyl groups, which are hydrolyzed to amine groups in an alkaline medium (Fig. 4).

Finally, we purify the extracted chitosan by filtration and washing.

### 2.3 Elaboration of rGO-Chitosan Composite

We synthesize the rGO-Chitosan composite (rGO-Cs) thin layer and powder by mixing graphene and chitosan in a dilute acetic acid solution with proportions rGO/ Cs 50/50 w/w and liquid/solid proportion 1/10 v/w, under vigorous stirring for 6 h.

We pour the solution into a petri dish on baking paper to prevent the film from sticking to the glass of the petri dish and leave it to dry at 90 °C in the oven for 6 h to eliminate acetic acid.

We obtain powder by scraping the film of the composite with a spatula in stainless steel.

#### **3** Results and Discussion

The techniques used for the characterization of the synthesized products are: FTIR tests of conductivity, solubility and voltamperometry.

#### 3.1 Appearance and Yield

The rGO is obtained in the form of a black powder.

Regarding the production of chitosan:

- In the first three steps, the powder has a light orange color.
- It becomes white after bleaching.
- The percentage of returns for each stage is presented in Table 1.

	Deacetylation		Off-white color	23.80
	Bleaching		White	92.80
n of chitosan	Deproteinization		Light orange	85.53
fferent steps of extraction	Demineralization		Light orange	70.37
nce and yield of products in dif	Preparation		Light orange	1
Table 1   Appeara		Appearance	Color	Yield % w

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#### 3.2 Conductivity and Solubility

Reduced graphene oxide (rGO) is a good conductor because of the existence of the conjugation of the structure and the weak presence of oxygen functions, while chitosan and chitin are not conductors because they are organic compounds. Chitosan is soluble in acetic acid, while rGO is poorly soluble. The elaborated rGO-chitosan (rGO-Cs) composites are conductors and insoluble in acetic acid Table 2.

### 3.3 FTIR Characterization

The infrared spectrum of the reduced graphene oxide–chitosan composite in powder form shows the same characteristic peaks of chitosan, namely:

- The amide group peaks at 3455 cm<sup>-1</sup> (N–H and O–H stretching), 1633 cm<sup>-1</sup> (C=O stretching), and 1560 cm<sup>-1</sup> (N–H bending)
- The C–H stretching peak at 2883 cm<sup>-1</sup>
- The C–O–C stretching peak at 1020 cm<sup>-1</sup>

In addition to these peaks, the composite spectrum shows a peak at 2100 cm<sup>-1</sup>, attributed to the skeletal vibrations of the graphite domains (the aromatic Sp<sup>2</sup> C=C) of graphene.

A broad peak is also observed between 2900 and  $3450 \text{ cm}^{-1}$ , which may be due to the presence of the OH of acetic acid, used for the synthesis of the composite. This acid contributes to the formation of hydrogen bonds between the chitosan chains and graphene, which strengthens the mechanical properties of the composite (Fig. 5).

#### 3.4 Voltamperometry Tests

Deposition of chitosan on reduced graphene oxide electrodes is a promising method for improving their electrochemical properties. The process is reversible and can be repeated multiple times (Fig. 6). The addition of KCl to the electrolyte increases the conductivity of the solution, which results in an increase in the current intensity.

The deposition of CS on reduced graphene oxide (rGO) electrodes was carried out in a three-electrode cell. The working electrode was the rGO electrode, the counter electrode was a platinum electrode, and the reference electrode was an Ag/AgCl electrode. The electrolyte was a solution of CS in 0.75 M acetic acid. In the second case, 1 M KCl was added to the electrolyte to increase its conductivity.

The potential sweep was carried out between -600 and +600 mV versus Ag/AgCl. A peak of oxidation was observed at 200 mV, which decreased with the number of cycles.



121



Fig. 5 FTIR spectrums for prepared rGO/graphene ref, chitosan and rGO-Cs composite



Fig. 6 Voltamperometry tests of deposition of chitosan on rGO electrodes

Voltammogram obtained from the deposition of CS on rGO electrodes (Fig. 6) show a peak of oxidation at 0.3 V and a peak of reduction at 0.1 V. The current intensity decreases with the number of cycles, which suggests that the deposition process is reversible.

Deposition of chitosan (CS) on reduced graphene oxide (rGO) electrodes is a simple and effective method for improving their electrochemical properties, such as conductivity and capacitance. This makes them promising candidates for use in a variety of electrochemical applications, such as energy storage devices, sensors, and actuators.

Tests on the  $[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-}$  system were performed on the elaborated rGO-Cs electrode, the voltammograms show two peaks: the oxidation peak at 0.3 V/Ag–AgCl and the reduction peak at 0.128 V/Ag–AgCl.

#### 4 Conclusion

We have synthesized rGO by electrochemical exfoliation and extracted chitosan from shrimp shells. We then synthesized rGO-Cs, a composite material with promising electrochemical properties, using a simple chemical method. The method involves mixing rGO and chitosan in a diluted acetic acid solution.

We also used an electrochemical method to synthesize rGO-Cs. This method involves the deposition of chitosan on a rGO electrode.

Our results showed that adding KCl to the electrolyte increased the conductivity of the solution, which resulted in an increase in the current intensity. The deposition process is reversible and can be repeated multiple times.

The rGO-Cs is a promising material for electrochemical applications, such as energy storage devices, sensors, and actuators. These studies could focus on optimizing the deposition conditions to further improve the electrochemical properties of rGO-Cs.

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## Structural and Hydrophobic Properties of Cobalt Doped ZnO Thin Films Prepared by Electrodeposition Method



Zehira Belamri D

**Abstract** In this work, thin films of cobalt-doped ZnO were prepared by thermal oxidation method of electrodeposited zinc layer on aluminum substrates for fabrication of hydrophobic coatings. XRD, Raman spectroscopy, and FEG-SEM methods used for characterization of studied samples. By measuring the contact angle between the film's surface and a deposited water drop, the wettability characteristics of the synthesized films were evaluated (WCA). The manufactured ZnO thin films were found to be polycrystalline with Wurtzite hexagonal structures, growing predominantly along the (101) plan, according to structural characterisation by XRD. No secondary phase for the cobalt-doped sample; this is confirmed by Raman spectroscopy. FEG-SEM images reveal that the grains shape is spherical for cobalt-doped ZnO thin film, however the undoped sample exhibit a compact grains with nanostructured pyramidal shape. Incorporation of cobalt into zinc ions sites leads to the decrease of crystallites size from 39 to 31 nm and enhanced the hydrophobic property of studied ZnO thin film.

Keywords Co-doped ZnO · Nanostructure · Thermal oxidation · Hydrophobic

## 1 Introduction

Zinc Oxide (ZnO) stays a principal nanostructured technological Group II-VI material. It is a semiconductor with a direct band gap of 3.2–3.4 eV at room temperature. Varying the value of the conductivity by doping processes, the gap can be changed. ZnO exhibits a natural n-type electrical conductivity which is due to the presence of the interstitial zinc atoms. The dopants usually used for ZnO generally belong to groups III and IV of Mendeleïev's table. In this case, they will replace the zinc atoms

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by occupying their atomic sites. Doping can also be done using elements from group VII of the periodic table.

In recent years, ZnO has attracted considerable attention; it's used in the fabrication of many devices, such as gas sensors [1], solar cells and photovoltaic [2, 3] fine hydrophobic property [4]. In order to create self-cleaning glass, Rabeel et al. [5] developed ZnO thin films that were deposited on glass substrates using a spray pyrolysis technique. The concept of preparing these surfaces presents enormous opportunities in the field of corrosion inhibition of metals and alloys.

The main objective of this present work is the fabrication of hydrophobic coating based on ZnO, using the thermal oxidation method of electrodeposited zinc thin film on metallic substrates. The study is devoted to the effect of doping by Co on the physical and wettability properties of these thin layers.

#### 2 Materials and Methods

Before deposition, the substrates undergo a mechanical polishing until the desired surface shape and thickness of 2 mm is obtained. They are cleaned in ultrasound baths for 15 min with distilled water and methanol, respectively.

The Zn layers are electrodeposited at room temperature from an aqueous zinc acetate precursor solution of 0.2 mol/L, with agitation under -10 V for 15 min. this is with respect to the distance between the aluminum substrate (cathode) and the platinum (anode) of 1.5 cm as represent in Fig. 1. ZnO thin films were obtained by thermal oxidation at 500 °C for 2 h of electrodeposited Zn layers. The concentrations of doping cobalt element are chosen of 0.01% (the doped sample is noted CZnO).

The structural characterizations were carried out using a PANALYTICAL Empyrean diffractometer ( $\lambda_{cu} = 1.540$  Å) and HORIBA labRAM HR evolution type Raman spectrometer at room temperature with a monochromatic radiation source of 473 nm. For the morphological study, a Field Emission Gun Scanning Electron Microscope (SEM, Jeol FEG JSM-7100 F) equipped with an energy dispersive X-ray spectrometer (EDX) was used. the hydrophobicity was measured by contact



Fig. 1 Image represents the steps of the experiments

angle measurements at room temperature using an optical system composed of a lamp delivering white light and projecting the image of the drop deposited on the sample [leybold type light source (6 V, 30 W)], and a projection lens allowing the enlargement of the image of the drop projected on a screen of size  $(30 * 30 \text{ cm}^2)$ .

#### **3** Results and Discussion

#### 3.1 X-Ray Diffraction Study

The XRD spectra (Fig. 2) reveal that undoped and CZnO thin films were polycrystalline. They show multiple peaks corresponding to (100), (002), (101), (102), (110), (103), (112), (201) and (202) planes related to the hexagonal Wurtzite crystal structure (according to ICDD file N° 01-070-2551) with a preferential orientation along (101). No new peaks associated with Co oxides appeared in CZnO sample. This confirms the successful substitution replacement of Co ions in Zn sites in the ZnO lattice. Zinc phase indicate by circle and the aluminum phase due to substrate indicate by star in Fig. 2.

The three principal peaks (100), (002), (101) in XRD spectrum of CZnO sample, shift towards smaller angles (Fig. 3) without changing the Wurtzite structure of ZnO, this is evidence of cobalt ions incorporation into the ZnO crystal lattice where the ionic radius of Co (0.058 nm) is less then to that of Zn (0.074 nm) which leads to



Fig. 2 XRD spectra of undoped and CZnO thin films treated 2 h at 500 °C



Fig. 3 XRD spectra of undoped and CZnO thin films treated 2 h at 500 °C show the shift of ZnO principal peaks towards smaller angles for CZnO sample

decrease of crystallite size, this is confirmed by lattice parameters values a and c (Table 1).

Average crystallite size calculated using Scherrer formula [5, 6]:

$$D = \frac{K\lambda}{\beta\cos\theta_B} \tag{1}$$

where

K a constant known as shape factor (k = 0.94),

- $\lambda$  The X-ray wavelength of Cu (1.5406 Å),
- $\theta_B$  The Bragg diffraction angle of (101) peak,

 $\beta$  FWHM of (101) peak.

The lattice parameters were evaluated using the following formula available in the literature on hexagonal crystal structure [7]:

$$a = \frac{\lambda}{\sqrt{3} * \sin \theta} \tag{2}$$

Sample	2θ <sub>101</sub> (°)	FWHM (°)	D (nm)	c (Å)	a (Å)
ZnO	36.299	0.225	39	5.206	3.250
CZnO	36.142	0.281	31	5.222	3.015

Table 1 Average crystallite size, a and c values of undoped ZnO and CZnO thin films

Structural and Hydrophobic Properties of Cobalt Doped ZnO Thin Films ...

$$c = \frac{\lambda}{\sin\theta} \tag{3}$$

129

where

 $\lambda$  The wavelength of X-rays (1.5406 Å).

 $\theta$  The diffraction angle of (100) for a parameter and the peak (002) for c parameter.

c<sub>0</sub> 5.207 Å.

## 3.2 Raman Spectroscopy Study

Vibration properties of undoped and cobalt-doped ZnO thin films (CZnO) were investigated by Raman scattering technique in this work. Figure 4 shows the Raman spectra of studied samples, they consist of four modes:  $E_2^{Low}$ ,  $E_2^{(high)}-E_2^{(Low)}$ ,  $E_2^{high}$  and  $A_1(LO)/E_1(LO)$  of the hexagonal ZnO structure phonon. Also, the polar mode of A1(LO)/E1(LO) at around 570 cm<sup>-1</sup> has been presented more intense for doped sample. The peaks intensity for the doped sample is greater than that of the undoped sample especially the peak  $E_2^{high}$ . This linked to the incorporation of Co ions the ZnO nanostructure. The appearance of A1(TO) mode on the spectrum of CZnO sample, reflects the crystallization quality of the ZnO thin films of the hexagonal Wurtzite structure which confirms the XRD analysis results.



Fig. 4 Raman spectra of undoped and cobalt-doped ZnO thin films

#### 3.3 Morphological and Wettability Characterizations

Figure 5a shows that the undoped ZnO film exhibits a compact morphology with pyramid-shape nanostructure attached to each other with a well-defined grain boundary and few nanorods. However, the surface morphology changed for cobalt doped sample; FEG-SEM image of cobalt-doped ZnO thin film (Fig. 5b) reveal more uniform and compact morphology with homogeneously dispersed spherical ZnO nanostructure. EDS analysis show the presence of zinc and oxygen in ZnO thin film (Fig. 5c) and no Co are detected in doped sample (Fig. 5d), which can be due to the low concentration of Co. The wetting properties of studied layers were analyzed by measuring the water contact angle of these layers. Measurements show that the obtained contact angle is 120.91° for undoped ZnO (inserted image in Fig. 5a) which indicates that the undoped ZnO film structure is inherently hydrophobic. The shape of the droplet on the surface of CZnO sample was more specific (inset of Fig. 5b) with contact angle of 128°, this indicates that Co improved the hydrophobic property of ZnO thin film.



Fig. 5 FEG-SEM image and the inset show the image of water drop of undoped ZnO thin film (a) and of cobalt-doped ZnO thin films (b). (c) and (d) corresponding EDS with suitable indexing

## 4 Conclusion

In this work, the study is devoted to the cobalt-doping effect on the structural and morphological properties of the ZnO thin film which in turn affects the hydrophobicity of their surface. A low concentration of cobalt leads to a decrease in the average crystallite size and improves the structural state of the ZnO thin film. The change in the surface morphology after cobalt-doping enhances the hydrophobicity of the studied ZnO layer.

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## Design of a New Photo-Diode Based on (α-PbO)/(α-SnO) Lateral Heterostructure



133

Ali Bakhtatou 💿 and Ali Hamidani 💿

**Abstract**  $\alpha$ -SnO and  $\alpha$ -PbO monolayers are two stable nanostructures that are separately synthesized by epitaxial growth on the same substrate (SiO<sub>2</sub>/Si) with superior functionalities, making them industrially important material for many applications. We have theoretically predicted a new lateral heterostructures  $(\alpha - PbO)_n/$  $(\alpha$ -SnO)<sub>n</sub> formed by periodically repeating narrow SnO and PbO strips joined along their adjacent interface and investigated the structural, mechanical and electronic properties by using first-principles calculations. We demonstrate that creating these lateral heterostructures by  $\alpha$ -PbO and by  $\alpha$ -SnO monolayer materials will allow for adjusting various physical and chemical parameters such as tunable band gap, which are required to fit wide spectral range in optoelectronics applications. We obtained that the  $(\alpha$ -PbO)<sub>7</sub>/ $(\alpha$ -SnO)<sub>7</sub> heterostructure shows an Anderson type-II band alignment where CBM is located at  $\alpha$ -PbO domain while VBM is located at  $\alpha$ -SnO domain. Consequently, the photon-generated electron-hole pairs are spatially separated, resulting in much longer exciton lifetime compared to that of the two monolayers separately which needs to be confirmed by further experimental measurements. This new structure can be used as a forward p-n diode and offer an interesting optoelectronic properties.

Keywords Two-dimensional materials  $\cdot \alpha$ -PbO monolayer  $\cdot \alpha$ -SnO monolayer  $\cdot$  Lateral heterostructures  $\cdot$  Band alignment

## 1 Introduction

Alpha lead-oxide ( $\alpha$ -PbO) and alpha tin-oxide ( $\alpha$ -SnO) 2D sheets were demonstrated to offer the possibility for oxide opto-electronics [1, 2].

Bulk  $\alpha$ -PbO is a semiconductor with an indirect band gap of about ~ 1.9 eV [3]. Monolayer and multilayered  $\alpha$ -PbO have been successfully synthesized [1].

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Fig. 1 Schematic representation of  $(\alpha \text{ PbO})_7/(\alpha \text{ SnO})_7$  relaxed heterostructure cell with n = 7. Pb, Sn and O atoms are represented by grey, violet and small red balls respectively

Experimental results have suggested that these atomic sheets show hydrophobicity, microwave stability, thermal robustness, anti-corrosive behavior and acid resistance [1]. Moreover,  $\alpha$ -PbO monolayer can be exploited in many applications in different fields; electronics, optoelectronics, photocatalysis, sensors and energy storage [1].

Bulk  $\alpha$ -SnO has a small indirect band gap of about ~ 0.7 eV [4]. SnO monolayer was successfully synthesized and can be exploited in sensing as well as catalysts [5].

Here, we design theoretically novel electronic materials by stacking PbO and SnO horizontally to form lateral heterostructures (LHSs). These LHSs are labeled  $(\alpha$ -PbO)<sub>n</sub>/( $\alpha$ -SnO)<sub>n</sub>, where n is the number of primitive cells in the stripe of  $\alpha$ -PbO or  $\alpha$ -SnO, n ranges from 1 to 10. The atomic representation of the heterostructure  $(\alpha$ -PbO)<sub>7</sub>/( $\alpha$ -SnO)<sub>7</sub> is presented in Fig. 1. We study theoretically the structural and electronic properties of these LHSs by first-principles calculations and prove that  $(\alpha$ -PbO)<sub>7</sub>/( $\alpha$ -SnO)<sub>7</sub> lateral heterostructure could function as a photodiode leading to device applications with remarkable functionalities.

#### **2** Computation Details

The calculations reported in this paper work are performed within the projector augmented wave formalism (PAW) [6]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [7] is used to approximate the exchange and correlation part as implemented in the Vienna ab initio simulation package (VASP) code [8]. A plane-wave basis set is take on with a kinetic-energy cutoff of 570 eV. For the electronic properties, the number of k-points in the reciprocal directions was chosen roughly in proportion to the size of the reciprocal lattice. 13 × 13 × 1 k-grid was under taken for  $\alpha$ -PbO and  $\alpha$ -SnO mono-layers. For the heterostructures we have used 13 × 6 × 1. The convergence criterion of energy value was chosen as  $10^{-6}$  eV between two consecutive steps. Allowed maximum Hellmann–Feynman

force convergence, on each atom in the cell, was set to  $10^{-2}$  eV Å<sup>-1</sup>. All calculations were performed with van der Waals correction (vdW) [9].

#### **3** Structural Properties

2D  $\alpha$ -PbO and  $\alpha$ -SnO are isostructural with the space group P4/nmm. At room temperature, they crystallize in the tetragonal structure (Fig. 2a). The structure is multilayered (sheets) form parallel to the xOy plane (Fig. 2b).  $\alpha$ -PbO monolayer (as well as  $\alpha$ -SnO monolayer) is formed of a planar of oxygen atoms intercalated between two planes of Pb (Sn) atoms. (Fig. 2c, d). A lead or tin atoms are surrounded by four oxygen atoms at the corners of a tetrahedron (Fig. 2e, f). Our calculated lattice parameter of  $\alpha$ -PbO (4.013 Å) and  $\alpha$ -SnO (3.811 Å) are in good agreement with experiment values [1, 5].

The primitive cell of  $\alpha$ -PbO (or  $\alpha$ -SnO) is construct from 2 lead atoms (or 2 tin atoms) and 2 oxygen atoms. Lattice mismatch between  $\alpha$ -PbO and  $\alpha$ -SnO is 4.74%.  $(\alpha$ -PbO)<sub>n</sub>/( $\alpha$ -SnO)<sub>n</sub> contains 2n Pb atoms, 2n Sn atoms and 4n O atoms. Lateral heterostructure is extends in the y direction which give the width of the heterostructure. As well as, the lattice constant, *a*, is the interface length on the x side (Fig. 1). The calculated fundamental lattice parameters of 2D  $\alpha$ -PbO and 2D  $\alpha$ -SnO, the optimized lattice constants *a* and *l* of the heterostructures are shown in Table1.

#### 4 Energetic Stability

The energetic stability of an interface can be characterized by its formation energy  $E_{form}$ . Defined as the energy required to create it from its constituent materials. The energy cost per primitive cell per unit length along the interface [10]:

$$E_{form} = (E_T - n(E_{PbO} + E_{SnO}))/(2a.n)$$
(1)

where  $E_T$  is the total energy of the heterostructure  $(\alpha$ -PbO)<sub>n</sub>/ $(\alpha$ -SnO)<sub>n</sub>, n is the number of primitive cells in the 2D strip of  $\alpha$ -PbO (or  $\alpha$ -SnO).  $E_{PbO}$  and  $E_{SnO}$  are the energy per primitive cell for  $\alpha$ -PbO and  $\alpha$ -SnO monolayers. *a* is the periodic length along the interface; factor 2 for the two interfaces within a supercell. According to this definition, negative  $E_{form}$  favors the creation of the interface. The calculated  $E_{form}$  values are shown in Table 1 for takes the values from 1 to 10. The calculated  $E_{form}$  values are negative for n = 1 to n = 8 and mean that the formation of these heterostructures is feasible. The interface is unstable for n = 9 and n = 10.



**Fig. 2** a Tetragonal lattice structure of  $\alpha$ -PbO bulk. **b** Layered structure of  $\alpha$ -PbO. **c** Front view of a  $\alpha$ -PbO monolayer. **d** Top view of a  $\alpha$ -PbO monolayer. **e** Square pyramid of the lead atom with the 4 oxygen atoms. **f** Zigzag Pb–O bonds in the Oy direction (same shape in the Ox direction). *Remark*  $\alpha$ -SnO bulk or monolayer have the same structures as the  $\alpha$ -PbO structures above

#### 5 Mechanical Stability

To investigate the mechanical stability of the heterostructures, we have calculated their independent four elastic constants such as  $C_{11}$ ,  $C_{12}$ ,  $C_{22}$  and  $C_{66}$  for  $\alpha$ -PbO,  $\alpha$ -SnO structures and eight  $(\alpha$ -PbO)<sub>n</sub>/ $(\alpha$ -SnO)<sub>n</sub> heterostructures. The obtained elastic constants are shown in Table 2. The Born criteria stability [11]:  $C_{11} > 0$ ,  $C_{66} > 0$  and  $C_{11} > |C_{12}|$  for  $\alpha$ -PbO and  $\alpha$ -SnO monolayers, and the three elastic stability criteria  $C_{11} > 0$ ,  $C_{66} > 0$  and  $C_{11}$ . $C_{22} > C_{12}$ . $C_{21}$  for the heterostructures are met which confirms their mechanics stability.

	a	1	Eform	$E_g$
	(Å)	(Å)	eV/nm	eV
2DPbO	4.013			2.57 (d)
2DSnO	3.811			3.02 (i)
n = 1	3.966	7.696	- 0.103	2.45 (i)
n = 2	3.942	15.492	- 0.055	2.41 (d)
<i>n</i> = 3	3.940	23.299	- 0.035	2.28 (d)
n = 4	3.939	31.089	- 0.023	2.22 (d)
<i>n</i> = 5	3.935	38.896	- 0.016	2.17(d)
<i>n</i> = 6	3.932	46.710	- 0.010	2.14 (d)
n = 7	3.932	54.472	- 0.006	2.14 (d)
<i>n</i> = 8	3.932	62.264	- 0.003	2.12 (d)
<i>n</i> = 9	3.929	70.098	+ 0.001	
<i>n</i> = 10	3.930	77.880	+ 0.001	

**Table 1** Optimized lattice parameters, formation energy  $(E_{form})$  and Band gaps  $E_g$  of 2D PbO, 2D SnO and  $(\alpha$ -PbO)<sub>n</sub>/ $(\alpha$ -SnO)<sub>n</sub> heterostructures, n ranges from 1 to 10

(d) and (i) indicate direct and indirect band gaps respectively

**Table 2** Elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{22}$  and  $C_{66}$  of bare 2D  $\alpha$ -PbO,  $\alpha$ -SnO and  $(\alpha$ -PbO)<sub>m</sub>/( $\alpha$ -SnO)<sub>m</sub> heterostructures, *n* ranging from 1 to 8

////	, 00			
	C11 N/m	C12 N/m	C22 N/m	C66 N/m
2DPbO	42.4	28.2	42.4	28.9
2DSnO	49.1	40.4	49.1	39.7
n = 1	44.1	33.3	45.7	33.0
n = 2	43.6	33.0	46.2	32.9
<i>n</i> = 3	43.7	32.8	45.7	32.8
n = 4	43.6	32.7	45.7	32.7
<i>n</i> = 5	43.5	32.6	45.5	33.0
n = 6	43.5	32.6	45.5	32.9
<i>n</i> = 7	42.6	32.8	46.0	32.9
<i>n</i> = 8	42.8	33.1	45.4	33.1



Fig. 3 Band structure of  $\alpha$ -PbO and  $\alpha$ -SnO monolayers, and  $(\alpha$ -PbO)<sub>n</sub>/ $(\alpha$ -SnO)<sub>n</sub> lateral heterostructures along the high symmetry directions of BZ for n ranging from 1 to 8.  $E_{g-d}$  and  $E_{g-i}$  indicate direct and indirect band gaps respectively

#### 6 Electronic Structure

#### 6.1 Band Structure

In this part, we calculated the electronic properties of the  $\alpha$ -PbO and  $\alpha$ -SnO monolayers, as well as the eight ( $\alpha$ -PbO)<sub>n</sub>/( $\alpha$ -SnO)<sub>n</sub> heterostructures. Figure 3 shows the calculated electronic band structures. We found that 2D  $\alpha$ -PbO is a direct band gap semiconductor of E<sub>g-d</sub> = 2.57 eV while 2D  $\alpha$ -SnO is a large indirect gap semiconductor of E<sub>g-i</sub> = 3.02 eV which is consistent with previous theoretical results [12, 13]. We also note that among these lateral heterostructures, only the ( $\alpha$ -PbO)<sub>1</sub>/( $\alpha$ -SnO)<sub>1</sub> heterostructure has an indirect band gap of 2.45 eV, and its minimum direct band gap occurs at the  $\Gamma$  point with a value of 2.55 eV. The other heterostructures show a direct band gap at the  $\Gamma$  point.

The calculated band gap values are listed in Table 1. We found that the band gaps of the  $(\alpha$ -PbO)<sub>n</sub>/ $(\alpha$ -SnO)<sub>n</sub> lateral heterostructures are smaller than the band gap values of PbO and SnO monolayers and also than their average value of 2.80 eV. As well as, all the band gaps of  $(\alpha$ -PbO)<sub>n</sub>/ $(\alpha$ -SnO)<sub>n</sub> LHSs exhibit in visible band which is rare among semiconducting 2D materials [1].

#### 6.2 1D Quantum Well Structure

We have also calculated the planar averaged potential and the macroscopic-averaged potential V(y) in y direction as shown in Fig. 4. The maximum potential value between PbO and SnO sides is 0.876 V.



Fig. 4 Average electronic potential energy V(y) along y direction in  $(\alpha PbO)_7/(\alpha SnO)_7$  heterostructure

In Fig. 5, we plotted valence band maximum (VB), conduction band minimum (CB) and Fermi level ( $E_F$ ) of  $\alpha$ -PbO and  $\alpha$ -SnO monolayers before and after junction of ( $\alpha$ -PbO)<sub>7</sub>/( $\alpha$ -SnO)<sub>7</sub> heterostructure. The work function is the Fermi level counted from vacuum which is positioned at 0 eV. It can be seen that the work function of  $\alpha$ -PbO and  $\alpha$ -SnO monolayers and heterostructures are -4.438 eV, -5.258 eV and -4.642 eV, respectively.

The work function difference between the two monolayers is equal to their Fermi level difference. For  $\alpha$ -PbO and  $\alpha$ -SnO, this difference is 0.820 eV, which is very



**Fig. 5** Band alignment of  $\alpha$ -PbO and  $\alpha$ -SnO monolayers, and the  $(\alpha$ -PbO)<sub>7</sub>/( $\alpha$ -SnO)<sub>7</sub> heterostructure

similar to the maximum difference of the macroscopic potential (0.876 eV) calculated above. When  $\alpha$ -PbO and  $\alpha$ -SnO monolayers are joined, electrons will move from n-type PbO with a higher Fermi level (lower work function) to p-type SnO with a lower Fermi level (higher work function) in the junction region. Thus, the Fermi level of SnO (PbO) moves up (down) and finally reaches the same level. Therefore, SnO accumulates a negative charge while PbO accumulates a positive charge, forming a built in electric field directed from PbO towards SnO, involving a built-in potential inside the heterostructure  $\alpha$ (PbO)<sub>7</sub>/( $\alpha$ SnO)<sub>7</sub> which is the average macroscopic potential shown in Fig. 4. These intrinsic electric field and built-in potential confine the holes and the electrons in the PbO side and the SnO side, respectively.

In keeping with the electrical performance, this new device can function as a forward p-n diode. As seen in Fig. 5, this lateral structure shows an Anderson type-II band alignment where VB is located in the SnO domain and CB is located in the PbO domain. Because the VB and CB sites are separated, the photon-generated electron-hole pairs can therefore be spatially separated, leading to a much longer exciton lifetime and the possible presence of exciton condensation between the layers, which may be beneficial for image development, diodes, photoelectric devices and lasers.

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# Numerical Investigation of Laminar Forced Convection Heat Transfer Nanofluids Flow Using Different Base Fluids



#### A. Laichi, A. Bouhezza, H. Köten, and O. Kholai

**Abstract** In this paper, Numerical investigation of laminar forced convection heat transfer nanofluids flow through a horizontal circular pipe under a constant heat flux using different base fluids. In the first part, it has been studied the effect of using several base fluids such as water, engine oil and mercury at different temperature ranging from 280 to 320 K and at different Reynolds number values ranging from 100 to 2100 on average Nusselt number and pressure drop. In the second part, it has been studied the effect of suspended of Al<sub>2</sub>O<sub>3</sub> at 3% volume fraction, 295 K and Reynolds number equal 1460 on heat transfer coefficient and local Nusselt number. The governing equations have been modeled using finite volume method approach with SIMPLE algorithm helping with ANSYS FLUENT software. The results indicate that the average Nusselt number and pressure drop for all base fluids increase as Reynolds number increase and decrease as temperature decrease. Engine oil has a higher average Nusselt number and pressure drop while mercury has a small average Nusselt number and pressure drop. Also, mercury has a small change with temperature. Moreover, average Nusselt number is only function of Prandtl and Reynolds number but pressure drop varies with Reynolds number. Add of Al<sub>2</sub>O<sub>3</sub> nanoparticle to the base fluids enhanced the heat transfer coefficient and local Nusselt number for all nanofluids. It has been found that mercury has a higher heat transfer coefficient and small Nusselt number due to higher thermal conductivity and small thermal boundary layer thickness.

Keywords Heat transfer · Fluid flow · Nanofluids · Transport phenomenon

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# 1 Introduction

The enhancement of heat transfer characteristic of base fluid using in industries such as, heat exchangers, electronics and energy storage and transportation is one of important research. There are two conventional methods using for enhancement the heat transfer, the passive method using the extended surface and rough surface and the active method using external power. Two methods doesn't sufficient for find a high performance of heating and cooling systems. The use of ultra-fine particle such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> dispersed in water has been reported by Masuda [1]. The author showed that the thermal conductivity of Al<sub>2</sub>O<sub>3</sub>-Water and TiO<sub>2</sub>-Water nanofluids increased with increasing of volume concentration and no change for SiO<sub>2</sub>-Water nanofluid. Also, for the effective dynamic viscosity increased with increasing of volume concentration and decreased with increasing of temperature. Moreover, it observed that the suspension has a higher dispersion for spherical nanoparticle. A new class of fluid call Nanofluids contained a small size of nanoparticle less than 100 nm has been found by Choi [2]. It reported that the dispersion of Cu nanoparticle in water enhanced the heat transfer coefficient as the thermal conductivity and flow rate increased. Palm et al. [3] studied the laminar forced convective heat transfer enhancement using Al<sub>2</sub>O<sub>3</sub>-Water nanofluids in radial flow cooling systems considering temperature-dependent properties. It found that the average heat transfer coefficient at 4% volume concentration increased with 25% than water base fluid. However, the modeling using temperature-dependent nanofluids properties gave a better heat transfer enhancement predictions as well as lower wall shear stresses than when considering constant properties throughout the domain. Convective heat transfer for water based Alumina nanofluids in a single 1.02 mm tube have been studied by Lai et al. [4]. The results showed that the heat transfer coefficient increased with volume flow rate and volume fraction of nanofluids. In addition, in the developing region, the HTC enhancement decreased with increasing axial distance from the test section entrance and it was higher for large volume fraction and volume flow rate, the fully developed region showed a small enhancement of HTC because stabilized of boundary layer. Many experimental studies have been reported for this reason, Kim et al. [5]. It studied the effect of dispersion of  $Al_2O_3$  in water on the convective heat transfer coefficient in laminar and turbulent flow condition and found that the maximum enhancement showed when used Al<sub>2</sub>O<sub>3</sub> in turbulent flow condition. In this study, the first one we describe the effect of different base fluid such as water, engine oil and mercury, Reynolds number and temperature on enhancement of heat transfer and pressure drop, in the second part, we describe the effect of addition Al<sub>2</sub>O<sub>3</sub> nanoparticle to water, engine oil and mercury at 3% volume fraction on local heat transfer coefficient. 2D Laminar forced convective heat transfer in horizontal circular pipe are investigated.

#### 2 Mathematical Model

Figure 1 shows representation of geometry using in this study. The flow is steady, axisymmetric laminar forced convective in horizontal circular pipe has a 4.57 mm diameter and 2 m length, nanoparticle and base fluid are in thermal equilibrium and single phase model is applied, no-slip condition and constant heat flux at the wall 2089.56 W/m<sup>2</sup>.

The properties of different base fluids at different temperatures used in this study presented by Bergman et al. [6]. Also, the properties of different nanofluids at 295 K and 3% volume concentration of  $Al_2O_3$  show in Table 1.

# 2.1 Continuity

$$\frac{1}{r}\frac{\partial}{\partial x}(\rho_{nf}V_x) + \frac{\partial}{\partial x}(\rho_{nf}V_r) + \frac{\rho_{nf}V_r}{r} = 0$$
(1)



Table 1 1	Nanofluids	properties
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Fluid	Density (kg/ m <sup>3</sup> )	Specific heat capacity (J/ kg K)	Dynamic viscosity (N s/m <sup>2</sup> ). 10 <sup>-6</sup>	Thermal conductivity (W/m K). 10 <sup>3</sup>	Prandtl number
Al <sub>2</sub> O <sub>3</sub> [7]	3970	765	1	40,000	1
Water-Al <sub>2</sub> O <sub>3</sub>	1087.16	3806.77	1275.18	659.6	7.3594
Engine oil-Al <sub>2</sub> O <sub>3</sub>	979.5385	1751.89	987,300	158.3	10,926.35
Mercury-Al <sub>2</sub> O <sub>3</sub>	13,254.06	145.12	2065	8902	0.03366

#### 2.2 Momentum

$$Vr\frac{\partial Vx}{\partial r} + Vr\frac{\partial Vx}{\partial x} = -\frac{1}{\rho_{nf}}\frac{\partial P}{\partial x} + \upsilon_{nf}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial V_x}{\partial r}\right) + \left(\frac{\partial^2 V_x}{\partial x^2}\right)\right]$$
(2)

$$Vr\frac{\partial Vr}{\partial r} + Vr\frac{\partial Vr}{\partial x} = -\frac{1}{\rho_{nf}}\frac{\partial P}{\partial r} + \upsilon_{nf}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial V_r}{\partial r}\right) + \left(\frac{\partial^2 V_r}{\partial x^2}\right) - \frac{V_r}{r^2}\right] + g_r$$
(3)

#### 2.3 Energy

$$V_r \frac{\partial T}{\partial r} + V_r \frac{\partial T}{\partial x} = \alpha_{nf} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \left( \frac{\partial^2 T}{\partial x^2} \right) \right)$$
(4)

where

$$\alpha_{nf} = \frac{K_{nf}}{\left(\rho c_p\right)_{nf}}$$

### 2.4 Heat Transfer Coefficient

$$q'' = h_x (T_w - T_m) \tag{5}$$

where hx, Tw and Tm are the local convective heat transfer coefficient, local wall temperature and the mean temperature at the same axial position respectively.

The mean temperature calculate with energy balance as:

$$T_m = \frac{2}{R^2 U_m} \int_0^R u(r) T(r) r dr$$
(6)

$$\phi = q''(\pi D_h L) = mc_p (T_{mi} - T_{mo})$$
(7)

$$\phi = Sh_{ave}(T_w - T_m) \tag{8}$$

 $Sh_{ave}$ ,  $T_w$  and  $T_m$  are the average convective heat transfer coefficient, average local wall temperature and the mean temperature of fluid respectively,  $\phi$  is the rate of heat transfer.

# 2.5 Nusselt Number

Nusselt number is the ratio between the convection heat flux and conduction heat flux.

$$Nu = \frac{h}{k_{eff}} D_h = \frac{convection heat flux}{conduction heat flux}$$
(9)

where h, keff and Dh are the heat transfer coefficient, effective thermal conductivity and hydraulic diameter respectively. keff depend on the mean temperature of the fluid flow.

# 2.6 Nanofluids Properties

Thermo physical properties of nanofluids such as density, effective thermal conductivity, effective dynamic viscosity and heat specific capacity are calculated using different empirical model, which are:

Effective density of nanofluids is calculated using the model of Pak and Cho [8]:

$$\rho_{eff} = (1 - \varphi)\rho_f + \varphi\rho_s \tag{10}$$

where  $\rho_f$ ,  $\varphi$  and  $\rho_s$  are density of base fluid, volume concentration and density of nanoparticle respectively.

Effective specific heat capacity is calculated using the model of Xuan and Roetzel's [9] and it is obtained in thermal equilibrium mixture of base fluid and nanoparticle.

$$C_{p\,eff} = \frac{(1-\varphi)(\rho C_p)_f + \varphi(\rho C_p)_s}{\rho_{eff}}$$
(11)

The effective thermal conductivity is calculated using the model of Hamilton and Crosser [10] for spherical nanoparticles:

$$\frac{k_{eff}}{k_f} = \frac{k_s + 2k_f - 2\varphi(k_f - k_s)}{k_s + 2k_f + \varphi(k_f - k_s)}$$
(12)

The effective dynamic viscosity is calculated using the model of Maïga et al. [11] for spherical nanoparticles:

$$\frac{\mu_{nf}}{\mu_f} = \left(1 + 7.3\varphi + 123\varphi^2\right)$$
(13)



# **3** Numerical Method

We studied laminar forced convective heat transfer and fluid flow using different base fluid in the first step, after studied the effect of add nanoparticle on heat transfer enhancement and hydrodynamic behavior. ANSYS FLUENT 2020 R1 Computational fluid dynamic language used in this study. The steady state incompressible coupled non-linear partial differential equations have discretized using the finite volume method. A second order upwind scheme uses for pressure, momentum and energy while the SIMPLE algorithm applied for the velocity–pressure coupling. Converged solutions have been considered when the residual in each equation  $10^{-6}$ . The non-uniform grid has been adopted in the radial direction, which is finer at an adjacent tube wall and uniform grid for axial direction. To find a grid independence solution, several element grids have studied at Reynolds number equal 1620.

For this study using different element grid 7500, 10,000, 15,000, 30,000, 60,000, 80,000, 100,000 and the average Nusselt number error between 60,000 grid and 80,000 less than 1%, finally selected 60,000 elements grid, which is captured the maximum variation of parameters studied. The variation of Nusselt number function of number of element shows in Fig. 2.

# 4 Results and Discussion

For illustrate the accuracy of results Fig. 3. It Shows a comparison between different theoretical and numerical results with the present model of local Nusselt number function of dimensionless axial position with Shah and London equation [12] and numerical result of Javad Bayat [13] at Reynolds number 1620 for water at 295 K.



#### 4.1 Shah and London Equation

We have two equations of Shah and London [12], Eq. (14) using for thermal developing region and Eq. (15) using for thermal fully developed region.

$$Nu(x) = 1.953 \left( RePr \frac{D_h}{x} \right)^{1/3} \text{ For } RePr \frac{D_h}{x} \ge 33.3$$
(14)

$$Nu(x) = 4.364 + 0.0722 \left( Re Pr \frac{D_h}{x} \right)^{1/3} \text{ For } Re Pr \frac{D_h}{x} < 33.3$$
(15)

# 4.2 Effect of Temperature on the Average Nusselt Number for Different Base Fluids

Figure 4 shows the variation of the average Nusselt number of water base fluid at three different temperatures and different Reynolds numbers. It observes linear increasing of average Nusselt number with increasing of Reynolds number because the increase of Reynolds number decrease the thickness of boundary layer due to enhance the heat transfer. Average Nusselt number decrease with increasing of temperature because temperature affects the thermo physical properties of water, this effect shows in Prandtl number when decrease 2.72 times in temperatures ranging from 280 to 320 K and when increase Reynolds number between 100 and 2100. This results confirmed that the average Nusselt number change function of Reynolds and Prandtl number (thermo-physical properties especially dynamic viscosity). Figure 5 shows the variation of average Nusselt number of engine oil base fluid at three different temperatures and different Reynolds numbers. The same variation of engine oil showed with water but it is not linear, average Nusselt number of engine oil at 2100 and 280 K higher than.



Fig. 4 The average Nusselt number of different base fluids at different Reynolds numbers and different temperatures



Fig. 5 The average Nusselt number ratio of engine oil and mercury compared with water at different Reynolds numbers and temperatures

Water with 10 times, because higher Prandtl number of engine oil 27,500 compare with Prandtl number of water 10.26. Prandtl number affects the thermal boundary layer thickness. Figure 6 shows the variation of average Nusselt number of mercury base fluid at three different temperature and different Reynolds numbers. Mercury has inverse behaviour with temperature and Reynolds number, average Nusselt number is great at high temperature and low Reynolds number, low temperature and high Reynolds number, but this variation is not large because of small Prandtl number and this cause due to small average Nusselt number of mercury than water and engine oil.

Figure 5 shows the ratio of average Nusselt number of engine oil and mercury respectively compared with water base fluid at different temperatures. It observed that at Reynolds number 2100 and temperature 280 K average Nusselt number of engine oil higher that water with 10 times, mercury is less with 25% than water at the same conditions of Reynolds number and temperature. The thermo physical properties such as dynamic viscosity affect the heat transfer behavior and it has high sensibility with temperature.



Fig. 6 Pressure drop of water, engine oil and mercury at different temperature and Reynolds numbers

# 4.3 Effect of Temperature on Pressure Drop for Different Base Fluids

The better base fluid whose has a higher heat transfer and lower pressure drop, in this reason we present compared study of pressure drop of different base fluids at different temperatures. Figure 6 illustrate the effect of temperature on pressure drop for several base fluids water, engine oil and mercury respectively, as a function of Reynolds. Pressure drop increase with increasing of Reynolds number and decrease with increasing of temperature for all base fluids. Temperature affects especially the dynamic viscosity, density with small change, it mean Prandtl number. It shows that higher pressure drop due to higher Prandtl (dynamic viscosity) equivalent to engine oil base fluid, it has a higher pressure drop than water and mercury. The effect of temperature shows especially for engine oil and water but it is small for mercury.

# 4.4 Effect of Nanoparticle on Local Heat Transfer Coefficient of Different Base Fluids

The effect of suspended of spherical nanoparticle  $Al_2O_3$  with 3% volume concentration with water, engine oil and mercury at Reynolds number 1460 and at temperature equal 295 K on axial variation of the heat transfer coefficient shows in Fig. 7. All nanofluids have a higher heat transfer coefficient than water base fluid. Moreover, mercury and engine oil have higher average values of heat transfer coefficient higher than 8000 W/m<sup>2</sup> K and 2000 W/m<sup>2</sup> K respectively because mercury has a small thickness of thermal boundary layer and engine oil has a higher Prandtl number. Heat transfer coefficient of  $Al_2O_3$ -Mercury shows a uniform change state variation compared with other nanofluids. Water- $Al_2O_3$  nanofluid in the present study gives a good agreement with experimental data of Kim et al. [5].





# 4.5 Effect of Nanoparticle on Local Nusselt Number of Different Base Fluids

Figure 8 present the effect of different nanofluids water- $Al_2O_3$ , engine oil- $Al_2O_3$  and mercury- $Al_2O_3$  at 3% volume concentration, temperature equal 295 K and Reynolds number equal 1460 on the axial local Nusselt number. Engine oil- $Al_2O_3$  nanofluid give a higher estimation of local Nusselt number with 10 order than Water- $Al_2O_3$  and Mercury- $Al_2O_3$  nanofluids because of higher convection heat flux than conduction heat flux at the surface of the tube. Mercury- $Al_2O_3$  nanofluid has a higher thermal conductivity about 8.902 W/m K so; the conduction heat flux is favorable in this case.

# 5 Conclusion

To investigate of 2D laminar forced convective heat transfer nanofluids flow in circular pipe under a constant heat flux we use a three different base fluids water, engine oil and mercury at different temperatures and different Reynolds numbers in the first step. Second step the same studied using  $Al_2O_3$  nanoparticle at 3% volume concentration and at Reynolds number and temperature equal 1460 and 295 K respectively. Average Nusselt number increase with increasing of Reynolds number because decrease of thickness of dynamic boundary layer whiles its decrease with increasing of temperature because decrease of Prandtl number (decrease of dynamic viscosity and increase of thermal conductivity), this results showed for water and engine oil while does not show a large effect for mercury. Engine oil has a higher average Nusselt number than mercury because a higher Prandtl number. It illustrate that average Nusselt number change with Reynolds and Prandtl number Nu =

f (Pr, Re). Pressure drop increase with increasing of Reynolds number and decrease with increasing of temperature for all base fluids. However, pressure drop has higher values when using engine oil at higher Reynolds number and small temperature. Pressure drop is only function of Reynolds number. In the second part using Al<sub>2</sub>O<sub>3</sub> nanoparticle suspended in water, engine oil and mercury at 3% volume concentration, Reynolds number 1460 and temperature 295 K. Add nanoparticle increase the heat transfer coefficient for all nanofluids, this results confirmed with compared of Water- $Al_2O_3$  nanofluids with experimental data of water Kim et al. [5]. Mercury- $Al_2O_3$  and Engine oil-Al<sub>2</sub>O<sub>3</sub> nanofluids show a large heat transfer coefficient than water and the maximum shows for Mercury-Al<sub>2</sub>O<sub>3</sub> nanofluid because has small thickness of thermal boundary layer. Mercury-Al<sub>2</sub>O<sub>3</sub> nanofluid has a uniform evolution of axial heat transfer coefficient. Local Nusselt number of Engine oil-Al<sub>2</sub>O<sub>3</sub> nanofluid is higher with 10 orders than Water-Al<sub>2</sub>O<sub>3</sub> and Mercury-Al<sub>2</sub>O<sub>3</sub> nanofluids and it has maximum in developing region and decrease in fully developed region because the thermal boundary layer is constant. Also, Prandtl number affect the local Nusselt number, higher evolution local Nusselt number shows in higher Prandtl number of Engine oil-Al<sub>2</sub>O<sub>3</sub> nanofluid, small local Nusselt number shows for Mercury-Al<sub>2</sub>O<sub>3</sub> nanofluid because it has higher conductivity. Temperature affects the heat transfer and hydrodynamic behavior. Nusselt number and heat transfer coefficient are function only with Reynolds number and Prandtl number. Dynamic viscosity has a higher effect on pressure drop for all base fluids. The use of nanoparticle enhances the heat transfer coefficient and it is change with base fluids. The use of nanofluids based on its heat transfer condition, base fluid application and environmental.

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# **Electronic Properties and Magnetic Stability in Binary Iron Pnictide**



Nabila Benmeddah and Fatma Temmar

**Abstract** In this work, we presented a first-principle study of the structural, electronic and magnetic properties of iron selenide in its pure state. The calculations were performed by the Pseudo-Potential method which is based on the density functional formalism (DFT), using the local spin density approximation (LSDA). The lattice parameters and total energy of FeSe were calculated for three different cases of magnetism in order to examine magnetic stability and electronic properties. We discussed the most stable state as well as the one closest to the creation of the phenomenon of superconductivity in this binary iron pnictide.

Keywords Magnetism  $\cdot$  Superconductivity  $\cdot$  DFT study  $\cdot$  Fe-pnictides  $\cdot$  Band structures  $\cdot$  Fermi surfaces

# **1** Introduction

Superconductivity was discovered in 2008, by the team of Japan Hideo Hosono at the Tokyo Institute of Technology, in iron-based compounds (Fe-pnictides), at temperatures almost as in cuprates ( $T_c$  up to 55 K, [1–5]) which attracted enormous interest. It has been induced in RFeAsO by doping with fluorine, cobalt [1], thorium [2], strontium [3], oxygen vacancies [4], or by applying high pressure [5, 6].

All of the parent compound (RFeAsO, R = La, Ce, Nd, Pr, Sm, Gd) display a similar antiferromagnetic phase transition from tetragonal to orthorhombic structural distortion on cooling from 250 to 100 K [7, 8]. When these materials are doped, the structural and magnetic transitions are suppressed and superconductivity appears [9–13].

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157

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FeSe, another iron-based superconductor, reaches a critical temperature above "100 K" by growing a thin layer on a  $SrTiO_3$  substrate, thus surpassing all other iron-based superconductors [14, 15] and opening the way to superconductors in thin layers as well as to the synthesis of complex materials.

In short, the discovery of new iron-based superconductors has opened a new horizon for superconductivity at high critical temperature. In this work, we focus the study on one of the parent of the binary compound FeSe type iron pnictides, we discuss the magnetic stability and the electronic structure, in particular his band structures and Fermi surfaces while relying on the FP-LAPW method based on the DFT.

#### **2** Computational Details

We compute the **FeSe** electronic band structure in the framework of Density Functional Theory implemented in the Wien2K full-potential APW+lo package [16, 17], we considered 200 k points in the BZ and checked that all the properties presented in this paper were converged with this mesh. The results that we present here, have been obtained within the LDA to the exchange-correlation potential [18, 19].

Our calculations of electronic properties were done by using the muffin-tin radii  $R_{\rm MT}$  for both of atoms Fe, Se initialized to be 2.0 a.u. [20].

The electronic states of the atoms in the crystal have been chosen with the valence configurations of

Fe<sup>26</sup>: 
$$1S^2 2S^2 2P^6 3S^2 3P^6 3d^6 4S^2$$
.  
Se<sup>34</sup>:  $1S^2 2S^2 2P^6 3S^2 3P^6 3d^{10} 4S^2 4P^4$ .

To ensure convergence, the LAPW basis set was defined by the cutoff  $R_{MT}K_{max}$ = 7 (the minimum of  $R_{MT}$  and the maximum plane-wave cut-off parameter  $K_{max}$ ). 6 × 6 × 6 *k*-point grid was used to perform the Brillouin Zone integration [21, 22] in the self-consistent calculations with charge convergence until 10<sup>-3</sup> eV.

Iron-based superconductor FeSe belongs to tetragonal structure with space group P4/nmm (#129). The equilibrium lattice parameters of FeSe have a value of a = 3.762 Å and c = 4.420 Å [20].

Iron selenide has the simplest crystal structure of all iron-based superconductors. FeSe is, like pnictides, an almost two-dimensional material, being only a stack of iron-selenium planes. It is stand out by the fact that it does not contain any interplanar atoms and, obviously, that it contains only two atomic species. By minimizing the total energy, the lattice constants and atomic positions will optimized.

Figure 1 shows the optimized structures of FeSe, Fe, Se atoms arrange in parallel planes in a supercell of 24 atoms according to the direction (1, 1, 2) thus, the distribution of the two Fe, Se atoms in the conventional mesh is presented on the right of the figure.





Table 1         Structural           parameters of FeSe with         1	Compound	Structural parameter (Å)	Atomic positions	
space group: P4/nmm #129	FeSe	$a = 3.762^{a}$	Fe $\left(\frac{1}{4}, \frac{3}{4}, 0\right)$ [20]	
		$c = 4.420^{a}$	Se $(\frac{1}{4}, \frac{1}{4}, z)$ [20]	

<sup>a</sup>Experimental value, with Z = 0.2402 [20]

The experimental structural parameters and atomic positions used in the calculation are shown in Table 1.

# **3** Results and Discussions

#### 3.1 Magnetic Stability

In order to study the stability of FeSe compound we performed the optimization calculations. In Fig. 2, we represent the variation of the total energy as a function of the volume for our material in three different cases (non-magnetic, ferromagnetic and finally antiferromagnetic) in the tetragonal structure.

From Fig. 2, we find that the most stable phase for the compound is the nonmagnetic (without spin polarized) phase (NM) thus coinciding with the volume closest to the associated experimental study.

The structural parameters such as the lattice constant, the modulus of compressibility as well as the minimum energy obtained during the calculations are given in Table 2.

By analyzing Table 2 we find that the lattice parameters decrease, the total energy E and the modulus of compressibility B increase, when changing from the magnetic state to the no magnetic state for the FeSe compound. However, the experimental results are slightly overestimated compared to our results, in particular the parameter





Table 2 Structural parameters and total energy calculated in magnetic and nonmagnetic states

Compound	Lattice parameters	Results	Expérimental results
FeSe with SP	a (Å) c (Å)	3.6588 5.2988	3.765 5.518 [23]
	B (GPa)	99.9142	
	В′	4.7328	
	Emin (Ry)	- 14,812.133918	
FeSe without SP	a (Å) c (Å)	3.6349 4.3753	3.775 5.512 [ <b>24</b> ]
	B (GPa)	123.9174	
	Β′	4.8190	
	Emin (Ry)	- 14,812.134479	

c. The most stable state is that of the no magnetic FeSe, which we will prove again in the next section. We have relaxed our material using the experimental structural parameters [20], to be able to compare with the literature and to reproduce better the correct electronic structure of the studied system.

#### 3.2 Electronic Properties

In this section, we present the results for the bi-atomic FeSe compound from the family of the iron-based superconductors. The band structure for the compound have been presented in Fig. 3. The letters  $\Gamma$ , X, M, Z, A, R represent the points of high symmetry of this structure. Two hole-like bands are centered at the  $\Gamma$  point and two electron-like bands at the M, R points. The calculated band structure along the  $\Gamma$ –Z line suggests that, because the dispersion of the bands is linear in kz-direction this

system can be treated as a two-dimensional one. This result agrees qualitatively with the previous calculations.

To get an idea of the origin of the energy bands, we calculated the total and partial density of states of the FeSe compound (Fig. 4).

Fe atom has the greatest density near the Fermi level, as the results of the previous figure have shown.

The density of states at the Fermi level is largely dominated by iron d electrons, while the other contributions at this level are marginal in comparison, also Se contribution exceeds Fe contribution at -15 eV further  $E_F$ .



Fig. 3 Band structure of FeSe, in the tetragonal structure, calculated with the functional DFT. a Non-magnetic state, **b** antiferromagnetic state



Theoretical  $z_{Se}$ , which reduces the Se-height above the Fe plane, affects the individual Fe-derived d-bands around  $E_F$  differently due to the orientation of the d-orbitals [23] (Fig. 5).

The main contribution of the PDOS is due to the *Fe-d* orbitals, which are the most dominant so, Fe atom orbitals are the most influencing on the electronic properties of the structure, for this, we have evaluated the densities of states of all *Fe-d* orbitals (Fig. 6).



Fig. 5 Total and partial DOS of Fe, Se atoms in FeSe compound obtained by functional DFT-LSDA



Fig. 6 Density of states projected into the 3d orbitals of the iron atom

The orbital  $d_{XZ} + d_{YZ}$  represents the maximum density at Fermi level thus, the other orbitals all present intense peaks near the Fermi level, in particular the  $d_Z^2$  and the  $d_{XY}$ , which suggests an attenuation limited by the behavior of iron electrons.

#### 3.3 Fermi Surface of the FeSe

The Fermi surface of FeSe is illustrated in Fig. 7. Two bands intersect the Fermi level, giving rise to two distinct cylindrical surfaces parallel to the  $k_z$  axis. The curvature of the surfaces along this axis is low due to the almost two-dimensional nature of the material. The surface is plotted on a two-dimensional Brillouin Zone in Fig. 7. The two cylinders become two pockets of very similar areas, composed of two holes in the center of the Brillouin zone. The other cylinders are resulting from electrons contribution in non-magnetic state.

The superconducting FeSe obtained in thin layers, whose Tc is much higher attending 100 K, has a different Fermi surface. Generally, the true electronic structure of Iron-based superconductors has 4 (or 5) Fermi surfaces: 2 (or 3) hole (cylinders) in the center of the first Brillouin zone, as it was presented for the FeSe antiferromagnetic Fig. 7b, and 2 other zone-corner showing electrons contribution at Fermi surfaces, as it was presented for the FeSe no-magnetic.

Superconductivity coincides with the non-magnetic state when we consider the number of hole and electron contribution at Fermi level.



Fig. 7 Fermi surface: a non-magnetic state b antiferromagnetic state

# 4 Conclusions

In summary, FeSe with its critical temperature  $T_C = 8$  K undergoes a structural transition from the tetragonal to the orthorhombic phase at  $T_s = 87$  K with nonmagnetic order, but with emerging nematic electronic structure. On the other hand, the calculations based on density functional theory (DFT) predict magnetic states for FeSe [25–28]. Recently, exotic states with hidden magnetic order were proposed. Our calculations based on LSDA allowed us to study the electronic and magnetic properties based on purely experimental parameters, we find that lattice constants (a, c) decrease from magnetic to non-magnetic state thus, the total energy increase proving the non-magnetic character of FeSe at low temperature. A complement study was added to compare different properties when the probability of antiferromagnetic state is present. The band structure in the nonmagnetic state. In both cases of magnetism, the density of state marks a remarkable contribution of the iron atom in particular Fe-d where the orbital  $d_{XZ} + d_{YZ}$ ,  $dz^2$  and  $d_{XY}$  represent the big contribution at E<sub>F</sub> successively.

Since the number of distinct pockets forming the Fermi surface gives the maximum number of different gaps that can exist on this surface, the non-magnetic state reinforced quantitatively the superconducting state while the magnetic state shows the same quality of the pockets.

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# Structural and Morphology Characterization of an EVA/ZnO Polymer in Thin Film Form for Solar Applications



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**Abstract** The objective of this work is to develop and study the structural properties, as well as the morphology of thin films of ZnO nano powders prepared by the solgel method, based on the fact that reducing grain size to the nanoscale introduces new physical characteristics and opens promising prospects for solar applications. The first part is an experimental study on the fabrication of ZnO. The second part is an experimental study on the organic polymer EVA. We used THF-soluble EVA and doped it with  $In_2O_3$ . Experimental analysis using XRD and SEM techniques is conducted to examine the doping rate, efficiency, and performance of the materials.

Keywords EVA · ZnO · Morphology · Structural

# 1 Introduction

Nanoparticles have always existed in nature, but they also exist as a result of human activity. Currently, research on nanoparticles is focused on improving and developing new properties to be used in various products in our daily lives. Nanoparticles are defined as synthetic particles with one or more dimensions measuring less than 100 nm. However, the terminology regarding different aspects of nanotubes is still subject to discussion. These particles are synthesized due to their unique properties specific to their dimensions [1–7].

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167

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There are natural nanoparticles (such as sea salt) and unintentionally anthropogenic artificial nanoparticles, such as domestic and industrial fumes, as well as intentionally manufactured ones with new properties, like oxides and polymers, for example [7–11].

Polymer materials are increasingly used in solar applications due to their interesting optical and mechanical properties. Ethylene-vinyl acetate (EVA) is an example of a polymer material widely used in the solar panel industry because of its transparency to sunlight and ability to adhere to other materials. However, to enhance the performance of solar panels, it is often necessary to incorporate zinc oxide (ZnO) nanoparticles into the polymer matrix. ZnO nanoparticles possess unique optical properties, such as a broad absorption spectrum and good electrical conductivity, which can improve solar panel efficiency [11–19].

Hence, the study and optical characterization of these EVA/ZnO polymer materials in the form of thin films are of great importance to understand their optical behavior and properties related to light transmission, absorption, and reflection. Commonly used techniques for characterizing EVA/ZnO polymer thin films include photoluminescence spectroscopy, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). These techniques allow for the measurement of material's optical properties like refractive index, light transmission, and reflection, as well as the morphology and structure of the thin films. This information is essential for optimizing solar cell design and improving their energy efficiency.

#### 2 Experimental Procedure

We prepare a mass of zinc oxide weighed on an analytical balance (m = 12 g). After weighing it, we place it in a beaker and add a volume of water (v = 60 ml). We also prepare a mass of citric acid weighed on an analytical balance (m = 1 g). After weighing it, we place it in a beaker and add a volume of ethanol (v = 60 ml). To obtain homogeneous solutions, we place them on a stirrer for 20 min. After stirring, we mix the two quantities in a third beaker, which allows us to obtain a layer of ZnO gel. Then, we filter this layer using filter paper (Fig. 1).

Drying: The first step of the thermal treatment of our gel is to place the ZnO gel in an oven for 24 h to obtain nanoscale ZnO powder.

Annealing: The second step, which is also the most important in our thermal treatment, is the annealing process. After drying the ZnO gel, we obtain a white powder. This powder is amorphous, so we proceed with a 2-h annealing at a temperature of T = 450 °C to crystallize our powder into a Wurtzite-type hexagonal structure. After annealing, we obtain a crystallized white or gray powder, which corresponds to pure ZnO. These powders are shown in Fig. 2.



Fig. 1 Equipment used for sample preparation



Fig. 2 ZnO gel before and after annealing

On the other hand, we prepare a mass of EVA weighed on an analytical balance (m = 0.5 g). After weighing it, we place it in a beaker and add a volume of (V = 20 ml) of THF (Tetrahydrofuran) to obtain a viscous liquid after two hours of magnetic stirring.

We use ethyl vinyl acetate (EVA) containing 18% vinyl acetate (Fig. 3).

We introduced 0–30% ZnO/In<sub>2</sub>O<sub>3</sub> into the EVA. At the end of this process, we obtain two samples that we will examine later: pure ZnO/EVA, and EVA/ZnO doped with 30% In<sub>2</sub>O<sub>3</sub>.



(a)

(b)

Fig. 3 EVA pure and gel before and after

### **3** Results

This is the main part of the study, where we present the most significant results obtained when using various characterization methods at the University of Constantine1 and at the Algerian Semiconductor Technology Research Center for Energy (CRTSE). These techniques were applied to samples prepared from pure ZnO/EVA and doped with  $In_2O_3$ .

DRX characterization was performed using an Empyrean Panalytical diffractometer, where X-ray radiation emitted from cobalt K $\alpha$  with a wavelength of  $\lambda = 1.789$  Å was used (Fig. 4).



Fig. 4 X-ray diffraction analysis of pure and doped ZnO



Fig. 5 Scanning electron microscopy (SEM) image of ZnO \* 10,000. In<sub>2</sub>O<sub>3</sub>/ZnO (30%)

The first observation that can be made from the spectra of pure ZnO and doped ZnO is that we observe the peaks of the hexagonal Wurtzite structure of ZnO, whether it is pure or doped. This indicates a structure with the same structural characteristics as that of bulk ZnO, whether it is pure or doped with  $In_2O_3$ . As for the  $In_2O_3$ -doped layers, we can say that  $In_2O_3$ -doped ZnO up to a concentration of 30% forms solid solutions: the  $In_2O_3$  atoms are placed in substitution or interstitial sites.

The second observation concerns the intensity of the peaks, where a decrease in the peaks is clearly evident, whether they are intense peaks or others. This is explained in terms of crystallinity, where the intensity of pure ZnO decreases significantly with increasing  $In_2O_3$  concentration, while the intensity of  $In_2O_3$  peaks gradually increases with increasing dopant concentration.

The morphology of the deposited ZnO/EVA layer was observed by scanning electron microscopy. Figure 5 depict the morphology of the undoped and  $In_2O_3$ -doped ZnO/EVA layer deposited on glass using the sol-gel technique.

In Fig. 5, a SEM image of ZnO and 10%  $In_2O_3$ -doped ZnO with a magnification of 10,000×, it can be observed that the powder exhibits a homogeneous particle size distribution. The grains are nano-sized particles with a size of 0.01 nm or smaller. In Fig. 5, a SEM image of 30%  $In_2O_3$ -doped ZnO with a magnification of 10,000×, it can be observed that the powder exhibits a uniform compact homogeneous particle size distribution with some irregularities. However, there are grains that are not nano-sized particles, possibly because the material was not ground properly due to the high amount of doping added compared to the initial amount.

#### 4 Conclusion

The study using X-ray diffraction (XRD) has shown that our powders become crystalline with a Wurtzite hexagonal structure after being subjected to a thermal annealing at 450 °C. Additionally, doping with a high percentage has an impact on

the average grain size. The morphological characterization conducted by scanning electron microscopy (SEM) has confirmed the structure observed by XRD and has also revealed the homogeneity of our powders, indicating a high lifetime. In conclusion of this study, ZnO emerges as an ideal semiconductor for solar applications as a thin film, potentially enhancing efficiency. The performance of ZnO can be enhanced by introducing highly thermally conductive semiconductor nanoparticles as dopants. In terms of dopants, we focused on the effect of  $In_2O_3$  doping in ZnO. It was observed that for all doping levels, the absorbance increases with the doping rate.

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# Synthesis and Characterization of $Zn_{(1-x)}Ni_{(x=0.01-0.03)}O$ Nanofilms Under Specific Conditions: Enhancement of Red Emission, and Photodegradation Retarding Behavior



# Abdelhalim Ouhaibi, Bachir Eddine Messaid, Rafik Serhane, Abdelhalim Zoukel, and Abderezak Zellagui

**Abstract** In this work, undoped and Nickel (1, 2, and 3%) doped ZnO nanofilms were synthesized on glass substrates by ultrasonic spray method. The structure was studied by X-ray diffraction (XRD). Optical properties of samples were analyzed by photoluminescence (PL) spectroscopy. Subsequently, sprayed nanofilms were used as catalysts in an experiment for the degradation of methylene blue (MB) under UV irradiation. XRD spectra confirmed the hexagonal 'wurtzite' structure with polycrystalline nature of undoped and Ni doped nanofilms, and revealed that no compound containing Nickel appeared confirming the good quality of the structures. Photoluminescence spectra showed that all samples exhibited strong UV emission with blue emission. The absence of green emission in all the spectra is obvious and unexpected. A regular red emission is strangely observed in the spectra of doped nanofilms only, which can be exploited by the development of photo or electroluminescent devices based on Ni doped ZnO. Phtodegradation of undoped ZnO exhibited high degradation rate activity by 87.1% compared to 61.4%, 49.7%, 72.7% of Ni doped ZnO

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175

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(1%, 2%, and 3%) respectively. Therefore, Ni doping lowered the photocatalytic efficiency of ZnO nanofilms.

Keywords Spray · ZnO · Ni doping · Photoluminescence · Photodegradation

### 1 Introduction

ZnO is among the most interesting materials in its powder, thin films or nanofilms forms having multitude applications in several fields [1–7]. Particularly in recent years, many research have been focused on photodegradation of pollutant caused by chemical or biological products such as organic chemicals, bacteria, industrial dyes, and antibiotics that have a direct negative influence on the environment [8]. ZnO has a wide band gap of  $\sim 3.37$  eV and high energy binding of excitons of 60 meV.

When irradiated by an energy greater than or equal to its gap, electron and hole  $(e^{-}/h^{+})$  pairs energy will be created in conduction band (CB) and valence band (VB) respectively. The generated  $(e^{-}/h^{+})$  pairs are the main actors in oxidation–reduction reaction of adsorbed organic molecules on the samples surface. The  $(e^{-})$  react with O<sub>2</sub> molecules dissolved in the aqueous solution in forming superoxide O<sup>-</sup><sub>2</sub>, while the  $(h^{+})$  react with OH<sup>-</sup> or H<sub>2</sub>O to form hydroxyl radicals (·OH), which act in the degradation of the organic pollutant [9].

ZnO nanofilms can be nanostructured by many chemical and physical techniques namely magnetron thermal evaporation [10], sputtering [11], sol–gel [12], hydrothermal [13], chemical vapor deposition (CVD) [14]. In the present work, ultrasonic spray was used in the elaboration of samples due its simplicity and low cost [15]. The main goal of the study is to synthesize undoped and Ni-doped ZnO nanofilms in order to study the role of Nikel doping on the photocatalytic activity as well as on the generation of visible emissions, in particular the rare red emission in ZnO.

# 2 Experimental

Utrasonic spray technique was used to elaborate undoped and Nikel-doped ZnO nanofilms on glass substrates preheated to 400 °C. The starting solution of 0.3 M concentration of ZnO was prepared by dissolving Zinc acetate  $(Zn (CH_3OO)_2, 2H_2O)$  in 25 ml of Methanol. Nikel dichloride (NiCl<sub>2</sub>, 6H<sub>2</sub>O) was used as Ni dopant. The molar ratio concentration Ni/Zn in the initial solution was varied to obtain Ni/ZnO atomic ratios of 1, 2 and 3%. Resulting aqueous solution was stirred for 1 h before use. Glass substrates have been cleaned as follow: 15 min in dilute acetone, 15 min in ethanol and 5 min of rinsing in deionized water before being dried with compressed air. The process of the ultrasonic spray technique used in this work is detailed in our

old paper [16] except that the deposition operation of the present work was carried out in a clean room.

#### **3** Characterization Details

The crystal structures of sprayed nanofilms were studied using X-ray diffractometer (XRD, BRUKER AXE D8 ADVANCE) with Cu Ka radiation (wavelength of 1.54 Å) in the range of diffraction angles between 20° and 85°. Photoluminescence characterization was carried out by FL3-DFX-iHR320 Photoluminescence equipment. Finally, the photodegradation activity was analyzed by measuring the decomposition rate of methylene blue (MB) solution exposed to UV irradiation in the presence of ZnO samples.

#### 4 Result and Discussion

#### 4.1 X-Ray Study

Nanoparticles X-Ray diffraction (XRD) patterns of ZnO are shown in Fig. 1. All the obtained peaks can be indexed to single phase hexagonal wurtzite structure of ZnO with p63mc space group and polycrystalline nature according to standard values (JCPDS Card Number 36-1451) [17, 18]. No signal of the metallic Zn is detected by XRD. In addition, there are no peaks corresponding with the Ni compounds, suggesting the incorporation of Ni atoms into ZnO. The average grain size of Ni-doped ZnO nanoparticles was estimated using Scherer's equation [19]

$$D(hkl) = \frac{0.9\lambda}{\beta \cos\theta}$$
(1)

The following relations calculated the lattice parameters 'a' and 'c' [20]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$
(2)

And

$$2d(hkl)\sin\theta = n\lambda \tag{3}$$

where  $\lambda$  is the wavelength of Cu K $\alpha$  radiation,  $\beta$  is the full width at half maximum (FWHM) of corresponding peak, and  $\theta$  is the diffraction angle.



Fig. 1 XRD spectra of undoped and Ni-doped ZnO

Table 1 summarizes the calculated values of the different ZnO nanocrystallite sizes using the most intense (101) and (002) diffraction planes.

The average nanocrystallite size values increased slightly from 18.62 nm for pure ZnO to the maximum value of 21.26 nm for 1% Ni-doped ZnO, which is possibly due to the closeness of the ionic radius of Ni + 2 (0.69 A°) and Zn + 2 (0.74 A°).

So, the incorporation of Ni atoms with a maximum percentage of 3% did not modify the lattice architecture of ZnO. These results agree well with the literature [21].

Sample	(hkl) plane	a (Å)	c (Å)	<d> (nm)</d>
ZnO	(002) (101)	3.239	5.189	18.62
ZnO_Ni1	(002) (101)	3.235	5.202	21.26
ZnO_Ni2	(002) (101)	3.239	5.189	19.08
ZnO_Ni3	(002) (101)	3.237	5.188	19.66
Reference (JCPDS card number 36-1451)	-	3.249	5.206	-

Table 1 Grain size an lattice parameters of undoped and Ni doped ZnO Nanoparticles

The definition of significance of bold in the table: Ref (JCPDS card number 36-1451) is the XRD reference data for ZnO wurtzite



Fig. 2 Photoluminescence spectra of undoped and Ni doped ZnO

#### 4.2 Optical Measurement

#### 4.2.1 Photoluminescence Spectroscopy

Photoluminescence spectroscopy was used to obtain detailed insight into the effect of Ni dopant incorporation on the band gap, defects density as well as luminescence characteristics of ZnO. As shown in Fig. 2, normalized PL spectra of undoped and Ni doped ZnO nanofilms have a strong UV band peak around 379 nm (Eg ~ 3.27 eV). A narrow excitonic peak forms undoped ZnO PL spectrum indicating the good crystallinity of the structure. Besides, Ni doped ZnO PL spectra are composed of wide peaks ranging fromUV to visible region. The violet emission peaks located between 402 and 410 nm were attributed to the transition of electrons from a set of shallow levels below the conduction band to the valence band and interstitial oxygen atoms (O<sub>i</sub>) [22]. The observed emission peak around 415 nm was assigned to the electronic transition energy from the conduction band to Zn vacancies [23]. The blue emission peaks between 441 and 480 nm are due to the transition of electrons from interstitial Zn<sub>i</sub> zinc atoms to the top of the valence band. Beside, an important, rare, and uniform red emission appeared at 650 having oxygen interstitial (Oi) and oxygen vacancy (V<sub>O</sub>) as origins [24, 25].

#### 4.3 Photocatalytic Activity

The photocatalytic activity of undoped and Nikel-doped ZnO thin nanofilms was evaluated by the degradation of methylene blue (MB) dye solution as an organic pollutant under UV lamp. The degradation mechanism is described in the literature by the following chemical reactions [25]:
$$ZnO + hv \rightarrow e^{-}CB + h^{+}VB$$
 (Electron/hole pair generation) (4)

$$OH^- + h^+ VB \rightarrow OH (Hydroxyl radical)$$
 (5)

$$O_2 + e^-CB \rightarrow O_2^-$$
(Superoxide radical) (6)

$$MB Molecule + \cdot OH^{-} \rightarrow CO_{2} + H_{2}O(MB dye degradation)$$
(7)

The hydroxyl radicals (·OH) and super-oxide ions ( $\cdot O_2^-$ ) are highly reactive species with a property of organic compounds degradation. The absorbance measurements are grouped in Table 2. The following relation calculated the photocatalytic degradation percentages:

$$Photodegradation(\%) = (A_0 - A) \times 100 A_0$$
(8)

Where,  $A_0$  and A are the initial absorbance of dye and the absorbance after UV irradiation respectively.

From Fig. 3, it is observed that undoped ZnO exhibited higher photocatalytic activity with 87.1% comparatively to Ni doped ZnO nano films 1%, 2% and 3% which reached 61.4%, 49.7%, 72.7% respectively. The high photocatalytic activity of undoped ZnO can be attributed mainly to the migration of charge carriers ( $e^-$  electrons and  $h^+$  holes) towards the catalytic surface during UV irradiation, as well as their participation in the redox reaction with the adsorbed dye, which is confirmed by the PL results. The photodegradation activity results revealed that Ni-doped ZnO restricted the degradation of MB under UV. Therefore, this result can be exploited in specific applications. The obtained result can be merged with some techniques in control theory [26–31].

Time (mn)	0	30	60	90	120	150	180	210
Undoped ZnO	0.40	0.27	0.23	0.19	0.17	0.13	0.09	0.05
ZnO_Ni1	0.40	0.26	0.25	0.24	0.23	0.20	0.17	0.15
ZnO_Ni2	0.40	0.36	0.36	0.29	0.29	0.25	0.22	0.20
ZnO_Ni3	0.40	0.37	0.33	0.26	0.24	0.18	0.14	0.11

**Table.2** Absorbance values of the irradiated MB each 30 min for 210 min at  $\lambda = 663$  nm



Fig. 3 MB degradation rate as a function of UV irradiation time for undoped and Ni-doped ZnO nanofilms

#### 5 Conclusion

In the present work, Zinc oxide nanofilms were deposited by ultrasonic spray technique on glass substrates at 400 °C. The effects of doping by Nikel on structural, optical, and photocatalytic properties were analyzed. The X-Ray diffraction revealed the wurtzite polycrystalline structure of undoped and Ni doped nanofilms. The PL spectra of all sprayed ZnO nanofilms exhibited the presence of UV and visible light emission. The peaks located around 379 nm are attributed to the recombination of (electron/hole) in the valence band. Visible peaks from 402 to 480 nm were attributed to the electronic transitions from conduction band to Zn vacancies, interstitial atoms (Zn<sub>I</sub>) to valence band and oxygen vacancies respectively. An important red emission appeared at 650 having oxygen interstitials (Oi) as origin. Ultimately, photocatalytic results showed that the best photocatalytic efficiency joined 87.1% by undoped ZnO nanofilms compared to Ni doped ZnO which restricted the degradation.

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# Synthesis and Characterization of Nickel Doped Fe<sub>3</sub>O<sub>4</sub> Nanoparticles Using Solvothermal Method



E. Aliouat, N. Belmokhi, B. Mihoubi, H. Filali, R. Bouhroum, and N. Boukheit

Abstract Over the past 20 years, research on nanomaterials has made remarkable progress not only in the controlled synthesis and the study of novel properties, but also in the multiple applications of matter at the nanoscale. Currently,  $Fe_3O_4$  magnetite nanoparticles continue to pose an enigma, as the understanding of certain fundamental properties remains unclear despite vigorous efforts and substantial progress in research. In fact, these materials have attracted considerable attention in the fields of new technology with different but complementary motivations using various types of experimental techniques and theoretical approaches. In this work, we present the results obtained from a thorough analysis of  $Fe_3O_4$  nanoparticles with various Nickel concentrations synthesized through a simple solvothermal method. Characterization methods are mainly structural (XRD, SEM) and physical (UV–Vis, FTIR, ...). The SEM images show that the prepared NPs exhibit spherical shape with nanometric size confirmed by X-ray diffraction. Furthermore, the Nickel substitution of iron cations into the crystalline structure had an impact on the average crystallite size. Raman spectra of  $Fe_3O_4$  magnetite nanoparticles are very consistent with the literature.

Keywords Magnetite · Magnetic properties · Nanoparticles

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185

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# 1 Introduction

In recent years, the high demand for magnetic materials in biomedical applications has prompted researchers to explore innovative approaches for synthesizing iron oxide nanomaterials [1–3]. In addition to its very high magnetic properties and electronic conductivity [4, 5], magnetite's biocompatibility [6, 7] and low toxicity have made it the driving force behind research efforts aimed at a multidisciplinary field of study. These experimental studies have revealed that magnetite has made significant progress both in the controlled synthesis of nanoparticles and in the exploration of new properties, which is intensifying its use in advanced medical technology applications [8–11].

Several synthesis methods for iron-based nanoparticles have been developed, including co-precipitation [12], micro/nano-emulsion [13], green (biosynthesis) [14], and solvothermal methods [15–17]. Each synthesis method has a different yet significant impact on a specific biomedical application.

Despite the relatively low quantities of materials produced through the solvothermal route, this technique appears well-suited for synthesizing nanoparticles smaller than 25 nm, in various shapes, with superior performance. However, it is essential to note that stability and sensitivity to aggregation pose major challenges. Consequently, researchers have focused on surface coatings to preserve stability and properties of nanoparticles when suspended in physiological environments [18, 19], which is particularly important because magnetic nanoparticles in water- and protein-rich environments are exposed to different PH conditions during preparation and biomedical applications [20].

Furthermore, new perspectives on enhancing the magnetic properties of magnetite nanoparticles have intensified research activities through doping reactions with transition metals.

In this study, a simple solvothermal method was employed to synthesize nickel doped  $Fe_3O_4$  nanoparticles. Advanced microstructural and magnetic analyses using usual characterization techniques (XRD, FTIR, Raman, VSM...), provided necessary insights for a better understanding of their properties.

#### 2 Preparation Method

Synthesis of the  $Ni_xFe_{3-x}O_4$  NPs was carried out based on solvothermal method, in which Ferric chloride (as iron source), Diethanolamine (DEA), Sodium hydroxide, Ammonium acetate and Ethylene glycol (as reducing agent) were used.

At first, iron chloride and nickel acetate were used by respecting the reports, 48 mmol of Sodium hydroxide and 240 mmol of Ammonium acetate were dissolved separately in 20 ml, 10 ml, and 40 ml of ethylene glycol respectively under magnetic stirring to form clear solutions. Then, 4 cm<sup>3</sup> of DEA was mixed with the solutions and stirred for 2 h at room temperature. The obtained mixture was transferred to a

Teflon-lined autoclave and maintained at 200  $^{\circ}$ C for 12 h. Finally, the sediment was washed with distilled water and dried at 100  $^{\circ}$ C.

### **3** Results and Discussion

Analysis of the X-ray diffraction patterns of nickel-doped  $Fe_3O_4$  nanoparticles (Fig. 1) shows good agreement with those of magnetite, which crystallizes in a spinel structure in the cubic space group Fd-3m with a lattice parameter of 0.8396 nm (JCPDS card no. 19-629). Thus, the solvothermal method enabled the synthesis of nickel-doped magnetite without second phase of Ni or one of its compounds. Moreover, the reaction precursors inducing magnetite formation were not detected by XRD. In view of this result, we can conclude that the  $Fe_3O_4$  formation reaction is complete. This confirms the formation of a single-phase solid solution with no secondary phase [20].

Table 1 summarizes the influence of doping on the lattice parameter and crystallite size estimated, from the main reflection, by Scherer equation.



Fig. 1 XRD patterns of Fe<sub>3</sub>O<sub>4</sub> nanoparticles doped with a 0.5% Ni; b 1% Ni

Table 1         Lattice parameter           and crystallite size of nickel	Sample	Average grain size (nm)	Lattice parameter (Å)	
doped nanoparticles	0.5% Ni	22.62	8.385	
	1% Ni	17.59	8.392	

The lattice parameter values of nickel-doped nanoparticles are very close to those of magnetite reported in the literature. Surface oxidation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles could explain the difference between the calculated and theoretical parameters. It has been reported that the thickness of the oxide layer can reach 3 nm [21]. What's more, the lattice parameter of the nanoparticles increases relatively slightly with the rate of nickel doping. This confirms the insertion of nickel into the magnetite lattice [22]. The main purpose of this insertion was to enhance the magnetic properties of magnetite nanoparticles. As the syntheses were carried out under similar conditions, the variation in the lattice parameter can be explained by the difference in the ionic radii of the two cations, but also by their preference for a specific coordination. On the other hand, studies of zinc doping of magnetite have reported that Zn<sup>2+</sup> can occupy both octahedral and tetrahedral sites, and the sites that  $Zn^{2+}$  actually occupies depend on the amount of dopant (Zn) and the method of synthesis [23]. Thus, if we consider not only the ion radii (R Fe<sup>3+</sup> = 64 pm, R Ni<sup>2+</sup> = 0.69 pm) but also the size of the octahedral and tetrahedral sites of the spinel structure, the slight increase observed strongly suggests the substitution of ferric ions by nickel ions in the tetrahedral sites for rates of less than 3%. Indeed, the insertion of the Ni<sup>2+</sup> cation, which is larger than the Fe<sup>3+</sup>cation, into the tetrahedral site induces a slight broadening of the structure and thus a slight increase in the crystalline parameter. A substitution of ferrous ions by nickel ions should lead to a narrowing of the structure, since the Fe<sup>2+</sup>cation is larger than  $Ni^{2+}$  [24].

The reduction in crystallite size of nickel doped magnetite is certainly due to the replacement of some smaller trivalent iron ions (0.63 Å) by larger divalent Ni ions (0.69 Å). Indeed, the size difference may also be responsible for the ionic forces confining the Ni<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> solid solution to the crystal structure, resulting in a spontaneous reduction in particle size [25].

However, for 5% nickel doping, as evidenced by the insertion of Zn into the magnetite lattice at high doping levels. The  $Ni^{2+}$  ion replaces  $Fe^{2+}$ , while electrical neutrality is maintained, making it impossible to distinguish a difference.

Optical transmission spectra are performed on nickel-doped nanoscale powders as shown in Fig. 2a. The two similar spectra show that magnetite doped with nickel is transparent at room temperature in the spectral range from 300 to 800 nm. High values of average optical transmission are observed on illustrative nanoparticles of NixFe<sub>3-x</sub>O<sub>4</sub> powders with x = 0.5 and 1% between 500 and 800 nm. It reaches 80% for 0.5% and 90% for 1%, respectively, as a doping rate. This result clearly highlights the influence of doping on transmission. We note that the difference between the two spectra is significant, approximately, it is about 5%. The transparent magnetite is very often explained by the inter-band electronic transition, due to decreasing of band gap energy [26].

As a precision tool compared with the tauc plot method, the technique based on the first derivative of the transmission with respect to energy is introduced. The latter method offers the applicability advantage in wide range of experimental conditions and validating its adequately compared with second method. The two methods' consistency leads to a good reliability of calculation [27]. The dT/dE Ni<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> curves (Fig. 2b) with x = 0.5 and 1% clearly show that the difference in the powder



Fig. 2 Transmittance spectra (a) and dT/dE curves (b) of nickel-doped magnetite

gap is not significant, it is around 1.79 eV. The values of these gaps are important and confirm the semiconductor nature of our powders (Fig. 2).

Infrared spectroscopy analysis enables the determination of different vibrational bonds and the location of characteristic bands of chemical molecules present in metal oxide spinel systems. Figure 4 presents the FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> nanoparticles doped with x = 0.5 and 1%, recorded in the range of 400–4000 cm<sup>-1</sup>. The two



Fig. 3 FTIR spectra of nickel-doped magnetite



Fig. 4 Spectral deconvolution into Gaussian-shaped bands of Raman spectra of nickel-doped magnetite

obtained spectra are usable and comparable to each other, with no significant differences observed. As a result, the analysis of the profiles reveals three distinct regions: the first region between 400 and 700 cm<sup>-1</sup>, characterized by the peak at 542 cm<sup>-1</sup>, attributed to the vibration of the Fe–O bond in Fe<sub>3</sub>O<sub>4</sub>; the second region between 700 and 3000 cm<sup>-1</sup> is attributed to the stretching vibrations of the CH, C=O, and C=C groups of sodium oleates absorbed on the surface of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles; and the third region corresponds to the stretching vibrations of OH, which is attributed to OH absorbed by the Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the precursor [28] (Fig. 3).

In recent years, Raman measurements were performed on magnetite by several groups of researchers. Some of these measurements were directly derived from Verwey's model, whose validity has recently come under increased scrutiny, mostly after a number of neutron and electron diffraction studies, but also NMR studies, have suggested that magnetite exhibits a more complex crystalline structure at low temperatures than that in Verwey's model. Careful consideration of the sizeable literature on the Raman spectroscopy of magnetite ( $Fe_3O_4$ ) shows variety not only in the number of the observed Raman modes, but also in their spectral positions and their attribution to underlying mechanisms. Because of this diversity, researchers turned to the spinel structure to perform a symmetry analysis and determine the phonon modes attributable to the observed Raman bands. It is now accepted that magnetite has an inverse spinel structure described by the cubic space group Fd3m (OFh). Symmetry considerations predict five Raman-active modes that can be summed up by the following equation:

$$G = A1g + Eg + 3T2g \tag{1}$$

Nanometric nickel-doped magnetite powders were characterized using Raman spectroscopy. Figure 4 shows the spectral deconvolution into Gaussian bands of the Raman spectra of the powders recorded between 250 and 800 cm<sup>-1</sup>. Analysis of

the two spectra reveals the absence of the 220, 290 cm<sup>-1</sup> doublet, characteristic of hematite, and thus the formation of hematite in our samples is excluded. On the spectrum in Fig. 4a, obtained from the powder doped with 0.5% nickel, three peaks at 337.98, 497.14, and 669.98 cm<sup>-1</sup> and a shoulder at 718.56 cm<sup>-1</sup> are observed [29–32]. Given the specificity of the spectrum on Fig. 4a, the attribution of the modes to the observed bands is done following the extant literature. Hence, the three peaks are attributed respectively to the Eg, F2g (2), and A1g. The shoulder at 718.56 cm<sup>-1</sup> essentially proves the superficial oxidation of magnetite into maghemite. The spectrum in Fig. 4b, obtained from the powder doped with 1% nickel, confirms that superficial oxidation with the presence of a shoulder at 718.85 cm<sup>-1</sup>. In addition to the three bands, Eg, F2g (2), and A1g, at 318.21, 488.97, and 668.01 cm<sup>-1</sup>, respectively [29–32], a fourth, weak-intensity band is observed at 377.19 cm<sup>-1</sup>. We think, as shown by Monika Hanesch [33], that it is the sign of the onset of the transformation of magnetite into maghemite. This is due to the fact that the divalent iron renders magnetite easily prone to oxidation.

Moreover, the spectra show that the observed Raman bands are wide, a phenomenon usually explained by the conduction mechanism in magnetite, but also by the electronic disorder associated with the random arrangement of the  $Fe^{2+}$  and  $Fe^{3+}$  ions on the octahedral sites [30].

The iron oxide  $Fe_3O_4$ , a magnetized substance known for an extended period, has been a subject of extensive study in the field. The multitude of research efforts carried out on the magnetism of transition metal oxides, particularly magnetite, highlights the growing interest in this material [34–36]. In fact, the magnetism of  $Fe_3O_4$  has long been a topic of discussion due to numerous controversies regarding the comprehension of some of its fundamental properties. Nowadays, this issue is addressed through purely quantum concepts based on two hypotheses that assimilate ions to magnetic dipoles:

The first, often overlooked, strictly treats the magnetic moment of the nuclei, which provides much information about nuclear magnetism.

The second that considers that the interactions are essentially due to only the spins of the  $Fe^{2+}$  and  $Fe^{3+}$  ions.

In the case of magnetic, its ferrimagnetic character is largely contingent upon the alignment of spin magnetic moments of  $Fe^{2+}$  and  $Fe^{3+}$  ions. It has been demonstrated that in octahedral sites, the moments are aligned in a parallel position, whereas in tetrahedral sites, ferric ions are distributed in an antiparallel alignment. Considering this configuration, the magnetic moments of ferric ions completely compensate each other. Thus, an overall magnetization of  $Fe_3O_4$  resulting from the magnetic moments of ferrous ions is perceptible even in the absence of an external magnetic field [37–40].

The magnetic response of  $Ni_xFe_{3-x}O_4$  powders with 0.5and 1% nickel was measured using a Vibrating Sample Magnetometer (VSM), allowing the extraction of general characteristics (saturation magnetization, coercivity, and remanence) for both powders [23]. Figure 5 compares the evolution of the magnetization as a function of the applied magnetic field of the two powders. The magnetization deduced from the curves and the mass of the powders is given in "emu/g". It is observed that both products exhibit superparamagnetic behaviour, featuring an open hysteresis loop



Fig. 5 Magnetic hysteresis loops of nickel-doped magnetite

Characteristics	Fe <sub>3</sub> O <sub>4</sub> with 0.5% Ni	Fe <sub>3</sub> O <sub>4</sub> with 1% Ni	
Saturation magnetization Ms (emu/g)	70.8	67.23	
Coercivity Hc (emu/g)	9.8	8.75	
Remanent magnetization (Oe)	90.77	72.99	

Table 2 Magnetic characteristics of the magnetite

with non-zero coercive field (Hc) and remanent magnetization (Mr). The saturation magnetization, coercivity, and remanence characteristics are summarized in Table 2.

A decrease in these characteristics is observed with increasing nickel doping rate. We attribute this decrease in the magnetic properties of nickel-doped magnetite to the difference in chemical composition of the two powders, by reason of their very close sizes. For both samples, saturation magnetization is achieved at an applied magnetic field of approximately 1.25 Oe.

### 4 Conclusion

The work presented in this paper aims to study nickel-doped magnetite nanoparticles synthesized by solvothermal technique using iron chloride and nickel acetate. The synthesis experimental parameters were optimized to obtain quasi-spherical nanoparticles with controlled size. Various characterization techniques were used to address the microstructural and magnetic properties of nickel-doped magnetite. The analysis of the results shows that the incorporation of nickel into the spinel structure of magnetite induces a slight evolution in the lattice parameter, as demonstrated by X-ray diffraction. In addition, variations in the magnetic properties have been recorded.

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# Effect of Ni-Doping on ZnO Nanostructures Properties



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**Abstract** In this work we have prepared and characterized nanoparticles of zinc oxides (ZnO) pure and doped with Nickel by the Sol Gel method. This non-costly, easy method makes it possible to have more homogeneous powders with a finer particle size. XRD analysis confirmed hexagonal würtzite-like structure of ZnO nanoparticles. Sizes of these nanoparticles are in an order of magnitude of a few tens of nanometers. The doping of ZnO nanopowders with 5% Ni improved the crystalline quality; this is revealed by the increase in the intensity of the peaks. The infrared absorption spectroscopy (FTIR) made it possible to identify the nature of the bonds present in the ZnO nanopowders. FTIR spectra confirmed two characteristic bands attributed to Zn–O stretching bands. The degradation rate of methylene blue (D) of pure ZnO reaches 99.6% after 90 min. Nickel doping greatly reduced the degradation (D) from 99.6 to 21%.

Keywords ZnO · Doping · Sol gel · Nanoparticules · Photocatalytic activity

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197

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# 1 Introduction

In recent years has promoted itself as an interesting metal oxide material because of its properties like high refractive index, binding energy, high thermal conductivity, antibacterial and UV protection. ZnO could be used in many materials and product like include medicine, cosmetics, rubber, solar cells and foods [1]. Zinc oxide has high biocompatibility and fast electric transfer kinetics, such phenomena encourage the use of this material as a biomimic membrane to immobilize and modify the biomolecules [2]. The addition of impurity atoms, or doping [3, 4] to the zinc oxide changes the optical and electrical properties of the material, making it suitable for new applications and devices.

Substitution of foreign impurities modifies; bandgap, optical, electrical and magnetic properties [5, 6]. Photoluminescence spectra defect level was reducing in the ZnO nanoparticules (NPs), by increasing of Fe concentration in the ZnO lattice sites [7]. In literature, the Cu doped ZnO NPs reduction in the energy gap from 3.49 to 3.43 eV revealed the substitution of Cu<sup>2+</sup> ions in the ZnO lattice [8]. A variety of chemical techniques were used to synthesize ZnO NPs, such as solvothermal [9], hydrothermal [10], co-precipitation [11] and sol–gel methods [12], etc. Among these synthetic routes, sol Gel method has been popularly adopted to synthesize by using ZnO NPs due to its easy method, low cost and high yield of nanoparticles with uniform size. In the present work, Ni doped ZnO were synthesized by Sol Gel method. We have studied the structural and optical properties of the Ni doped ZnO NPs for using photocatalytic application.

### **2** Experimental Details

A first aqueous solution with a concentration of 0.1 mol/L of zinc acetate dihydrate  $(Zn(CH_3COO)_2.2H_2O)$  is dissolved in distilled water with continuous stirring at moderate speed at 80°C. In parallel, a second solution of citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> dissolved in ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) with magnetic stirring at room temperature for 15 min is then added drop by drop to the first solution with continuous magnetic stirring until a homogeneous gel. The gel is dried at 80 °C for 24 h to obtain Zinc oxide. After that, we crush the product manually in a mortar until the granules are then homogeneous and then we treat the powder obtained by annealing at a temperature of 400 °C for 4 h. Finally, we obtain the pure Zinc oxide nanoparticles.

#### **3** Results and Discussion

#### 3.1 X-Ray Diffractometer (XRD)

Figure 1 shows the X-ray diffraction (XRD) spectra of the pure ZnO sample. All the diffraction peaks observed are: (010), (002), (011), (012), (110), (013), (0220), (013) and (021) correspond to those of ZnO of hexagonal structure type würtzite (JCPDS 96-900-4180). All the peaks are intense, sharp and fine, affirm the good crystallinity of the elaborated nanostructures and their poly-crystalline natures and thus formed crystallites in different orientations. The three most intense and dominant peaks are located around the diffraction angle  $2\theta = 31.737^{\circ}$  and  $36.225^{\circ}$  correspond to the (010) and (011) planes respectively. The intensity of this last peak indicates that (011) is the preferred orientation. The variation in the intensity of the peaks implies a variation in the number of atoms which refract in each of the directions and the variation in the position of the peaks implies a variation in the structural parameters (cell parameters, cell volume, etc.). Indeed, the XRD spectra of the pure ZnO samples reveal an improvement in the intensity, thus indicating better crystallization. We also observe that there is no detected peak of the parasitic phase therefore all the lines observed belong to the hexagonal structure of ZnO.

The ZnO obtained was identified by comparison with the database (JCPDS card No: 96-900-4180). It has a hexagonal würtzite crystal system structure with space group P63 mc symmetry, with lattice parameters:

a = b = 3.2530 (Å) and c = 5.2070 (Å) and angles  $\alpha = \beta = 90^{\circ}$  and  $\gamma = 120^{\circ}$ . This result is in good agreement with the results obtained in the literature [13, 14].



Fig. 1 XRD pattern of pure ZnO nanoparticles

Figure 2 shows the X-ray spectra (XRD) of undoped and doped with 5% Nikel ZnO samples. The diffraction peaks obtained with intensities correspond to the (110), (002), (011), (012), (110), (013), (020), (112) and (021) planes. Indeed the two diagrams represent the same dominant peak (011) which is located around the angle of 36.22° and which means that the two spectra present a single poly-crystalline phase which correspond to the hexagonal structure of the würtzite type (JCPDS 96-900-4182). The average particle size has been determined from full width at half maximum (FWHM) of the diffraction peaks using Scherrer's equation (Table 1). The average particle size of un-doped zinc oxide nanoparticles has been found to be 28.5 nm. Nickel doping reduced average particle size to 16.39 nm.

There is a slight shift of peaks towards high values. This leads to a decrease in parameter c (Table 2). Some authors attribute this shift to the incorporation of Ni ions in the substitution sites [15, 16]. We also observe a peak, located at  $2\theta$ = 44.47° which can be attributed to the parasitic phase NiO with low intensity



Fig. 2 XRD pattern of un-doped and doped ZnO nanoparticles

Doping rate (%)	Phase	2θ (°)	(hkl)	FWHM (°)	D <sub>aver</sub> (nm)	$\delta (10^{14} \text{ lines/} \text{m}^2)$	ε (10 <sup>-4</sup> )
0	Wurtzite	31.781	(010)	0.2323	28.5	12.6	34.1
		36.274	(011)	0.2614			
5	Wurtzite	31.809	(010)	0.398	16.39	23.28	16
		36.287	(011)	0.496			

Table 1 Structural parameters of un-doped and doped ZnO nanoparticles

Strain ( $\epsilon$ ), dislocation density ( $\delta$ ), average crystallite size ( $D_{aver}$ ), full width at half maximum (FWHM), the diffraction angle ( $2\theta$ ) and Miller indices of diffraction planes (hkl)

Doping rate (%)	2θ (°)	(hkl)	d <sub>hkl</sub>	Lattice parameters (Å)		c/a	Volume V (Å)
				a (Å)	<i>c</i> (Å)		
0	31.7806	(010)	0.2813	3.2486	5.2030	1.6016	54.9003
	34.4464	(002)	0.2605				
5	31.8096	(010)	0.2810	3.2457	5.2002	1.6021	54.7818
	34.4657	(002)	0.2600				

Table 2 The cell parameters and volume for un-doped and doped ZnO nanoparticles

Spacing between consecutive parallel planes ( $d_{hkl}$ ), the diffraction angle (2 $\theta$ ) and Miller indices of diffraction planes (hkl)

can be negligible. An increase in intensity is also clearly observed, indicating an improvement in crystallization. The addition of 5% Nickel therefore promotes the state of crystallization of the material [17, 18].

The values of the lattice parameters a and c, deduced from the X-ray spectra, are indicated in Table 2. The orders of magnitude of a and c are characteristic of the würtzite structure of ZnO.

#### 3.2 Infrared Absorption (FTIR) of Zinc Oxide

The analysis of pure and doped ZnO powders by IR infrared spectroscopy allowed us to identify the specific vibrations as well as the characteristic peaks of the matrix of the samples produced. Figure 3 shows the transmission spectrum of the pure ZnO sample. The Zn–O bond was clearly observed at about 483.51 and 463.94 cm<sup>-1</sup> [15] and the C=C bond was observed at about 1530.03 cm<sup>-1</sup>. Two peaks of the absorption bands were observed at about 236.38 and 3740.44 cm<sup>-1</sup> corresponding to O–H vibrations.

# 3.3 Photocatalytic Test of Zinc Oxide

In order to evaluate the photocatalytic activity of pure and Nikel doped ZnO nanoparticles, we used methylene blue (MB) as a target under irradiation from a lamp with a power of 120 W and a wavelength of 365 nm. Figure 4a shows the evolution of the UV–Vis spectrum of methylene blue as a function of time in the presence of pure ZnO nanoparticles. We clearly notice that the absorption peak at 663 nm characteristic of MB decreases sharply with time. Figure 5 shows the variation of the C/C0 ratio which represents the level of methylene blue in the presence of non-degraded zinc oxide nanoparticles over time. The results obtained show that the degradation



Fig. 3 FTIR of pure ZnO

rate (D) reaches 99.6% after 90 min. Figure 4b shows the evolution of the UV– Visible spectrum of methylene blue as a function of time in the presence of ZnO nanoparticles doped at 5% Nickel doping greatly reduced the degradation rate (D) from 99.6 to 21%. The highest photocatalytic activity is obtained for pure ZnO. The maximum absorption is located at 663.07 nm for both cases. The addition of Ni strongly decelerated the degradation of MB. The degradation rate (D) decreased from 97 to 73%.



Fig. 4 Photocatalytic test for ZnO nanoparticles





# 4 Conclusion

We have prepared a pure and doped with 5% Nickel zinc oxide nanopowders using the Sol–gel process. These powders were analyzed using several characterization techniques: XRD, FT-IR and photo-catalytic test. The XRD spectra of the samples revealed the hexagonal Wurtzite-like structure of ZnO. Average crystallites size of un-doped zinc oxide nanoparticles has been found to be 28.5 nm. Ni-doping reduced average particle size to 16.39 nm. FTIR shows two characteristic bands at around 483.51 and 463.94 cm<sup>-1</sup>, which are attributed to the mode vibration of Zn–O. The photo-catalytic activity of ZnO shows that degradation rate (D) of pure ZnO reaches 99.6% after 90 min. Nickel doping significantly reduced the degradation rate (D) from 99.6 to 21%.

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# Synthesis, Characterization and Chemical-Sensor Applications of Zinc Oxide-Graphene Nanocomposite



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**Abstract** The proposed study focuses on the development of a gas sensor utilizing a quartz crystal microbalance (QCM) as the sensing platform. The sensor incorporates a nanocomposite of Zinc Oxide (ZnO) and Graphene as the sensitive layer. The synthesis of this nanocomposite involves a chemical method for thin film is deposition on OCM using spray pyrolysis technique. To evaluate the sensor's sensitivity, the frequency shift ( $\Delta f$ ) of the coated OCM electrode is monitored when exposed to different gas concentrations such as ethanol, propane, and humidity. The frequency shift serves as an indicator of the gas concentration being detected. The isotherm response characteristics demonstrate good reproducibility and reversibility, suggesting the reliability of the sensor. Several techniques are employed to analyze various aspects of the coated QCM electrodes. Contact angle measurements (CA) are utilized to assess the surface wettability, providing information on how the nanocomposites interacts with the surrounding environment. Chemical compositions of the coated electrodes have been investigated by employing attenuated total reflectance-Fourier transform infrared (ATR- FTIR) spectroscopy. Scanning electron microscopy (SEM) is utilized to study the surface morphology of the coated QCM electrodes, providing detailed information on the structure and topography of the sensor's sensitive layer.

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207

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**Keywords** Spray pyrolysis deposition  $\cdot$  Zinc oxide  $\cdot$  Graphene  $\cdot$  Gas sensor  $\cdot$  Quartz crystal micro-balance (QCM)  $\cdot$  Nanocomposites

### 1 Introduction

Over the past few decades, nanomaterials have gained significant attention and have found a wide range of applications across various industries particularly in electronic devices. due to their unique properties at the nanoscale. These materials are engineered to have specific properties based on their size, shape, and composition, making them versatile and valuable for numerous purposes [1-4].

Zinc Oxide (ZnO) nanoparticles are one of these metal oxyde nanomaterials and are highly used in solar cells, antibacterial applications, electronic optics, and chemical sensors. Chemical sensors play a crucial role in analyzers by converting chemical information into useful signals, enabling the detection and analysis of specific components or the overall composition of a sample [5-8]. Chemical sensors consist of a receptor part and a transducer part, and the ideal sensor is affordable, portable, and exhibits perfect selectivity and instantaneous response to the target analyte. The focus of current research lies in the development of Quartz Crystal Microbalance (QCM) gas sensors. QCM sensors are highly sensitive piezoelectric devices that can accurately detect mass changes due to the presence of molecules. The sensing material coated on the QCM's active electrode plays a crucial role in determining the sensor's characteristics. OCM sensors have been widely employed to selectively detect various gases (such as ammonia, alcohol, mercury, hydrocarbons, etc.) and humidity [9]. Strategies to enhance the selectivity of sensing materials on QCM platforms include heterostructure design, surface functionalization, and fabrication of nanocomposites. To improve the sensitivity of QCM sensors, researchers have incorporated sensing materials with high surface area, such as metal oxyde-graphene and its derivatives (graphene oxide and reduced graphene oxide) as nanocomposites [10, 11].

The proposed work aims 1—to investigate the synthesis of ZnO-graphene nanocomposites using solvothermal methods. 2—to elaborate a thin film using the as-prepared solution on commercial QCM electrodes using the spray pyrolysis technique. This technique allows for local deposition of thin films on the QCM electrode's surface in ambient air without causing damage to the piezoelectric quartz. 3—analyze various aspects of the coated QCM electrode by employing several techniques like Contact angle measurements (CA), Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy.in order to provide detailed information on the structure and topography of the sensor's sensitive layer, aiding in the understanding of the gas sensing mechanism and potential optimization of the sensor's performance and 4—evaluate the sensor's sensitivity, by monitoring the frequency shift ( $\Delta f$ ) of the coated QCM electrode when exposed to different gas concentrations such as ethanol, toluene, propane acetone and humidity.

### 2 Materials and Methods

#### 2.1 Synthesis of Zinc Oxide-Graphene Nanocomposites

The pure zinc oxide solution was obtained using a simple solvothermal process by dissolving Zinc acetate dihydrate ( $C_4H_6O_4Zn$ , 99.99% purity, Sigma Aldrich) in the methanol. The molar mass of  $C_4H_6O_4Zn$  is M = 219.51 g/mole. The methanol must completely dissolve the precursor (zinc acetate di-hydrate) in order to obtain a clear solution, calculate by chemical concentration relationship:

$$C = \frac{n}{V} = \frac{m/M}{V}$$

With

- C concentration's solution in (mol/l);
- n Mole number (mole);
- V volume's solution in (ml).
- m the dissolve's mass (g);
- M molar mass (g/mol).

A solution with a concentration of 0.4 M have been prepared using stirrer by adding and heating 4.3902 g of C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>Zn in 50 ml of methanol for 30 min.

In this study, graphite rods from electrical battery devices (as electrodes) and an electrolyte bath (electrochemical cell) composed of  $H_2SO_4$  and  $H_2O$  were used for the electrochemical exfoliation process to obtain high-quality, large-area Graphene thin sheets, the process has been presented in previous works by Bakli et al. [12].

Different amounts of graphene powder were dispersed in a 50 ml of ZnO solution. Then, the suspension was mixed at room temperature for 1 h with ultrasonicating. Then, the well dispersed ZnO-Graphene nanocomposites solution was obtained. The ratio of ZnO and Graphene were controlled by the volume of each solution.

#### 2.2 Coating of the Thin Films

In the described process, ZnO-graphene sensitive layers were prepared using the spray pyrolysis technique. Prior to deposition, all substrates were subjected to ultrasonic cleaning for 30 min in acetone, followed by rinsing with distilled water. The cleaned substrates were then placed on a hot plate maintained at a temperature of 350 °C with an accuracy of  $\pm 2$  °C. The as-prepared solution, containing the ZnO-Graphene nanocomposites, was loaded into a spray gun fixed at a distance of 20 cm above the substrate. To generate a fine mist of the precursor solution, compressed air was used as a carrier gas for spraying. The process parameters were set as follows: a spray time of 5 s, a break time of 1 s, and a total of 60 cycles. These parameters

were determined to ensure a uniform deposition of the solution onto the substrates, resulting in the formation of a consistent and homogeneous sensitive layer.

#### 2.3 Sensor and Measurement System

The principle of the QCM sensors is based on the change in the fundamental oscillation frequency  $\Delta f$  upon ad/absorption of molecules from the gas phase. To a first approximation, the frequency change  $\Delta f$  which results from an increase in the oscillating mass  $\Delta m$  and it was described by the Sauerbrey equation [13]. The piezoelectric crystals used were AT-Cut 6 MHz quartz crystal. The frequency shifts of the vibrating crystal were directly monitored measured using transistor Colpitts oscillator connected to the frequency counter TF930 TTi. The coated QCM-based sensor was evaluated for sensitivity by monitoring the frequency shifts of the quartz treated with different concentrations of VOC vapors with the aid of Labview interface software. A liquid of known volume and density was introduced in the testing cell by a Hamilton syringe and heated to induce free evaporation. Gas sensing measurement system is shown in Fig. 1.

The concentration of the introduced analyte was calculated in parts per million (ppm) according to:

$$C = \frac{\rho V_1}{V} = \frac{m_g}{V}$$

Fig. 1 Gas sensing measurement system



where

- C is the concentration in ppm,
- m<sub>g</sub> is the weight of analyte in milligrams,
- V is the volume of the testing cell in l,
- $\rho$  is the density of liquid sample in milligrams/l,
- $V_1$  is the volume of liquid sample in l.

After diffusion towards the electrode surface, the injected vapor was subsequently adsorbed on the functionalized QCM electrode which induced a frequency shift ( $\Delta$ f). After the adsorption process, the test chamber was purged with dry air until the vapor desorption process took place. The sensor sensitivity was evaluated against concentrations of propane, ethanol, and humidity vapours. Inside the chamber, the humidity and temperature evolution was monitored by THT22 temperature and humidity sensor with Arduino microcontroller.

#### **3** Results and Discussion

#### 3.1 Quartz Crystal Microbalance Responses

The kinetic responses of QCM-based sensor coated with thin layer of ZnO-Graphene nanocomposites are shown in Fig. 2a. The sensor responses in terms of frequency shift were plotted against time for concentrations of ethanol, propane, and humidity vapors ranging. For all vapors, the isotherms showed that the absolute value of the shift frequency increases gradually with time then reaches a steady state value. Between measurements, the sensor was exposed to dry air until full desorption was achieved. The frequency of the crystal back returning to its initial values indicates full desorption of analytes from the coated electrode surface. The elaborated sensor exhibited fairly rapid response, negligible baseline drift, and good reversibility for all vapors. From this figure, it is shown that the elaborated sensor presents a good affinity toward humidity vapors than other tested gases, indicating hydrophilic behaviour of the elaborated sensitive layer. In order to evaluate the response of sensor towards different types of gas. Further tests were carried out and responses have been recorded as shown in Fig. 2b. It is clear that, as a function of VOC concentrations, the saturated values of  $\Delta f$  increase proportionally with increasing analyte concentrations. As an example, the sensor response was determined to be 49, 82 and 100 Hz after contact with toluene ( $C_7H_8$ ) vapors at concentrations of 47, 89 and 142 ppm, respectively.

The sensitivity which is an important performance parameter of a QCM sensor is usually defined as frequency change ( $\Delta f$ ) divided by analyte vapors concentration change ( $\Delta C$ ). For this propose, the sensitivity was calculated by the slope of the regression curves. The sensitivity values are: 1.28, 0.4, 6.46 and 0.43 Hz/ppm for Ethanol, Propane, Acetone and Toluene, respectively. We can also observe that



Fig. 2 a Gases kinetic responses of QCM-based sensor and  ${\bf b}$  sensitivity toward different concentrations of VOCs vapors

Acetone  $(C_3H_6O)$  show the highest slope ratio compared to the other Vocs indicating the higher sensitivity toward acetone vapors which are polars molecules.

#### 3.2 Sensitive Layer Characterization

In order to explain the sensing behaviour, it is necessary to perform a characterization of the ZnO-Graphene nanocomposites thin film. 1-Contact angle measurements were carried out at room temperature and atmospheric pressure to assess the wettability of the coated QCM surface. A 5 µl droplet of water was carefully deposited on the surface of the coated QCM using a microsyringe. Five measurements were carried out, and the average value of the contact angle was of the order of 30° indicating the hydrophilic bihaviour of the elaborated film, this result is expected because zinc oxide and graphene have hydrophilic characters at it was reported by Srivastava et al. [14] and Accordino et al. [15]. 2-Chemical compositions of the coated electrodes have been investigated by employing attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. The spectrum was recorded in the frequency range of 400–4000 cm<sup>-1</sup> and was shown in Fig. 3. A broad and strong peak at 3600– 3300 cm<sup>-1</sup> is ascribed to the O-H stretching vibration of the hydroxyl group, the broadband observed around 2084-2350 cm<sup>-1</sup> indicating vibrations related to the C-O bond. The spectrum also reveals the presence of oxygen functional groups, carbonyl (C=O), alkoxy (C-O), epoxy (C-O-C), and aromatic (C=C), around 1726, 1218, 1041, and 1622 cm<sup>-1</sup> frequencies, respectively. On the other hand, a band around (400-800 cm<sup>-1</sup>), indicate stretching modes of Zn-O bonds, corresponding to hexagonal ZnO's vibrating mode. The absorbance peaks at about 1561 and 450 cm<sup>-1</sup> suggest the skeletal vibration of graphene sheets and the stretching vibration of Zn-O bonds, further supporting the concept of a composite structure involving both

ZnO and graphene [16, 17]. FTIR suggest the successful formation of a composite structure integrating ZnO and graphene. The identified vibrational modes and chemical groups provide clear evidence of the presence of these constituents within the composite material. FTIR analysis provides valuable information on the molecular composition and interactions within the composite, reinforcing the evidence for the existence of a ZnO-graphene matrix as well as hydrophilic behavior through the presence of hydroxyl groups, suitable for polar molecules detection which justifie good affinity toward acetone vapors.

SEM Zeiss EVO MA25 fitted with two Bruker xFlash 6l60 x-ray detectors for energy-dispersive X-ray spectroscopy «EDX» analysis was utilized to study the surface morphology and elemental analysis of the coated QCM electrodes, providing detailed information on the structure and topography of the sensor's sensitive layer (see Fig. 4a). The image suggest that the ZnO-Graphene nanocomposite has been successfully deposited on silicon substrates, forming a structure with decorated surfaces consisting of graphene nanoparticles and ZnO nanorods. The obtained EDX was shown in Fig. 4b, this analysis confirms that no contaminants are deposited and only carbon, zinc and oxygen are present in the deposited film on silicon substrate. All these results are in good agreement with the previous studies [18].



Fig. 3 ATR-FTIR spectrum of ZnO-graphene nanocomposite



Fig. 4 a SEM image and b EDX analysis of ZnO-graphene nanocomposite

#### 4 Conclusion

In this study, a gas sensor based on ZnO-Gaphene nanocomposite thin film coated on commercial quartz crystal microbalance as polar molecules sensor have been successfully fabricated using a spray pyrolysis method. The proprieties sensing in presence of gas vapors showed that the sensor was more sensitive to acetone vapors than others tested gases. Chemical and morphological properties' sensitive film have been studied, The FTIR results suggest the successful formation of a composite structure incorporating ZnO and graphene, with the presence of –OH hydroxyl groups indicating the hydrophilic behavior of the sensitive film developed, which correlates well with the CA measurement. SEM images and EDX analysis demonstrate that we obtained ZnO-Graphene nanocomposite thin film; the SEM images show that the film was decorated with graphene nanoflakes, Aggregated or agglomerated nanoparticles and ZnO nanorods and EDX analysis confirms that only carbon, zinc and oxygen are present in the deposited film on silicon substrate, respectively.

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# HMDSO/ZnO-Graphene Heterostructure Coated Quartz Crystal Microbalance Transducer for VOCs Sensing



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Abstract Accurate, reliable and fast, detection of different harmful volatile organic compounds (VOCs) is crucial criterion for medical, industrial, agricultural and environmental applications. To address the issue, in this study, porous HMDSO/ZnOgraphene heterostructure has been used as a sensitive layer. The thin HMDSO and ZnO-graphene nanocomposite layers have been elaborated on quartz crystal microbalance (QCM) transducer by plasma enhanced chemical vapor deposition (PECVD) and spray pyrolysis technique, respectively. The synthesized heterostructure was characterized by Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM). The sensing performance of the coated QCM-based sensor was evaluated by expositing it to various concentrations of organic molecules. The coated OCM sensor demonstrated high sensitivity values of 1.26, 1.05, 1.58 and 0.90 Hz/ppm and low detection limit of 2.38, 2.58, 1.90 and 3.33 for toluene, ethanol, benzene and methanol, respectively. The sensing performance of the elaborated sensor correlates well its chemical and morphological properties. The observed results demonstrate the successful strategy of retaining the excellent property of graphene (high specific surface area) with plasma surface activation to improve the active sites for gas absorption.

Keywords QCM · VOCs sensor · Heterostructure · ZnO-graphene · HMDSO

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217

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## 1 Introduction

Volatile organic compounds (VOCs) are a chemical composites in liquid form which can evaporate at room temperature. These organic molecules differ in their chemical physical properties and safe limit of concentration [1]. Even at low concentration level, the exposition of VOC molecules causes different health effects [2, 3]. In this context, chemical sensor which can detect different types of VOCs reflects one of the primary goals of the actual research in the sensor area for medical and environmental applications [4–6]. Although highly sensitive and selective VOCs sensors have been recently reported in the literature [7], their ability to detect VOCs at low concentrations level remain insufficient. As an alternative, the use of nanostructured materials as sensitive layer makes gas monitoring practical at low concentration levels [8]. The commonly used methods to enhance the gas sensing properties are the elaboration of porous sensing layers (facilitating the diffusion of gas molecules) and the decrease in the particle size (increasing the surface to volume ratio) [9]. Due to its large surface to volume ratio, good electrical and chemical properties, graphene material has attracted great attention in a broad field of applications as good nanomaterial, during the last decade [10]. Despite these attractive properties, graphene-based gas sensors had low sensitivity due to the strong sp2 hybridization making pure graphene chemically inactive to various VOCs vapors [11, 12]. To overcome these drawbacks, many reported works have shown that, constructing heterostructure sensing layers have become a simple and effective way to improve the gas sensing properties [13].

The aim of this work is to investigate a high-performance VOCs sensor based on quartz crystal microbalance (QCM) coated with hexamethyldisiloxane (HMDSO)/ZnO-graphene heterostructure. The approach consists essentially on retaining all the excellent properties of graphene (high specific surface) with plasma surface activation. The morphological and structural characterization of ZnO-graphene nanocomposite and HMDSO/ZnO-graphene heterostructure were performed by atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR), respectively. The VOCs sensing properties of the as-prepared HMDSO/ZnO-graphene heterostructure were evaluated towards various concentrations of toluene, benzene, methanol and ethanol ranging from 35 to 70 ppm.

# 2 Experimental

# 2.1 Deposition Method

Thin films of ZnO-graphene nanocomposite were firstly deposited on ultrasonically cleaned QCM surface using the pyrolysis spray deposition technique. For the preparation of the ZnO precursor solution, a 4.39 g of zinc acetate were dissolved in 100 ml of methanol and the solution was stirred vigorously. Then a 0.15 g of graphene was added to 25 ml of the ZnO precursor solution. The mixture was stirred with

a thermal stirrer for a suitable time to ensure uniform dispersion of the graphene. During deposition, the temperature, the distance between spray and substrate and spray number were set to 300 °C, 7 cm and 40, respectively. After the deposition of the ZnO-graphene nanocomposite on QCM substrate, an ultra-thin layer of HMDSO was deposited on the synthetized ZnO-graphene by plasma enhanced chemical vapor deposition (PECVD) technique. During plasma deposition, the monomer partial pressure, the plasma power and the deposition time were set to 0.5 mbar, 200 W and 5 min, respectively.

#### 2.2 Structural and Morphological Characterizations

The chemical structure of the ZnO-graphene and the HMDSO/ZnO-graphene heterostructure layers were characterized by FTIR spectroscopy. All spectra were acquired in absorbance mode in the 500–4000 cm<sup>-1</sup> range using a 6300 type A spectrometer. The surface morphology of the elaborated layers was recorded in nanometer range by means of atomic force microscope. AFM images were acquired in tapping mode using Angstrom Advanced (AA2000) microscope.

#### 2.3 QCM-Based Sensor Evaluation

Chemical sensing properties of the studied QCM-based VOCs sensor functionalized with HMDSO/ZnO-graphene heterostructure were evaluated towards methanol, ethanol, benzene and toluene molecules. The sensing properties of the fabricated sensor were evaluated in VOCs testing cell shown in Fig. 1. Organic liquid with specified volume and density are introduced in the measuring chambre by a micro syringe and allowed to evaporate freely on a hot plate. The chamber's temperature and atmosphere were meticulously controlled throughout all the experiments. The absorption of the analytes molecules induces a shift in the resonance frequency ( $\Delta f$ ) of the quartz according to Sauerbrey equation in gas phase [14]. The responses of the elaborated sensor to the presence of different concentrations of VOCs vapors were recorded using LabVIEW software. The sensing properties of the heterostructure coated QCM sensor was monitored in presence of different concentrations of toluene, benzene, methanol and ethanol in the range of 35–70 ppm. After reaching the adsorption steady state, dry air has been introduced in the measurement chambre in order to obtain full desorption of VOCs molecules from the sensing layer.


Fig. 1 Schematic representation of the testing system

## **3** Results and Discussion

#### 3.1 Structural and Morphological Analysis

The FTIR spectra recorded on ZnO-graphene and HMDSO/ZnO-graphene heterostructure are presented in Fig. 2. The FTIR spectrum related to ZnO-graphene nanocomposite presents a vibration peak at  $540 \text{ cm}^{-1}$  corresponding to the stretching mode of the Zn–O. The spectrum also shows the presence of the C=C peak around  $1600 \text{ cm}^{-1}$  indicating the existence of graphene nanosheet [15–18]. The observed of Zn–O and C=C peaks in the FTIR spectrum indicates the formation of the nanocomposite in the synthesis [19]. For the HMDSO/ZnO-graphene heterostructure, the FTIR spectrum shows all the peaks related to the ZnO-graphene nanocomposite in addition to the presence of the Si–O–Si bond around 1020 cm<sup>-1</sup> related to HMDSO layer and the CHx peak at 2924 cm<sup>-1</sup>. The work of I. S. Bae et al. has shown that the structure of the film deposited by PECVD was more porous due to the existence of high proportion of CHx groups [20, 21]. The increase in the film porosity improves the gas sensing performance by facilitating the diffusion of gas molecules.

Figure 3a, b show AFM images (5  $\mu$ m × 5  $\mu$ m) obtained on the surface of the ZnO-graphene nanocomposite and the HMDSO/ZnO-graphene heterostructure, respectively. The elaboration heterostructure resulted in relatively rougher surface with the value of the Rms (root mean square roughness) of about 21.3 nm compared to 8.81 recorded on ZnO-graphene surface (Fig. 3). Increasing layer surface roughness causes the augmentation in the surface to volume ratio (specific surface area). In this case, the sensitive layer accommodates greater number of adsorption sites, leading to the enhancement of the sensor's adsorption properties.



Fig. 3 Surface morphology of the: a ZnO-Graphene nanocomposite and b HMDSO/ZnO-graphene heterostructure

## 3.2 Sensor Response Evaluation

The sensing mechanism of the elaborated QCM-based sensors rely on the absorption of VOCs molecules accompanied by the shift in the resonant frequency of the coated quartz. Figure 4a shows the real time frequency response (in absorption and desorption mode) to 70 ppm concentration of toluene recorded on two different QCM sensors; one coated with ZnO-graphene nanocomposite and the other with HMDSO/ZnO-graphene heterostructure. When comparing the two responses, it is clearly noticed that the sensing behavior are drastically different for the two coating layers. The QCM sensor coated with ZnO-graphene nanocomposite was practically non sensitive to toluene molecules although the later has a high specific surface area. This behavior is probably due to the strong sp2 hybridization which makes graphene intrinsically inert to many gas molecules [12]. However, in case of heterostructure coating, the sensitivity to toluene vapor increases significantly confirming the



Fig. 4 Real time frequency response of: a ZnO-Graphene and heterostructure to 70 ppm of toluene and b heterostructure towards different VOCs concentrations

successful strategy of the heterostructure. In fact, plasma surface functionalization provides a lot of absorption sites for different analyte molecules.

Figure 4b depicts the dynamic frequency responses of the QCM sensor coated with HMDSO/ZnO-graphene heterostructure towards varying concentrations of toluene, ethanol, benzene and methanol ranging from 35 to 70 ppm. The responses are recorded in absorption mode (upon exposure to VOCs vapors) and in desorption mode (during purge with dry air). For all type of VOC molecules, the dynamic responses indicated that the value of the shift in the resonant frequency of the quartz rises with exposition time then reaches an equilibrium value when absorption and desorption processes occur simultaneously. The restoration of the quartz resonant frequency (the back returning of the sensor to its baseline value) was considered as an indication of complete desorption of analytes molecules from the coated QCM surface. The results also show that the studied sensor has good affinity to toluene molecules.

Figure 5 depicts the variations of the shift frequency (saturated values) as a function of analyte concentration. For all VOC molecules, the maximum response value increase with increasing VOC concentration and the sensing behavior is fairly linear. The sensors sensitivity S is defined as the ratio of the shift frequency ( $\Delta f$ ) to the change in analyte concentration ( $\Delta ppm$ ) and the limit of detection (LOD) is calculated by the ration  $3\sigma/S$  (where  $\sigma$  is the noise level estimated to 1 Hz). The calculated sensitivity was in the order of 1.26, 1.05, 1.58 and 0.90 Hz/ppm for toluene, ethanol, benzene and methanol, respectively. These values are very good compared to other QCM-based VOCs sensor [22, 23]. Concerning the LOD, the sensor coated with HMDSO/ZnO-graphene heterostructure presents a lower LOD values. It can detect up to 2.38, 2.58, 1.90 and 3.33 ppm of toluene, ethanol, benzene and methanol, respectively.



### 4 Conclusion

The aim of this study is the fabrication of a potential VOCs sensor using HMDSO/ ZnO-graphene heterostructure as sensitive layer and QCM as transducer. In an attempt to improve the sensor sensitivity, an ultra-thin layer of HMDSO has been elaborated by PECVD over ZnO-graphene layer in order to create more active sites by plasma surface functionalization. The structural analysis deduced from FTIR results indicated the incorporation of groups related to the HMDSO material and the AFM data revealed the growth of rougher surface with high specific surface area, that can accommodate more absorption sites for the gas sensing. The fabricated QCM-based VOCs sensor showed good affinity to toluene molecules than other tested organic molecules. The performance of the fabricated sensors in terms of LOD and sensitivity, resulted from the measurements at various VOCs concentrations, indicates that the later showed improved detection properties in comparison with VOCs sensors reported in the literature. The fabricated sensor is therefore potentially useful in environmental and human health care applications.

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# **Correlation Between Structural and Optical Properties of CuO Nanoparticule Prepared by Sol–Gel Method: Degradation of Mythylene Blue**



225

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Abstract Highly feature Copper Oxide CuO nanoparticles were prepared by solgel method at different temperature (400, 500 °C). The Copper chloride dehydrate, ethanol and citric acid were used as precursor, solvent and stabilizer, respectively. The influence of annealing temperature on the structural and optical properties of CuO nanoparticle was also investigated. In order to determine the information on our samples several characterizations were carried out structural characterization: X-ray diffraction (XRD); Optical properties: optical absorption and photodegradation of blue methylene of nanopowder. X-ray diffraction shows monoclinic structure with high crystallinity of all powder with preferential orientation and crystallite size is 22 nm. The intensity of peaks greatly increased with increasing of annealing temperature. An extreme absorption onset has been observed for all powder in the region between 380 and 650 nm. This attributed to the absorption of light by copper oxide (CuO) nanoparticle. The band gap was determined to be 1.47–1.39 eV (decreased with annealing temperature) that is significantly smaller than the band gap of bulk copper. These CuO nanoparticule show an excellent degradation of MB reach to 95% by advanced oxidation using  $H_2O_2$  which enhanced the photocatalysis applications.

Keywords CuO nanoparticle · Structural properties · Photocatalysis

# 1 Introduction

Nanomaterials are the basis of a new scientific and technological revolution, and occupy a very important place in our lives. The interest of studying these nanomaterials in different forms lies mainly, on the one hand in their new properties which differ significantly from those at the macroscopic scale (massive materials), and on the other hand, their use in the industrial field [1]. Among these nanomaterials,

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nanoparticles of metals and metal oxides give rise to more and more interest. CuO is one of the most useful metal oxides for many applications in different fields such as solar cells and photovoltaic materials [2], electrochromic coatings [3], catalytic applications [4] and gas sensors [5].

Copper oxides (CuO) have attracted the attention of the scientific community because of their applications in various fields thanks to their chemical properties, their non-toxicity, and their low cost compared to other metals. These oxides are considered effective catalysts for the heterogeneous conversion of hydrocarbons into carbon dioxide and water and the degradation of organic molecules. The band gap (2.17 eV) of this material favors its use in applications oriented towards photoconduction, photothermic and solar cells [6, 7].

The development of a high quality nanoparticle of copper oxide (CuO) is a very important and delicate step; several techniques have been used for the production of CuO, among them the sol–gel technique [8]. They lead to products of high purity and make it possible to control the composition of the final material at the molecular level. They also allow a control of the doping of the coating particle; it can be very low thus offering a lower use of the product, a low toxicity emission and therefore a minimum of production cost.

The objective of this work is the elaboration of copper oxide (CuO) nanoparticles by sol–gel technique at different annealing temperature, then the structural and optical characterization of the samples obtained are investigated by different technic such as: XRD, UV-visible spectroscopy and degradation methylene blue for photocatalytic application.

#### 2 Materials and Method

## 2.1 Materials

In our work, the CuO nanopwders was obtained by dissolving copper chloride dehydrate (CuCl<sub>2</sub>.2H<sub>2</sub>O) in solvent (Ethanol) with magnetic stirring at 50° C, after 30 min a volume of acid citric was added in a molar ratio (n (AC)\n (chloride) = 1), in order to dissolve motives of work hydroxide, the volume total of the solution is Vt = 15 ml. The solution is then brought to magnetic stirring at 80 °C for 2 h, the solution becomes yellow-green changed gradually to a gel stability, then dried at furnace for 24 h. Finally, the nanoparticles obtained and annealed at different temperature for 4 h (Fig. 1).



Fig. 1 Different step of preparation of CuO nanoparticles by sol-gel process

## 2.2 Characterization

The crystallography of the co-doped TiO2 was determined by Bruker D8 Advance Xray diffractometer with a high-intensity Cu K<sub>a1</sub> irradiation ( $\lambda = 0.1540562$  nm). The Photocatalytic activity studies were carried out using organic pollutant, Mythlyne blue. Moreover, the photocatalytic activities of CuO powder were estimated by using a 2.5 × 10<sup>-5</sup> mol solution of MB under UV light source ( $\lambda = 360$  nm, 2 W) placed about 10 cm above the solution under magnetic stirring. The test of duration without H<sub>2</sub>O<sub>2</sub> and with H<sub>2</sub>O<sub>2</sub> relevant the concentrations were calculated by a spectrophotometer. The maximum absorption peak ( $\lambda max$ ) of MB at about 666 nm was considered to estimate the remaining concentration of MB [9]. The photodegradation of MB was usually determined by  $\frac{C_0 - C_1}{C_0} \times 100$  where C<sub>0</sub> (initial absorbance) and C<sub>t</sub> are the concentrations of MB at time (0) and (t), respectively. Subsequently, the photocatalytic activities of the photocatalyst were considered proportional to the relative degradation of MB.

#### **3** Results

#### 3.1 Structural Properties

#### 4 XRD Analysis

X-ray diffraction patterns (XRD) shown in the Fig. 2 indicate the structural evolution of the CuO powders as a function of the annealing temperature from 400 to 500 °C for 4 h. They show that the powders crystallize greatly increases with increasing of annealing temperature. The XRD spectrum shows diffraction peaks located at 20(°): 32.49°, 34.99°, 35.51°, 38.72°, 43.72°, 48.81°, 53.46°, 58.25°, 61.56°, 66.12°, 68.018°, 72.40°, 75.13°. These peaks are assigned to reflection planes: (110), (002), (111-), (111), (200), (202-), (112), (202), (113-), (022), (220), (311), (004). All diffraction peaks correspond to the monoclinic phase of CuO (Tenorite) (JCPDS No. 48 1548), a space group C2/c with lattice constants a = 4.684 Å, b = 3.425 Å, c = 5.129 and  $\beta$  = 99.47 [10, 11]. We also see a quick increase in the intensity of the peaks as the annealing temperature increases. This result reflects an increase in the crystallinity rate of the material, which improved by an increase in grain size. Indeed, when the annealing temperature increases, the atoms have enough energy to diffuse and occupy a low-energy at normal position in the lattice, which results in an increase in rate of crystallinity and the crystallites size of the CuO. These results are in good agreement with the work [12–15]. The crystallite sizes D of CuO nanoparticle are calculated using a Debye-Scherrer equation and found around 15-22 nm approximately, this measured sizes of CuO nanopowders also found by Nithya et al. [16]. The sizes of crystallite are cited in Table 1



Fig. 2 XRD diffraction pattern of CuO nanopowders treated at different temperatures (400 and 500  $^{\circ}$ C) for 4 h. •: CuO

				1
Powder	Temperature (C°) and annealing time (h)	Phase	(hkl)	Size of crystallite D (nm)
CuO	400 °C for 4 h	Tenorite	(110)	15,26
			(002)	20,84
			(111)	18,55
			(111–)	16,97
	500 °C for 4 h	Tenorite	(110)	16,76
			(002)	22,88
			(111)	19,30
			(111–)	17,27

Table 1 The sizes of crystallite of CuO nanoparticles at different temperature

# 4.1 Optical Properties

The UV-Visible absorption spectra of CuO nanoparticles measured in the range 200–800 nm (Fig. 3). The band gap energy calculated from  $E = 1240/\lambda$  relation by plotting the absorption edge of CuO were found decrease from 1.47 to 1.39 eV by increasing of annealing temperature from 400 to 500 °C. CuO nanoparticle showed maximum absorption at wavelength 380 mm with red shift region which can be attributed to improved crystallinity of the CuO nanoparticles, which is confirmed by XRD results compared with bulk copper oxide. These results are in good agreement with this reported by other works [16].



Fig. 3 UV-visible absorption spectra of CuO nanopowder at different annealing temperature



Fig. 4 Evolution of U.V-visible absorption spectra of methylene blue of CuO nanopowder annealed at different temperature (400, 500 °C) irradiation for 1 h without and with  $H_2O_2$ 

### 4.2 Photocatalysis Application

The evolution of UV-Vis absorption spectra of BM as a function of annealing temperature in absence and in the presence of  $H_2O_2$  for copper oxide (CuO) nanopowders is represented in Fig. 4. These spectra show a very small decrease in BM after the addition of copper oxide without  $H_2O_2$ , indicating that BM degradation is almost constant. On the other hand, the BM spectra of CuO in the presence of  $H_2O_2$  obtained show that the absorbance decreased more rapidly compared to the state without  $H_2O_2$ . Consequently, the addition of  $H_2O_2$  causes the degradation of BM by the heterogeneous Fenton process (Cu +  $H_2O_2$ ) advanced oxidation, this acceleration may be due to the presence of copper nanoparticles which facilitate the decomposition of  $H_2O_2$ and the formation of hydroxyl radicals OH, which is necessary for photocatalysis. These results are in agreement with the results obtained in the literature [17].

# 5 Conclusion

The main conclusions from this work are that the XRD pattern shows a monoclinic structure of CuO nanoparticles with an average grain size of approximately 22 nm. Moreover, The UV-visible pattern of CuO nanoparticles showed maximum absorption at 380 nm with red shift and the band gap energy decrease by increasing of annealing temperature to 1.39 eV. Finally, a test of photodegradation of methylene blue reaches to 95% of absorbance in the presence of  $H_2O_2$  which enhance the photocatalysis application.

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**Renewable Energy** 

# Deposition of Copper Oxide Thin Films by Spray Polarisis Technique with Copper Chloride Solution for Different Spray Number



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Abstract In this study, CuO thin films were produced using spray pyrolysis technique on glass substrates at a fixed temperature of 350 °C. The films had a 0.1 M deposit using (CuCl<sub>2</sub>, 2H<sub>2</sub>O) as precursor, Using a spray number that ranges between 25 and 150 spray with a step of 25 spray to observe how this parameter affects the structural characteristics of our material. According to the plan (002), X-ray diffraction (XRD) analysis demonstrates the development of pure polycrystalline CuO with tenorite phase, which is a monoclinic structure. the characterizations utilized, such as X-ray diffraction (XRD), demonstrate the development of pure polycrystalline CuO with tenorite phase, which is a monoclinic structure. The parameter of the monoclinical cell a vary according to the spray number between 4.78 and 4.67 Å. also c vary according to the spray number between 5.12 and 5.3 Å. The variation in parameters was due to stresses. and Raman spectroscopy was used to perform the optical characterisation. What we discovered using XRD is confirmed by Raman spectroscopy.

**Keywords** Copper oxide  $\cdot$  XRD  $\cdot$  Spray pyrolysis  $\cdot$  Spectroscopy Raman  $\cdot$  Spray number  $\cdot$  Copper chloride solution

# 1 Introduction

Properties of metal oxide thin films are what distinguish them most from other types of technological applications. Among these, extensive research has focused on cuprous oxide thin films as an encouraging substance with potential applications in

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235

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various industries. There are three types of copper oxides (cupric oxide or tenorite (CuO), the cuprous oxide or cuprite (Cu<sub>2</sub>O) and  $cu_3O_4$ , The most stable of them is cupric oxide (CuO) moreover, band gap ranging from 1.3 to 2 eV [1]. Cupric oxide which has a monoclinic polycrystalline structure. It is confirmed that the p-type conductivity of CuO thin films [2]. It has garnered significant attention over time due to its noteworthy electrical and optical characteristics [3]. Additionally, The material has attracted considerable interest from businesses due to its high optical absorption rate [4, 5], outstanding electrical conductivity [6], non-toxic nature [7]Furthermore, because of its strong solar absorbance and little thermal emittance [8]. Copper oxide (CuO) thin films found utility in various applications such as: gas sensor [9], solar cells [10], lithium battery [11] and material for the magnetic storage [12]. CuO can be acquired through both physical and chemical methods such as magnetron sputtering [13], molecular beam epitaxy [14], thermal evaporation [15], chemical precipitation [16], polyol process [17], spray pyrolysis [18], sol-gel method [19], solvo thermal [20], hydrothermal methods [21], etc. Chemical method are cheaper, faster, and more productive than physical method. This approach facilitates their straightforward adaptation for industrial purposes.

Among these methods, the growth of CuO thin films has conventionally been achieved through spray pyrolysis on various types of substrates. This is a straightforward and convenient method for depositing a range of metal oxide thin films. The two significant advantages of this approach are its operation at atmospheric pressure and its suitability for large-area deposition. The effect of deposition factors regarding the qualities of CuO thin films has been the subject of extensive research.

In this paper, we describe the creation of CuO thin films at the nano-scale using a cost-effective technique called discontinuous chemical spray pyrolysis. We explore the structural and optical properties of these films while altering the number of spray.

### 2 Experimental Methods

### 2.1 Elaboration of CuO Thin Film

By spraying an aqueous precursor solution of 0.1 M containing an acceptable amount of copper chloride dehydrate dissolved in an appropriate volume of distilled water, nano-sized CuO thin films have been produced. The precursor solution was discontinuously sprayed onto cleaned glass substrates with dimension (1 cm \* 1 cm) that had been heated to 350 °C. Mechanically, spray was carried out utilising a perfume nozzle and air as the carrier gas. 25 cm separated the substrate from the nozzle. and the time between two successive 1 s. With a number of sprays ranging from 25 to 150 sprays with a step of 25 sprays.

where the formation of the CuO thin films begins following this reaction (Eq. 1)

$$CuCL_2 + H_2 + O \rightarrow CuO + 2HCL$$
(1)

We altered the deposition settings to generate good quality CuO films that were homogeneous, highly crystallised, and reproducible.

## 2.2 Characterization of Materials

The structural and optical characteristics of the deposition of CuO thin films against spray number were investigated using a variety of techniques. The symmetric—2 geometry was utilized to study the structural properties utilizing XRD on a Philips X'Pert diffractometer with a CuK $\alpha$  radiation source that has a wavelength of 0.154056 nm. The presence of the CuO phase was verified in this work using Raman spectroscopy. A Bruker Senterra Raman spectrometer with AlGaAs excitation at a 532 nm laser was used to record all Raman spectra over the range of 100–1400 cm<sup>-1</sup> with an exposure time of 20s.

## **3** Results and Discussions

#### 3.1 XRD Pattern

Figure 1 Show in XRD analysis was conducted to explore the structural characteristics of thin CuO nanostructured films formed on glass substrates using different numbers of spray.



Fig. 1 CuO thin films with various spray numbers as seen in their XRD patterns

Figure 1 depicts the thin film's XRD pattern. It shows the crystalline nature of copper oxide and the diffraction peaks are in excellent agreement with the pdf file (JCPDS n = ° 45-0937). The enhancement of the CuO tenorite phase was verified by the single crystallographic planes. They have concluded the formation of CuO single phase. The crystallisation of two particular designs (002) and (111) in the CuO phase was good. According to JCPDS card numbers 85-1326 for copper and 78-2076 for copper dioxide, no peak of either of the other phases of copper or copper dioxide was seen in our investigation.

As can be observed, the XRD peak intensity increases with the number of sprays and noticeably decreases for the film created with 125 sprays. This signifies an enhancement in the crystalline quality of the deposited films, potentially attributed to the thermal annealing process that occurs in the cuo films due to the catalytic reaction. The widening of the XRD peaks might be attributed to micro-strain, likely originating from the disparity in the thermal expansion coefficients between the substrate and the deposited films [22]. At the identical deposition temperature of 350  $^{\circ}$ C [23, 24].

As can be seen In the 1st layer spectrum of CuO with a spray count of 25 identified a matching polycrystalline CuO structure through spray pyrolysis. it is noticed that the film is composed of an amorphous fabric in which small crystallites are dispersed. In the 2nd to 6th layer spectra of CuO, the diagram exhibits the same spectrum. In all of the films, we did not observe any preferential orientation, but rather two directions: (111) and (002) with varying intensities, and minor peaks corresponding to (-111), (-202), (020), (202), (-113), (-311), (311). The CuO phase, where preferred orientation along (002) is seen, has also been described in other research [25–29]. The (-111) plane is also a favourable orientation, according to Roy et al. [30].

Figure 2 show in the lattice characteristics of the CuO films, a, b, and c, are displayed as a function of the spray number. is used to calculate the lattice constants a, b, and c The following Eqs. (2, 3)

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{\alpha^2 \sin^2 \beta} + \frac{k^2}{c^2 \sin^2 \beta} - \frac{2hlcos}{\beta} \alpha c \sin^2 \beta$$
(2)

$$\lambda = 2dsin\theta \tag{3}$$

Miller indices being h, k, and l. As determined by Bragg's Eq. (2) and taken from the JCPDS n = ° 45-0937, d is the lattice spacing. The lattice parameter values and those found in the literature agree rather well [31].

We notice that there are some differences in the values of a, b, and c compared to those given by the ASTM datasheet, which may be explained by the stresses caused during the formation of our films. The lattice parameter 'a' varied, depending on the number of sprays, between 4.78 and 4.67 Å, and similarly, the lattice parameter 'c' varied between 5.12 and 5.3 Å, depending on the number of sprays. These parameter values are lower than those of the bulk material due to the induced stresses. Also, We can observe that the lattice parameters reach values that are close to those of the bulk



Fig. 2 The lattice parameters change depending on the spray number

material at 100 sprays. There are no differences in the lattice parameters whether using copper acetate precursor or copper chloride.

The following relationships were used used to determine the size of crystallites D for the films and the microstrain due to crystal imperfection and distortion in Fig. 3. The following [3, 4]:

$$D = \frac{K}{\lambda}\beta\cos\theta \tag{4}$$

$$\varepsilon = \frac{\beta}{4\mathrm{tg}}\theta\tag{5}$$

The size of (002)-oriented grains is presented in Fig. 3 in relation to the quantity of sprays. In this figure, it is noticeable that the grain size expands. with two different rates until reaching 100 sprays, which have the largest grain dimension. Afterward, there is a decrease in grain size for 125 and 150 sprays. The growth in our curve indicates the enhancement in our films' crystalline structure (similar trend observed when using the copper acetate solution but with an improvement in grain size). At first to the quin relation indicates the improvement in our films crystalline structure. growth of grains during deposition (between 25 and 50 sprays) is faster than that observed between 75 and 100 sprays. Initially, our layers did not have a good crystalline structure, as shown in (see Fig. 1).

Figure 4 it can be observed a measure of the intensity of (002) orientation peak varies with quantity of sprays in a symmetrical manner, even when changing our



Fig. 3 Changes of the (002)-oriented crystallite size according on the spray number for both copper acetate (work already done in previous master's theses) and copper chloride solutions

precursor. The only difference is seen in the intensity, which is enhanced when using the copper chloride precursor compared to when using the copper acetate precursor. The maximum intensity is achieved at 125 sprays for both precursors.



Fig. 4 Variation of expressing the peak intensity I(002) in relation to the spray number for two precursor



Fig. 5 Changes in the crystal strain with respect to the spray number for two precursor

Strain are calculated using Eq. (4) and represented in Fig. 5. It can be observed that the strain decreases at two different rates: the first from 25 to 50 sprays and the second from 75 to 100 sprays. The latter has the minimum strain value, allowing room for grain growth, which makes up our thin CuO layers, thus indicating an improvement in the crystalline state Fig. 5. After 100 sprays, the stresses increase until reaching a maximum value at 150 sprays. This trend is consistent for both copper acetate and copperchloride precursors, but the strain is lower for the copper chloride solution compared to the copper acetate solution.

#### 3.2 Raman Spectra

Figure 6 displays three distinct peaks in the Raman spectra of the deposited films, situated at 277.2, 333.1, and 624.6 cm<sup>-1</sup>. The principal vibration modes of CuO, Ag(1), Bg(1), and Bg(2) are represented by these peaks, which have been documented in existing literature [22, 32].



Fig. 6 Deposited thin layers' Raman spectra

# 4 Conclusion

Using the discontinuous chemical spray pyrolysis method, nanoscale CuO thin films were deposited on a glass substrate. We explored how the spray number affected the structural and optical characteristics of the deposited layers. XDR was used to characterise the thin layers' structural properties, while Raman spectroscopy was used to characterise their optical properties. The XDR has validated the crystalline condition of our thin layers and the favoured direction of CuO formation in accordance with the plan (002). We were able to verify the existence of a thin CuO layer using the characterisation and Raman spectroscopy.

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# **Stability Analysis of Gradient Zone of a Solar Pond**



245

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**Abstract** Linear stability theory is applied to study the effect of feedback control on the onset of double diffusion convection in the non-convective layer of a solar pond. The system is stabilized using sensors and actuators that modify the intensity of the heat flow. The sensors are positioned at a given height of the layer. The influence of the application of active control on the appearance of convection in the case of an infinite layer is analyzed.

Keywords Active control · Solar pond · Double diffusion · Linear stability

# 1 Introduction

Solar energy is one of the most promising substitutes for traditional energy resources to produce clean and cheap energy. However, its intermittent and unstable nature is a major drawback, resulting in a mismatch between supply and demand [1]. A salinity gradient solar pond can provide an environmentally friendly, cost-effective and socially acceptable energy solution [2]. The characteristics that make it attractive are, on the one hand, a long-term storage capacity, which can provide enough heat for the year, and on the other hand, an annual capture efficiency of the order of 15-25% [3]. A review of the achievements and development of solar ponds over the decades is presented by [4]. A solar pond consists of three layers, an upper convective layer or zone of surface, a lower convective layer or zone of storage, and between these two layers there is the non-convective zone. The storage capacity of

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a solar pond mainly rests on the area not convective that exhibits vertical stratification in salinity and temperature. The diffusivities of these two components being very different, instabilities may appear and lead to convective movements. The main problem in a solar pond is the maintenance of stability of this gradient zone. This shows why the researchers have spent as much time analyzing and study the thickness and structure of this zone, for optimal performance of the pond solar. Many of the physical processes important fundamentals for the dynamics of a solar pond have been described by [5], who also presented the stability criterion for systems with double diffusion with linear gradients. Among the first works concerning the study the linear stability of the repository zone [6, 7]. This area was considered as a layer confined with the taking into account of the absorption of the solar radiation in the layer. A weak formulation of the basic equations has been used as well as the Galerkin method for obtain approximate solutions. The dynamic processes that involve the stability and behavior limits between the gradient zone and convection zones has been studied by [8]. It has been established that the good operation of a solar pond requires three things: maintaining the temperature of the area of storage by heat extraction and injection of brine, surface washing to control the upper layer and an initial stratification of salt well designed to avoid the formation of instability.

A linear stability study of the area of gradient was performed by [9] using the mathematical formulation proposed by [6]. There linear stability was used by [10] with a surface boundary condition describing the transfer of heat at the surface of the pond in terms of mechanisms of radiation, convection and of evaporation. A theoretical study was carried out by [11] on the influence of a porous layer on the control of the onset of convection in the zone of storage.

Recently the quality of the area stability non-convective of a gradient solar pond salinity has been studied by [12]. Annual profiles surface temperature, salinity and extractors are built to different combinations of thickness of the area of upper convection and the temperature of the storage area.

The formation and maintenance of the gradient of salinity are essential elements for good functioning of a solar pond. In the case of pure water, studies have shown the possibility of the stabilization of Rayleigh- convection Bénard by active control [13]. The objective of present work consists in studying the active control of double diffusive convection in the layer layer of a solar pond, using a proportional feedback control.

#### 2 Mathematical Modeling

In our study, we are mainly interested in the non-convective and insulating intermediate zone, height d (Fig. 1), because it is the stability of this area that depends on the proper functioning of the pond solar.

This area is modeled by a layer horizontal of infinite extension with surfaces upper and lower free, with constant concentrations  $C_1$  and  $C_0$  on both sides. We impose a heat flux by convection in top of the shell, and a conduction flux  $q_1$  at low, taking

**Fig. 1** Sketch of the solar pond structure



into account the heat extracted of the lower convective zone. In our work only the solar flux absorbed by the bottom of the pond and not that absorbed by the layer.

The equations governing the problem are the conservation of mass, quantity equations of motion, energy and species formulated together with the Oberbeck-Boussinesq approximation [9]. The basic equations are given by:

$$\nabla \cdot \mathbf{V} = 0$$
  

$$\rho_0 \left( \frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \cdot \nabla) \mathbf{V} \right) = -\nabla p + \mu \nabla^2 \mathbf{V}$$
  

$$-\rho_0 (1 - \beta_T (T - T_0) + \beta_C (C - C_0)) g \mathbf{K}$$
  

$$\frac{\partial T}{\partial t} + (\mathbf{V} \cdot \nabla) T = \alpha \nabla^2 T$$
  

$$\frac{\partial C}{\partial t} + (\mathbf{V} \cdot \nabla) C = D \nabla^2 C \qquad (1)$$

Here,  $\mathbf{V} = (u, v, w)$  is the fluid velocity vector, *t* is the time, *P* is the pressure,  $\mu$  is the dynamic viscosity of the water, *D*,  $\alpha$  are the mass and thermal diffusivities,  $\beta_T$ ,  $\beta_C$  are the coefficients of thermal and saline expansion respectively, *C* is the salt mass fraction, *g* is the acceleration due to gravity,  $e_Z$  is the unit vector along the z-axis.

The boundary conditions take into account the fact that the two horizontal free surfaces remain flat and impermeable; with continuity of velocities at each of the interfaces and that the fraction salt mass of the two free surfaces remains constant. This results in the following equations:

$$C - C_{1} = \lambda \frac{\partial T}{\partial y} + q_{1} = 0$$
  

$$w = \frac{\partial u}{\partial y} = 0 \quad \text{pour} \quad y = 0$$
  

$$C - C_{0} = \lambda \frac{\partial T}{\partial y} + h_{d}(T_{d} - T_{\infty}) = 0$$
  

$$w = \frac{\partial u}{\partial y} = 0 \quad \text{pour} \quad y = d$$
(2)

where  $\lambda$  is the thermal conductivity of water,  $h_d$  is the convective heat transfer coefficient natural,  $T_d$  is the temperature at the limit upper layer  $T_{\infty}$ , is the temperature of the upper convective zone.

The typical values of the physical parameters of a solar pond [6] make it possible to evaluate the Biot number ( $\beta_i = h_d d/\lambda$ ) of the upper boundary of the stratified layer. The order of magnitude of this last ( $\beta_i \approx 600$ ) makes it possible to consider the upper limit of the non-convective layer at constant temperature, equal to  $T_{\infty}$ .

If the thermal losses between the bottom of the pond and the ground are neglected, the heat flux of the storage zone must be equal to the difference between the total flux  $q_0$  absorbed in the storage zone and the flux  $q_{ext}$  extracted by the exchangers heat,  $q_1 = q_0 - q_{ext}$ . Since  $q_{ext}$  corresponds to a fraction f of the total heat flux absorbed:  $q_{ext} = f q_0$ , then we can deduce that:

$$q_1 = (1 - f)q_0 \tag{3}$$

The configuration of the non-convective layer is characterized by the fact that below the critical Rayleigh, the fluid is immobile and the heat transfer takes place by conduction and the mass transfer by diffusion. Above this threshold, a convection movement is generated, which changes the distribution of temperature and concentration. The idea of active control in this case is to adjust the heat flux  $q_1$  so as to delay the start of movement. To do this, a set of temperature sensors located at a height  $y_s$  detect temperature deviations from the conductive values  $T_{cond}$ . Then, heat source  $q_1$  is modulated proportionally to these deviations.

$$q(x, 0) = q_1 - G[T(x, y_s) - T_{cond}(x, y_s)]$$
(4)

where G is the gain of the proportional control.

The equations governing the problem are dimensionless using the length scale d, time scale  $d^2/\alpha$ , velocity scale  $\alpha/d$ , pressure scale  $\rho(\alpha/d)^2$ . We also introduce dimensionless temperature  $\theta = (T - T_0)/\Delta T$  and dimensionless concentration  $S = (C - C_0)/\Delta C$ . Using these scales, Eq. (1) can be transformed into the following dimensionless form:

$$\nabla \cdot \mathbf{V} = 0$$
  

$$\rho_0 \left( \frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \cdot \nabla) \mathbf{V} \right) = -\nabla P + \Pr \nabla^2 \mathbf{V} + \Pr (Ra_T \theta - Ra_s S) \mathbf{k}$$
  

$$\frac{\partial \theta}{\partial t} + (\mathbf{V} \cdot \nabla) \theta = \nabla^2 \theta$$
  

$$\frac{\partial S}{\partial t} + (\mathbf{V} \cdot \nabla) S = \frac{1}{Le} \nabla^2 S$$
(5)

where the dimensionless parameters:  $Ra_T = g\beta\Delta T^2 d^3/\alpha\nu$  is the thermal Rayleigh number,  $Ra_S = g\beta\Delta C d^3/\alpha\nu$  is the solute Rayleigh number,  $Pr = \nu/\alpha$  is the Prandtl number,  $Le = D/\alpha$  is the Lewis number,.

The dimensionless boundary conditions are given by the following equations:

$$\theta = (T - T_0) / \Delta T$$

The system (5) and (6) has a basic solution associated with a situation of pure double diffusion without active control given by:

$$S - 1 = \frac{\partial \theta}{\partial y} + (1 - f) - G(\theta_S - \theta_{CS}) = 0$$
  

$$w = \frac{\partial u}{\partial y} = 0 \quad \text{pour} \quad y = 0$$
  

$$S = \theta = 0$$
  

$$w = \frac{\partial u}{\partial y} = 0 \quad \text{pour} \quad y = 1$$
(6)

The system (5) and (6) has a basic solution associated with a situation of pure double diffusion without active control given by:

$$V_B = 0$$
  

$$\theta_B = (1 - f)(1 - y)$$
  

$$S_B = (1 - y)$$
(7)

#### **3** Linear Stability Study

We carried out a study of the linear stability of the previous basic solution relatively to infinitesimal disturbances, in the case of an infinite horizontal extension layer. The disturbances are developed in normal modes and introduced into the disturbance equations. These equations are discretized using finite differences. For N points of calculation we have a matrix system of dimension 3N. The analysis of linear stability is thus reduced to an eigenvalue problem, which can be found using the standard subroutine DGVCCG of the IMSL library of FORTRAN. There value of the Rayleigh number, for which the rate of growth of the amplitude is zero, is calculated by the iterative method of Newton. For details on the method and the solution procedure as well as its validation see [14].

## 4 Results and Discussions

The problem studied is governed by seven parameters, namely  $Ra_T$ ,  $Ra_s$ , Pr, Le, G,  $y_s$  and f. In the present study, the Prandtl number and the number are fixed at Pr = 7 and Le = 100 [6].

Figure 2 presents the marginal stability curves, in terms of the Rayleigh number, Ra, as a function of the wave number, a. The results were obtained for different values of the gain of control, G, when the sensors are located at position  $y_s = 0.725$ . For a given value of the gain, the minimum of the curve gives the critical Rayleigh number  $Ra_{Tc}$  and the corresponding critical wavenumber  $a_c$ . For an uncontrolled system (G = 0), we find that,  $Ra_{Tc} = 419$  to  $a_c = 1.77$ . A global view on the graph shows that the feedback control (G > 0) has a stabilizing effect on the system, so that  $Ra_{Tc}$  increases with increasing G. It should be noted that for all results presented in this work, it was found that the onset of convection occurs through an oscillatory instability (Hopf bifurcation).

The effect of sensor position,  $y_s$ , on the marginal stability curves is shown in Fig. 3 for G = 5, f = 0 and  $Ra_s = 2000$ . The results indicate that the position of the sensors affects the value of the critical Rayleigh number for the onset of convection. This point has been demonstrated in the past by [13] in the case of a classical Rayleigh-Bénard problem, i.e. a horizontal layer of pure water heated from below and cooled from above. The optimal position of the sensors is at the center of the layer height, i.e. at  $y_s = 0.5$ . This position gives the control the maximum efficiency in terms of stabilization of the layer, this value will thus be adopted for all the results which follow.

Figure 4 shows the variation of the critical Rayleigh number as a function of the control gain for different values of the fraction extracted from the heat flux. The curve for f = 0 corresponds to the case where there is no heat extraction from the solar pond.  $G \approx 13$ , which means that beyond this value the increase in control gain leads to the destabilization of the system instead of stabilizing it. All the curves show







a maximum at around G. We see that convection starts later for larger values of f, the system is more stable when more heat is extracted from the layer.

The effect of the control gain G on the critical Rayleigh number  $Ra_{TC}$  is shown in Fig. 5 for several values of the Rayleigh number solute  $Ra_s$ . For an uncontrolled system (G = 0), the critical Rayleigh number increases with increasing  $Ra_s$  (stabilizing effect). The shape of the curve changes with the increase in the value of the solutal Rayleigh number. For  $Ra_s = 105$  the proportional active control destabilizes the layer instead of stabilizing it.

The critical wave number  $a_c$  associated with the critical Rayleigh (Fig. 5) is shown in Fig. 6. We see that  $a_c$  varies with the gain of imposed control, the curves also have a maximum value which changes with the value of the Rayleigh solutal  $Ra_s$ imposed. When the critical wave number increases it means that the structure of the disturbances at the beginning of the instability is more confined, as shown in Fig. 7. The obtained result can be merged with some techniques in control theory [14–17].





Fig. 7 Streamlines (top), isotherms (middle) and isoconcentrations (bottom) at the onset of convection for f = 0 and RaS = 2000: **a** G = 0, ac = 1.77, **b** G = 10, ac = 2.69

# 5 Conclusion

A linear stability analysis was performed to investigate the active control of the layer with vertical temperature and concentration stratification, which represents the non-convective zone of a solar pond. It has been shown that the onset of diffusive double convection in this layer can be controlled. However, depending on the imposed solutal Rayleigh number, the control can become a destabilizing factor. The results show that the position optimal vertical position of the collectors is located in the center of the non-convective layer.

The optimal vertical position of the sensors is at the center of the non-convective layer. In the range of parameters considered in this study, the linear stability shows that the triggering of convection is via an oscillatory instability.

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# Heat Transfer Enhancement in a Parabolic Trough Solar Collector Using Inner Wall Fins and Nanofluids



Halla Diafi, Sihem Djouimaa, and Djemaa Guerraiche

**Abstract** In this study, two different absorber tube configurations were examined: a smooth absorber tube and an absorber tube with inner wall fins at the bottom. The study primarily focused on the effects of nanoparticle additives  $(Al_2O_3 \text{ and } SiO_2)$  to the base fluid, Syltherm 800. The nanoparticles were introduced at concentrations of 1, 2, 3, and 4% within a smooth tube. The study also explored their impact when introduced in a tube with inner wall fins at the bottom. The investigation centered on 2D heat transfers under turbulent flow conditions, with Reynolds numbers ranging from  $6.10^4$  to  $15.10^4$ . The research uncovered several key observations. The incorporation of nanofluids resulted in a 4.90% increase in the Nusselt number for the smooth tube. Additionally, the friction factor experienced a 2.64% increase, and the Performance Evaluation Criteria (PEC) improved by 1.04. Interestingly, a combination of SiO<sub>2</sub> with Syltherm 800 and the addition of fins exhibited even better performance, showcasing, 88.76% enhancement compared to individual nanofluids. This configuration led to a Nusselt number and PEC increase of 1.80, while the friction factor initially decreased by 9.10% at Reynolds numbers below 10<sup>5</sup>, and subsequently increased by 16.73%.

**Keywords** Parabolic trough collector · Nanofluid · Receiver tube · Forced convection · Nusselt number

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255

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#### **1** Introduction

Solar energy, especially from parabolic trough collectors (PTC), has proven to be an efficient source of power and high-temperature heat production [1] and heat at very high temperatures [2]. However, optimizing PTC performance remains a challenge. To address this, researchers have explored the use of nanofluids in heat transfer, which can enhance PTC performance. Various studies refer to the use of nanoparticles, among them, Vahidinia et al. [3] conducted an analysis study on PTC operating with different nanofluids. The results point to that the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>-Syltherm 800 hybrid nanofluid is the best choice with the greatest PEC of 1.76 with highest energy and exergy efficient. The study conducted by Guerraiche et al. [4] investigated the impact of incorporating nanoparticles into the operational Heat Transfer Fluid, using  $Al_2O_3/$ water based nanofluid at diverse volume fractions. Their results show significant enhancement in thermal efficiency, with an increase ranging from 3 to 14% for volume fractions of nanoparticles varying from 2 to 6%. The latest research revolves around altering the geometry of the PTC and introducing nanoparticles into the heat transfer fluid. Khan et al. [5] compared the smooth tube, the tube with longitudinal fins and the tube with twisted tape insert with Al<sub>2</sub>O<sub>3</sub>/water, when combining the nanofluids insertion with the twisted tape, the best thermal performance is attempts by 72.26%, but the results in a severe pressure drop that requires energy to pump. Amina et al. [6] presented the use of nanofluids of 1% fraction volume and the presence of two longitudinal fins in the tube side of the PTC, they noted that the introduction of fins increases the Nusselt number, and nanofluids have been shown to improve heat transfer.

The objective of this work is to improve heat exchange between the fluid and the absorber tube wall. The enhancement is done primarily by inserting nanoparticles into the fluid flow. Furthermore, the study requires an analysis and comparison of the performance of two distinct absorber tube configurations: one with a smooth absorber tube and the other with inner wall fins positioned in areas of elevated heat concentration along the lower wall.

#### 2 Physical Model

In our study, we consider a two-dimensional absorber tube of PTC shown in Fig. 1 with length 1 m, internal diameter  $D_{ri} = 64$  mm and 22 fins are placed in the lower region with 1 mm height. Figure 1c show the position of the fins used for the study.



(c) Receiver tube with nanofluid and fins

Fig. 1 2D receiver tube of PTC

# 3 Numerical Study

# 3.1 Governing Equations

The governing equations in the case of a monophasic, turbulent, incompressible and steady fluid flow in the receiver tube are given as [7]:

Continuity: 
$$\frac{\partial(\rho \overline{u_i})}{\partial x_i} = 0$$
 (1)

Momentum: 
$$\frac{\partial \left(\rho \overline{u_i u_j}\right)}{\partial x_i} = -\frac{\partial \overline{P}}{\partial x_i} + \frac{\partial}{\partial x_j} \left[ \mu \left( \frac{\partial \overline{u_i}}{\partial x_j} + \frac{\partial \overline{u_j}}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial \overline{u_i}}{\partial x_i} \delta_{ij} - \rho \overline{u'_i u'_j} \right]$$
(2)

where  $-\rho \overline{u_i u_j}$  and  $\delta_{ij}$  are Reynolds stress and Kronecker delta respectively

Energy: 
$$\frac{\partial}{\partial x_j} \left( \rho \overline{u_i} C_P \overline{T} \right) = \frac{\partial}{\partial x_i} \left( \lambda \frac{\partial \overline{T}}{\partial x_i} + \frac{\mu_T}{Pr_i} \frac{\partial (C_P \overline{T})}{\partial x_i} \right) + S_T$$
 (3)

where  $\mu_T$  and  $Pr_i$  are Eddy Viscosity (Pa.s) and the turbulent Prandtl number for energy

k equation: 
$$\frac{\partial}{\partial x_j} \left( \rho \mathbf{K} \overline{u_j} \right) = \frac{\partial}{\partial x_j} \left[ \left( \mu + \frac{\mu_T}{\delta_k} \right) \frac{\partial \mathbf{K}}{\partial x_j} \right] + G_K - \rho \varepsilon$$
 (4)

where k,  $G_K$  and  $\varepsilon$  are turbulent kinetic energy (m<sup>2</sup>/s<sup>2</sup>), Generation of turbulent kinetic energy (kg/ms<sup>3</sup>) and turbulent dissipation rate (m<sup>2</sup>/s<sup>3</sup>) respectively.

$$\varepsilon \text{ equation: } \frac{\partial}{\partial x_j} \left( \rho \varepsilon \overline{u_j} \right) = \frac{\partial}{\partial x_j} \left[ \left( \mu + \frac{\mu_T}{\delta_{\varepsilon}} \right) \frac{\partial \varepsilon}{\partial x_j} \right] + \rho C_{1\varepsilon} S_{\varepsilon} - \rho C_2 \frac{\varepsilon^2}{K + \sqrt{\nu \varepsilon}}$$
(5)

where  $\delta_{\varepsilon}$  is the turbulent Prandtl number for  $\varepsilon$ , and  $\nu$  is Kinematic Viscosity (m<sup>2</sup>/s)

$$G_k = \mu_T S^2 \tag{6}$$

where S is Rate of strain tensor (1/s)

The turbulent viscosity equation: 
$$\mu_T = \rho C_\mu \frac{K^2}{\varepsilon}$$
 (7)

The Eqs. (4) and (5) presents the transport equations of the realizable k- $\varepsilon$  turbulent model. The constants for the realizable k- $\varepsilon$  turbulent model are expressed bellow:  $C_2 = 1.9, \sigma_k = 1, \sigma_{\varepsilon} = 1, 2, \text{ and } S_T = \text{Source Term (concentrated flux).}$ 

# 3.2 Mathematical Modeling

The average Nusselt number: 
$$Nu = \frac{h.D_{ri}}{\lambda}$$
 (8)

The heat transfer coefficient: 
$$h = \frac{\varphi_u}{(\pi . D_{ri} . L) (T_r - T_{fm})}$$
 (9)

When the average working fluid temperature  $T_{fm}$  is equal to  $T_{fm} = \frac{T_{inlet} + T_{outlet}}{2}$ and  $T_r$  is temperature in the inner of an absorber tube.

The Reynolds number is given as: 
$$\operatorname{Re} = \frac{4.\dot{m}}{\pi . D_{ri}.\mu}$$
 (10)

where  $\dot{m}$  is the mass flow rate (kg/s).

The Prandtl number is given us: 
$$Pr = \frac{\mu C_P}{k}$$
 (11)
Density	$\rho = - \ 4.153495 \times T + 1.1057 \times 10^3$
Specific heat capacity	$C_P = 0.001708 \times T + 1.107798$
Thermal conductivity	$\lambda = -5.753496 \times 10^{-10} \times T^2 - 1.875 \times 10^{-4}T + 1.9 \times 10^{-1}$
Viscosity	$\mu = 6.672 \times 10^{-7} \times T^4 - 1.566 \times 10^{-3}T^3 + 1.388 \times T^2 - 5.54 \times 10^2$
	×T

Table 1 Correlations of liquid Syltherm 800

Table 2	Thermophysical
propertie	s of nanoparticles

Nanoparticles	$\rho$ (kg/m <sup>3</sup> )	K (W/m k)	C <sub>P</sub> (J/kg k)
Al <sub>2</sub> O <sub>3</sub>	3970	40	765
SiO <sub>2</sub>	2200	1.2	703

#### 3.3 Thermophysical Properties of Nanofluid:

The base fluid employed is Syltherm 800, and its thermophysical properties, which change with temperature, can be found in Table 1 [8]. These physical properties of the base fluid undergo modification when solid nanoparticles are introduced (see table 2).

The following formulas are semi-empirical correlations were used to calculate the thermophysical properties of nanofluid for Density [9], Heat capacity [10], Dynamic viscosity [11] and Thermal conductivity [12].

$$\rho_{\rm nf} = (1 - \varphi)\rho_{\rm f} + \varphi\rho_{\rm s} \tag{12}$$

$$(\rho C_p)_{nf} = (1 - \varphi)(\rho C_p)_f + \varphi(\rho C_p)_s \tag{13}$$

$$\mu_{nf} = \frac{\mu_f}{\left(1 - \varphi\right)^{2.5}} \tag{14}$$

$$\frac{k_{nf}}{k_{f}} = \frac{k_{s} + 2k_{f} + 2(k_{s} - k_{f})\phi}{k_{s} + 2k_{f} - (k_{s} - k_{f})\phi}$$
(15)

#### 3.4 Boundary Conditions

The boundary conditions for resolving differential equations are listed as follows.

At the inlet, the uniform and constant velocity and temperature conditions are imposed,  $u_x = u_{in}$ ,  $u_y = 0$ ,  $T = T_{in} = 500$  K.

At the outlet, the outflow (conservation of mass flow and energy) is used.



Fig. 2 Grid independence test for different cell numbers: a smooth tube, b tube with fins

The heat flux displays irregularity on both sides of the absorber tube, with a greater concentration observed at the tube's lower portion. This phenomenon occurs due to the concentration of solar radiation at the top of the collector, which is then reflected onto the lower section of the tube, as illustrated below:

The flux at the upper half is given by:  $q_{up} = \varphi_{solaire} \times \tau_{verre} \times \alpha_{absorbeur} = 912 \text{ W/}$ m<sup>2</sup> The flux at the lower half is defined as:  $q_{lower} = \varphi_{solaire} \times \tau_{verre} \times \alpha_{absorbeur} \times C_R$ = 26320 W/m<sup>2</sup>

Where  $(\tau_{verre})$  Transmissivity for the cover,  $(\alpha_{absorbeur})$  Absorptivity of the absorber tube,  $(\varphi_{solaire})$  Incident solar radiation (w/m<sup>2</sup>) and (*C<sub>R</sub>*) concentration ratio equal to 0.96, 0.95, 1000 and 28.86 respectively.

#### 3.5 Grid Independency

To create a mesh that is independent of numerical solution, we use a well-structured quadratic mesh for both tube shapes, after several refinements, it can be seen in Fig. 2 that the element of the mesh does not affect the results of the solution for different cell numbers for the smooth tube and for the tube with fins.

#### 4 Results and Discussion

The effect of a volume fraction on the average Nusselt number for two nanoparticles types  $Al_2O_3$  and  $SiO_2$  across different volume fractions, for both a smooth absorber tube and an absorber tube with fins, for  $Re = 6.10^4$  can be observed in Fig. 3a the average Nusselt number increases with increase of volume fraction. The heat transfer improvement achieved 2.51% and 8.20%, respectively, when  $Al_2O_3$  and  $SiO_2$  nanoparticles were introduced compared to the smooth tube using a basic heat



Fig. 3 a The Nusselt number versus volume fraction for different nanofluid with absence and presence of fins. b Friction factor versus volume fraction for different nanofluid with absences and presence of fins

transfer fluid. Moreover, the Nusselt number increases for the absorber tube with fins, and the enhancement in Nusselt values is most pronounced in the case of  $SiO_2/Syltherm 800$  with fins, showing an improvement of 8.76%. Adding nanoparticles led to improved thermal conductivity due to their high thermal efficiency. The fins implementation is also made to increase the thermal conductivity, and to provide heat homogenization.

This can be observed in Fig. 3b, which illustrates the variation in the friction factor for the two nanofluid types at various volume fractions, in both a smooth absorber tube and an absorber tube with fins. It becomes evident that the friction factor increases as the volume fraction rises. The increased concentration of nanoparticles results in a higher fluid density, leading to a corresponding rise in pressure drop. The inclusion of fins, on the other hand, leads to a reduction in friction factor values. Interestingly, in the area exposed to concentrated heat flux, the fluid's viscosity is reduced due to the expanded exchange surface. In the case of the tube with fins, the friction factor decreases by 12.46% when the nanofluid concentration is 4%, as compared to a smooth tube using nanofluid. Figure 4a presents the Nusselt number at different Reynolds number for various types of nanofluids studied, for a fixed volume fraction of  $\varphi = 3\%$  for both geometries. The results are compared with those of a smooth tube containing Syltherm 800 only. It's clear that the average Nusselt number increases as the Reynolds number rises. We observed that introducing nanofluid into a smooth tube yields better results with SiO2 nanoparticles, with a thermal improvement of 4.90%. This improvement can be attributed to the distinctive properties of SiO<sub>2</sub> nanofluid compared to Al<sub>2</sub>O<sub>3</sub>. Notably, the highest Nusselt number is observed in the case of a tube containing fins, where the thermal transmission was enhanced by the incorporation of nanofluids (SiO<sub>2</sub>/Syltherm 800) by 88.76%. In Fig. 4b, the relationship between the friction factor and Reynolds number is presented for a volume fraction of nanoparticles  $\varphi = 3\%$ . It is evident that as the Reynolds



**Fig. 4** a Nusselt number versus Reynolds number for different nanofluid with absence and presence of fin. **b** Friction factor versus volume fraction for different nanofluid with absence and presence of fins

number increases, the friction factor decreases. This phenomenon occurs due to the correlation between the Reynolds number and velocity. With an increase in Reynolds number, the velocity also increases, leading to a decrease in the friction factor. The presence of nanoparticles causes the friction factor to be higher in comparison to the base fluid, where we observed an increase in the friction factor by 2.64% at SiO<sub>2</sub>/Syltherm 800, this discrepancy is attributed to the effects of nanofluids on density and viscosity, both of which contribute to the higher friction factor. The presence of fin results in a reduced friction factor when compared to Syltherm800 by 9.10%.

Observed an increase in the friction factor by 2.64% at SiO<sub>2</sub>/Syltherm 800, This discrepancy is attributed to the effects of nanofluids on density and viscosity, both of which contribute to the higher friction factor. The presence of fins results in a reduced friction factor when compared to Syltherm800 by 9.10%. This outcome is due to the increased surface area provided by the fins, leading to a higher pressure drop. Consequently, this rise in the pressure drop lowers the friction factor. However, this trend holds true only for Reynolds numbers below  $10^5$ . Beyond this threshold, the friction factor begins to rise again by 16.73%.

To assess the improvement in heat transfer, we employed the Performance Evaluation.

Criteria (PEC), which is determined using the following relationship [13]:

$$PEC = \frac{Nu/Nu_0}{(f/f_0)^{\frac{1}{3}}}$$
(16)

The PEC of PTC receiver tube using nanofluid in smooth tube and tube with fins for different Reynolds number is illustrated in Fig. 5. As can be seen for these cases, the PEC values are greater than 1, the best performance evaluation criteria are when  $Re = 15.10^4$  and  $\varphi = 3\%$  for SiO<sub>2</sub>/Syltherm 800 in tube with fins. We can also



note that for the tube with nanofluids and without fins, the PEC does not make much difference when the Reynolds number increases.

#### 5 Conclusions

A 2D steady state turbulent flow numerical simulation of an absorber PTC was performed to study the effects of two types of nanofluids ( $Al_2O_3/Syltherm 800$  and  $SiO_2/Syltherm 800$ ) with and without adding fins with 1 mm high, to improve heat transfer and decrease the temperature concentration along the lower wall of the absorber tube. The outcomes drawn from our study are as follows:

The study found that introducing nanofluids and fins into the absorber tube of a PTC could enhance heat transfer. The choice of nanoparticles, particularly SiO<sub>2</sub>, resulted in significant improvements in heat transfer, with increased Nusselt numbers. The study also found that friction factor increased with nanoparticle volume fraction, but decreased with the addition of fins, especially at low Reynolds numbers. Overall, the study provided valuable insights into improving heat transfer in PTCs using nanofluids and modified tube geometries.

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# $Fe_2HfZ$ (Z = Si, Ge, Sn), Promising New Candidate Materials for Electronic and Thermoelectric Applications



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Abstract Full-Heusler materials have attracted intensive attention of scientific research in recent years due to their physical properties, the materials are considered potential candidates for high performance thermoelectric applications. Structural, elastic, and electronic properties of full-Heusler Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn) compounds have been studied using a pseudopotential plane-wave method within the framework of density functional theory, the exchange correlation effects have been treated using the generalized gradient approximation GGA-PBEsol as implemented in the CASTEP code. The calculated results for lattice constant, bulk modulus (B) and its pressure derivative  $B_{0'}$  are in good agreement with the theoretical data. We have calculated the elastic constants and checked the mechanical stability of the  $Fe_2HfZ$  (Z = Si, Ge, Sn) materials.  $Fe_2HfZ$  (Z = Si, Ge, Sn) are found to be mechanically stable. Independent single-crystal elastic properties like bulk modulus, shear modulus, Young's modulus and universal index for the corresponding polycrystalline phase indicate that  $Fe_2HfZ$  (Z = Si, Ge) are brittle and  $Fe_2HfSn$  is ductile. The values of Young's modulus demonstrate that, among the investigated materials, Fe<sub>2</sub>HfSi is the stiffer one. The universal anisotropy index differs significantly from zero, indicating that our materials are elastically anisotropic. We also calculated electronic band structures, total and partial electronic density of states. According to our calculations,  $Fe_2HfZ$  (Z = Si, Ge, Sn) compounds are not spin polarized. While  $Fe_2HfSn$ have a metallic behavior, Fe<sub>2</sub>HfSi and Fe<sub>2</sub>HfGe exhibit a semiconductor behavior with indirect band gaps of 0.325 eV and 0.097 eV respectively. The partial densities of states show that the valence bands due to Fe-d orbitals and the conduction band due to Fe-d and Hf-d orbitals.

**Keywords** Full-Heusler compounds • Density functional theory • GGA-PBEsol • Structural properties • Elastic properties • Electronic properties

265

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#### 1 Introduction

The increasing importance of sustainable and clean energy sources can be attributed to the serious energy crisis and environmental pollution. The science and industry communities have directed their attention towards thermoelectric materials for their capability to convert waste heat into electrical energy. The high stability and reliability of thermoelectric materials have made them a popular choice [1]. Full-Heusler materials have become a significant area of research due to their physical properties, which makes them potential candidates for high-performance thermoelectric materials [2, 3], this class of materials offers low band gaps, high electrical conductivity, low thermal conductivity and large thermopower [4]. The full-Heusler materials with a narrow band gap are promising for a variety of applications, including thermoelectric devices [5]. Particularly Fe-based alloys and many others [4, 6]. Full-Heusler materials typically consisting of  $X_2$  YZ formula, with X and Y being transition metals and Z being a p-block element (space group Fm3m; No: 225) [5]. Within the full-Heusler family investigating the electronic, elastic and structural properties of Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn) full-Heusler compounds is the main objective of this paper.

#### **2** Computational Details

The calculations were conducted using the Cambridge Serial Total Energy (CASTEP) Package based on the density functional theory (DFT) [7, 8]. The electron–electron interaction considered within the generalized gradient approximation GGA-PBE [9]. A 12 × 12 × 12 Monkhorst and Pack grid of k-points is used for integration in the irreducible Brillouin zone [10]. The plane wave basis set cut-off is set as 500 eV. where the convergence criteria on the total energy was set to 5 × 10<sup>-6</sup> eV/atom. The maximum force and displacement were set to be less than 0.01 eV/Å and 5 × 10<sup>-4</sup> Å respectively, and a maximum stress within 0.002 GPa. The stress–strain method approach [11] is used to calculate the single-crystal elastic constant Cij from the first principles calculation. The Voigt–Reuss–Hill (V–R–H) approximations were used to estimate the elastic moduli.

#### **3** Results and Discussion

#### 3.1 Structural Properties

The Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn) full-Heusler material crystallize in the space group Fm3m with Fe, Hf and Z atoms at 4c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2) and 4a (0, 0, 0) Wyckoff positions [5].



Fig. 1 Energy-volume curve for Fe2HfZ (Si, Ge, Sn) full-Heusler compounds

**Table 1** Calculated equilibrium lattice parameter (a), bulk modulus (B) and its pressure derivative for  $Fe_2HfZ$  (Z = Si, Ge, Sn) full-Heusler compounds

Compound	a (Å)	$B_0$ (GPa)	$B_0'$	References
Fe <sub>2</sub> HfSi	5.84	230.95	4.36	This work
	5.92	213.5	4.18	[13]
Fe <sub>2</sub> HfGe	5.1	217.72	4.47	This work
Fe <sub>2</sub> HfSn	6.13	196.92	4.46	This work

A common approach to determine structural properties such as lattice constant (a), bulk modulus (B) and the pressure derivative of bulk modulus  $B_0$ ' near equilibrium is to use the GGA-PBE scheme to calculate the total energy volume at different values and simulate the results combined into a semi-empirical equation of state.

The E(V) curve shown in Fig. 1 was fitted using the following Birch Murnaghan equation of state [12]:

$$E(V) = E_0 + \frac{9B_0V}{16} \left( \left[ \left(\frac{V_0}{V}\right)^{2/3} - 1 \right]^2 \left( 6 - B_0' \left[ \left(\frac{V_0}{V}\right)^{2/3} - 1 \right] \right) - 4 \left(\frac{V_0}{V}\right)^{2/3} \right)$$
(1)

Table 1 summarizes the structural parameter results of the  $Fe_2HfZ$  (Z = Si, Ge, Sn) full-Heusler compounds. These results are in good agreement with the theoretical data [13].

#### 3.2 Elastic Properties

We calculated the elastic constant Cij using the stress strain method [14], to determine the mechanical behavior of the Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn). The cubic structure has 3 independent elastic constants, namely  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  [15]. To ensure the

0.00013

Table 2 Calculated elastic constants $Cij$ (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), ratio of $G/$ B, Young modulus $E$ (GPa) and universal anisotropy	Compound	Fe <sub>2</sub> HfSi	Fe <sub>2</sub> HfGe	Fe <sub>2</sub> HfSn
	<i>C</i> <sub>11</sub>	437.65	388.40	352.09
	C <sub>12</sub>	149.37	110.86	119.68
	C44	112.39	143.95	117.41
index $A^U$ at zero pressure	В	245.46	225.43	197.15
	G	125.09	115.41	116.93
	B/G	1.96	1.90	1.68
	E	320.77	295.75	292.88

mechanical stability of cubic crystals, the elastic constants must satisfy the Born stability criteria [16, 17]:

 $A^U$ 

$$C_{11} > 0; C_{44} > 0; C_{11} > |C_{12}|; C_{11} + 2C_{12} > 0.$$
 (2)

0.07

0.01144

The calculated elastic constants satisfy these constraints as shows in Table 2, which means that the studied materials are mechanically stable. Since  $C_{11}$  and  $C_{12}$ are larger than  $C_{44}$  and  $C_{11}$  is larger than  $C_{12}$  the hardness in the direction of the x axis is larger than that in the direction of the y- and z-axes. Independent singlecrystal elastic properties like bulk modulus, shear modulus, Young's modulus and universal index for the corresponding polycrystalline phase have been calculated from the independent elastic constants Cij, the results are summarized in Table 2. The calculated bulk modulus values from the elastic constants Cij are very close to the estimation from Murnaghan's equation of state for these compounds.

We predicted the brittle or ductile nature of this compound based on the Pugh criteria (B/G ratio). That is, when B/G ratio is higher than 1.75, then a material shows ductile behavior otherwise the material is brittle [18]. The Pugh's ratio of Fe<sub>2</sub>HfZ (Si, Ge, Sn) indicate that Fe<sub>2</sub>HfSi and Fe<sub>2</sub>HfSn are brittle and Fe<sub>2</sub>HfSn is ductile. The Young's modulus related to the stiffness of materials [19]. The values of Young's modulus demonstrate that Fe<sub>2</sub>HfSi is the stiffer material.

Another important parameter to estimate elastic anisotropy is the so-called universal anisotropy index [20]. For isotropic crystals, A<sup>U</sup> equals zero, deviations from zero characterize the degree of elastic anisotropy. From the calculated A<sup>U</sup>, it can be inferred that the anisotropy factor of the studied compounds differs significantly from zero, indicating the presence of significant elastic anisotropy in these materials.

#### 3.3 Electronic Properties

In order to understand the electronic conduction of  $Fe_2HfZ$  (Z = Si, Ge, Sn), we calculate the energy band structures, total and partial electronic densities of states.



Fig. 2 Electronic band structure of Fe2HfZ (Si, Ge, Sn) full-Heusler compounds



Fig. 3 Total and partial density of state of Fe2HfZ (Si, Ge, Sn) full-Heusler compounds

The band structures of the studied compounds are shown in Fig. 2. According to our calculations, Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn) compounds are not spin polarized. Fe<sub>2</sub>HfSi and Fe<sub>2</sub>HfGe exhibit a semiconductor behavior, in which the valence band maximum is at  $\Gamma$  point and the conduction band minimum is at X point, with indirect band gaps of 0.325 eV, 0.097 eV for Fe<sub>2</sub>HfSi and Fe<sub>2</sub>HfGe, respectively. While Fe<sub>2</sub>HfSn have metallic behavior, where the valance band and the conduction band are overlapping. It is important to note that our results show reasonable agreement with other theoretical data. A. Azam et al., for example, have found an indirect energy band gap of 0.317 eV for Fe<sub>2</sub>HfSi through the use GGA-PBE [13].

Figure 3 shows the total and partial densities of states of the Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn) full-Heusler compounds. We can note that the valence bands are mainly due to Fe-d orbitals. In the conduction band above the Fermi energy level, the primary contribution comes from Fe-d and Hf-d orbitals. The obtained result can be merged with some techniques in control theory [21–25].

#### 4 Conclusion

Based on DFT calculations, the plane-wave pseudopotential method was utilized as implemented in the CASTEP code to investigate the structural, electronic, and elastic properties of Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn) full-Heusler materials. The structural properties calculations successfully determined the optimized lattice constant and bulk modulus, which showed excellent correlation with existing theoretical data. Notably, the calculated elastic constants confirmed the mechanical stability of our compounds. Furthermore, the Paugh ratio values revealed the brittleness of Fe<sub>2</sub>HfSi and Fe<sub>2</sub>HfSn, while Fe<sub>2</sub>HfSn demonstrated ductile behavior. Lastly, the calculated universal index of anisotropy indicating the anisotropic nature of our compounds. Fe<sub>2</sub>HfSi and Fe<sub>2</sub>HfGe compounds exhibit indirect semiconductors band gaps, while Fe<sub>2</sub>HfSn is to be classified as a metal. This research presents significant findings regarding the Fe<sub>2</sub>HfZ (Z = Si, Ge, Sn) full-Heusler compounds, which hold potential for thermoelectric applications. The narrow band gaps of Fe<sub>2</sub>HfSi and Fe<sub>2</sub>HfGe make them particularly attractive choices for such applications. The Fe<sub>2</sub>HfSn full-Heusler compound, with their metallic behavior, can be utilized as electrical contact in thermoelectric devices.

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# First-Principles Calculations of Structural, Elastic and Electronic Properties of Cubic CsBeI<sub>3</sub> Compound



Amel Meziani

**Abstract** The structural, elastic, and electronic properties of the cubic CsBeI<sub>3</sub> compound have been calculated using the full potential linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT). The exchange– correlation potential for structural and elastic properties has been evaluated using the generalized gradient approximation (GGA-PBE), while the modified Becke-Johnson potential (mBJ-GGA) has been employed in the calculation of the band structure. The structural parameters (lattice constant and bulk modulus) were found to be in reasonable agreement with the available data. Additionally, the elastic constants ( $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ ), elastic moduli and Debye temperature have been studied for the first time. We have predicted the electronic band structure and density of states, and CsBeI<sub>3</sub> exhibits semiconductor behavior with an indirect band gap of 0.4628 eV. The upper valence bands are essentially dominated by I-p states. The estimated elastic parameters of this material indicate that it is anisotropic, ductile in nature, and mechanically stable.

Keywords DFT · FP-LAPW · Electronic properties · Elastic properties · CsBeI<sub>3</sub>

## **1** Introduction

In recent years, halide-based peroveskites with the general formula ABX<sub>3</sub> (where A represents alkali, B represents metal, and X represents halide ions) have been the focus of many studies due to their physical properties and potential applications in optoelectronics and photovoltaics. The ideal perovskite structure is simple cubic and belongs to space group  $Pm\bar{3}m$  (No 221), with A located at the corners of the cube, B at the body center, and X at the centers of the faces. Only a few studies have been conducted on the electronic band structure of ABI<sub>3</sub> type perovskite. However,

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273

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there are no reports on the electronic and elastic properties from experimental or theoretical studies on the electronic band structure and elastic properties of cubic CsBeI<sub>3</sub>. Therefore, the objective of the present work is to investigate the structural, elastic and electronic properties of this compound using the FP-LAPW approach.

#### 2 Method of Calculation

In the cubic halide perovskite  $CsBeI_3$ , the atomic positions of the atoms are as follows: Cs: (0,0,0)a, Be: (1/2,1/2,1/2)a and I: (0,1/2,1/2)a, (1/2,0,1/2)a, and (1/2,1/2,0)a. The crystal structure of the  $CsBeI_3$  is depicted in Fig. 1.

The calculations were performed using the FP-LAPW method [1] implemented in WIEN2k code [2]. The exchange–correlation potential was evaluated using the generalized gradient approximation (GGA-PBE) [3]. The modified Becke–Johnson potential (mBJ-GGA) potential [4] was used in the calculation of the band structure. In our work, the number of plane waves was limited to  $R_{mt} \times K_{max} = 9$  (where *R* represents the smallest of the muffin-tin sphere radii and  $K_{max}$  is the maximum value of the wave vector *K*), and the expansion of the wave functions was set to  $l_{max} =$ 10 inside the muffin-tin spheres. The sphere radii values are 2.5 Bohr for Cs and I and 2.08 Bohr for Be. The *K* integration over the full Brillouin zone was performed using a 7 × 7 × 7 k-points mesh.





#### **3** Results

#### 3.1 Structural and Elastic Properties

The equilibrium structural parameters of this compound were determined by fitting the total energy as a function of volume to Murnaghan's equation of state [5]. Table 1 presents the calculated structural parameters (lattice constant  $a_0$ , bulk modulus B and its pressure derivative B') obtained from the GGA-PBE, along with the corresponding theoretical values.

The lattice constant  $a_0$  and the bulk modulus *B* were estimated to be 5.6103 Å and 23.1877 GPa, respectively. We found that our results are in good agreement with the available theoretical results. To our knowledge, there are no experimental results for the structural parameters of this compound.

In this work, we have also determined elastic properties such as the elastic constants  $C_{ij}$  and other elastic moduli using the IRelast package [7]. The computed elastic constants  $C_{ij}$  have been presented in Table 2. It is noteworthy that all the constants are positive and satisfy the mechanical stability conditions for cubic crystals [8]:  $(C_{11} - C_{12}) > 0$ ;  $(C_{11} + 2C_{12}) > 0$ ;  $C_{11} > 0$ ;  $C_{44} > 0$ , and the bulk modulus *B* also should satisfy a criterion:  $C_{12} < B < C_{11}$ .

Furthermore, Table 2 includes the estimation of other elastic parameters, such as the bulk (*B*) and shear modulus (*G*), Poisson's ratio ( $\nu$ ), Young's modulus (*E*) and Zener anisotropy factor (*A*). These parameters have been calculated using Voigt-Reuss-Hill approximations [9–11]:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \tag{1}$$

$$G = \frac{1}{2}(G_V + G_R) \tag{2}$$

Table 1         Calculated           structural equilibrium lattice		<i>a</i> <sub>0</sub>	В	<i>B</i> '
constant $a_0$ (in Å), bulk	This work GGA-PBE	5.6103	23.1877	4.8473
modulus $B$ (in GPa) and its	Theo [6]	5.555	18.844	-
pressure derivative $B'$ for CsBeI <sub>3</sub>				

**Table 2** Elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ), bulk modulus *B*, shear modulus *G* (in GPa), Poisson's ratio  $\nu$ , Young's modulus *E* (in GPa), Zener anisotropy factor *A* and *B/G* ratio for CsBeI<sub>3</sub>

	-							
<i>C</i> <sub>11</sub>	<i>C</i> <sub>12</sub>	C <sub>44</sub>	В	G	ν	Ε	Α	B/G
24.15	20.39	18.28	21.64	7.89	0.33	21.11	9.72	2.74

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \tag{3}$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}$$
(4)

$$\nu = \frac{3B - 2G}{2(3B + G)}$$
(5)

$$E = \frac{9BG}{3B+G} \tag{6}$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{7}$$

The elastic anisotropy factor is equal to one for an isotropic material, while any value smaller or larger than one indicates anisotropy. From Table 2, we can see that the value of the anisotropy factor A is 9.72. This indicates that our compound is anisotropic. The value of the B/G ratio is 2.74, which is larger than the critical value (1.75) separating ductile and brittle materials [12]. This suggests that CsBeI<sub>3</sub> belongs to ductile materials.

The Debye temperature  $\theta_D$  can be derived from the calculated elastic constants using the following equation [13]:

$$\theta_D = \frac{h}{k} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} v_m \tag{8}$$

where *h* is Plank's constant, *k* is Boltzmann's constant,  $N_A$  is Avogadro's number,  $\rho$  is the density, *M* is the molecular weight, *n* is the number of atoms in the molecule, and  $v_m$  is the average sound velocity, which is approximately given by:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-(1/3)}$$
(9)

where  $v_l$  and  $v_t$  are the longitudinal and transverse sound velocities, which are obtained by the following expressions [14]:

$$v_l = \left(\frac{3B + 4G}{3\rho}\right)^{1/2} \tag{10}$$

and

$$v_t = \left(\frac{G}{\rho}\right)^{1/2} \tag{11}$$

	$v_l$	v <sub>t</sub>	$v_m$	$\theta_D$	$Tm \pm 300$
This work	2558.57	1267.45	1422.61	129.092	695.7406

**Table 3** The transverse, longitudinal and average sound velocities  $(v_t; v_l; v_m \text{ in m/s})$ , Debye temperature ( $\theta_D$  in K) and melting temperature (Tm in K) for CsBeI<sub>3</sub>

Table 3 gives the calculated sound velocities, Debye temperature and melting temperature for cubic CsBeI<sub>3</sub>. The Debye temperature is predicted to be 129.092 K.

To our knowledge, there are no experimental or theoretical results available for the anisotropy factor, shear modulus, Young's modulus, Poisson's ratio, Debye temperature and melting temperature of  $C_sBeI_3$ . We can consider the present results as predictions for this compound.

#### **Electronic Properties** 3.2

Figure 2 shows the calculated band structure for CsBeI<sub>3</sub> along the high symmetry lines using the mBJ-GGA approximation.



structure of CsBeI3 using mBJ-GGA approximation

The valence band maximum occurs at the R point, whereas the conduction band minimum occurs at the  $\Gamma$  point. Therefore, CsBeI<sub>3</sub> has an indirect band gap (R- $\Gamma$ ) of 0.4628 eV. Unfortunately, to the best of our knowledge, there are no experimental or theoretical band gap studies to compare our results with. The obtained result can be merged with some techniques in control theory [15–19].

The calculated total and partial densities of states (DOS) are presented in Figs. 3 and 4 using the mBJ-GGA approximation. At lower energy, the structure situated at around -11.40 eV, below the Fermi level, reflects the I-s states. The peak centered at about -7.29 eV originates from the Cs-p states. The upper valence bands (between -5.5 and 0 eV) are essentially formed by I-p states with a small contribution of Be-s states. The lowest conduction bands are composed of Be-s and Be-p states. The conduction bands from 5 to 14 eV are essentially dominated by Cs-d states, with a small contribution of I-p and Be-p states.



Fig. 3 The total density of states (DOS) of CsBeI<sub>3</sub> using mBJ-GGA approximation





#### 4 Conclusion

We have examined the structural, elastic and electronic properties of the  $CsBeI_3$  compound using the FP-LAPW method. The structural parameters are in good agreement with the theoretical results. The electronic and elastic properties have been calculated for the first time in this study. The elastic constants were found to meet the criteria for the stability of the cubic crystal. The *B*/*G* ratio indicates that CsBeI<sub>3</sub>

is ductile in nature. The  $CsBeI_3$  compound exhibits semiconductor behavior with an indirect band gap of 0.4628 eV.

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# Impact of High Temperature and Germanium Rate on the Electrical Performance of the SiGe Heterojunction Bipolar Transistor with DPSA-SEG Architecture



Chems El Ghizlane Lachkhab, Maya Lakhdara, Abdelaaziz Boulgheb, and Saida Latreche

**Abstract** The aim of this work is to model and analyze the electrical characteristics of a SiGe Heterojunction Bipolar Transistor HBT integrated in BiCMOS055 technology with DPSA-SEG (Double Poly silicon, Self-Aligned, Selective Epitaxial Growth) architecture, using COMSOL Multiphysic software. The goal is to analyze the impact of high temperatures on component characteristics in the range from 300 to 450 K. At high temperatures, electrical performances decrease considerably, the maximum oscillation frequency/transition frequency drops from 397/334 to 343/268 GHz when the temperature ranges from 300 to 450 K. Secondly, we optimized the impact of the Germanium fraction rate introduced into the SiGe base of the HBT on electrical properties. For Germanium concentration less than 20%, static and dynamic performances improved but these performances decreased when germanium concentration is over 20%.

**Keywords** SiGe  $\cdot$  HBT  $\cdot$  BiCMOS55nm  $\cdot$  DPSA-SEG  $\cdot$  COMSOL  $\cdot$  High temperature  $\cdot$  Germanium fraction rate

### 1 Introduction

The bipolar transistor was the first active semiconductor component and it had a significant impact on the electronics industry. Despite this, the homojunction bipolar transistor has been supplanted by a new type of transistor the Heterojunction Bipolar Transistor HBT due to the technological limitations of its frequency increase. Today, these components provide fast responses at low cost, a reduction in energy consumption and a reduction in noise compared to standard Silicon technology [1, 2].

281

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The decrease in component size has resulted in frequencies of 300 THz for terahertz active imaging applications using innovations for high performance technology (IHP) [3, 4]. This scenario permits us to attain the terahertz frequencies while also achieving associated applications that are able to be mass-produced at a moderate cost.

The Heterojuction Bipolar Transistor (HBT) has the advantage of being implemented in a BiCMOS technology, since it employs both bipolar and MOS technology [5, 6].

This technology combines the benefits of both types of components, high operating frequencies and low noise for the bipolar technology, high integration density and low power consumption for MOS technology. Indeed, BiCMOS technology satisfies the present demands for speed and high integration density in circuit fabrication while enabling greater transition frequencies of up to 300 GHz [7, 8].

The aim of this work is to simulate the impact of temperature on the electrical performance of a SiGe Heterojunction Bipolar Transistor HBT integrated in BiCMOS55 nm technology. In addition, we will optimize the germanium profile in the SiGe alloy, which is the main element in the study of the HBT's electrical properties. As the base is the active part of the HBT it largely determines the static and dynamic component's performance to highlight the choices to make to achieve transistors with ultimate performance.

#### 2 The Considered HBT Structure

The studied structure is a SiGe Heterojunction Bipolar Transistor HBT integrated in a BiCMOS55nm, with a DPSA-SEG (Double Poly-silicon, Self-Aligned, Selective Epitaxial Growth) architecture. This structure includes a collector module consisting of a Selectively Implanted Collector (SIC), a highly doped buried layer and a collector well. The emitter–base module contains of an intrinsic monocrystalline SiGe base with a concentration of germanium of 20% and an extrinsic Polysilicon base. The polycrystalline emitter and internal spacers reduce the width of the emitter window and isolate the extrinsic base from the emitter [9–12]. Deep trench isolation DTI is used in this architecture to isolate the transistor from the rest of the plate environment, while shallow trench isolation STI separates the device core from the collector contact. This minimizes device size as well as collector/substrate capacitance [11, 13].

The drift-diffusion model (DDM), which based on the Poisson equation and continuity equations for electrons and holes is used in COMSOL software to model and analyze the semiconductor device.

Poison equation:

$$\nabla * (-\mathbf{e}_{\mathrm{r}} * \mathrm{V} * \nabla) = \mathbf{q} \left( \mathrm{P} - \mathrm{N} + \mathrm{N}_{\mathrm{D}}^{+} + \mathrm{N}_{\mathrm{A}}^{-} \right) \tag{1}$$

Continuity equations for electrons and holes:

Impact of High Temperature and Germanium Rate on the Electrical ...

$$\frac{\partial \mathbf{N}}{\partial \mathbf{t}} = +\frac{1}{q} (\nabla * J_n) - U_n \tag{2}$$

$$\frac{\partial \mathbf{P}}{\partial \mathbf{t}} = -\frac{1}{q} (\nabla * J_n) - U_p \tag{3}$$

 $e_r$ : relative permittivity,  $N_A^-$  and  $N_D^+$ : concentration of dopant, P and N: carrier concentrations, q: Electric charge.

In and Jp are the current densities of electrons and holes which are affected by concentrations N and P, carrier mobility  $\mu_n$ ,  $\mu_p$  and electron and quasi-Fermi hole potentials  $\phi n$ ,  $\phi p$  [14, 15].

$$J_n = +qN\mu_n \frac{d\phi_n}{d_x} \tag{4}$$

$$J_p = -q P \mu_p \frac{d\phi_p}{d_x} \tag{5}$$

The energies of the valence band and the conduction band ( $E_v$ ,  $E_c$ ) are presented in the Eqs. (6) and (7), Where  $\Delta E_g$  is the gap energy,  $\chi_0$  electronic affinity,  $E_g$  energy band discontinuity [15, 16].

$$E_c = -(V + \chi_0) \tag{6}$$

$$E_v = -\left(V + \chi_0 + E_{g0}\right) + \Delta E_g \tag{7}$$

Figure 1 illustrates the final structure of BiCMOS055, while Fig. 1a shows an image of a BiCMOS55 with DPSA-SEG structure and Fig. 1b shows the final structure with COMSOL software.



Fig. 1 Final structure of BiCMOS55nm a in STMicroelectronics [17], b under COMSOL [18]

#### **3** Results and Discussion

#### 3.1 Effect of High Temperature on the Electrical Characteristic of the HBT

The effect of temperature especially high temperature is a fundamental aspect of accurately characterizing the electrical properties of SiGe Heterojunction Bipolar Transistor. The use of these components in microwave applications that may be exposed to different temperatures and operate at high current densities accentuate is very common.

Static characteristics at high temperatures. The evolution of base and collector currents with increasing temperature (300, 350, 400 and 450 K) is shown in Fig. 2 where curve (a) illustrates the variation of collector current  $I_c$  and curve (b) shows the variation base current  $I_b$ . An increase in collector current is distinguished when the temperature rises, this is attributed to the decrease in mobility and band gap with the increase in temperature. However  $I_b$  has a coefficient of ideality  $\eta$  close to 1, this allows an increase of the base current more than the collector current.

In the case of high polarization of  $V_{BE}$ , the rate of increase of the current with the temperature is reduced because of the influence of the emitter and the base's access resistors.

Figure 3a illustrates the way that current gain changes with temperature. The current gain  $\beta$  changes inversely with the increase of the temperature, we observe that when the temperature increases (more than 300 K), the maximum value of gain decreases and shifts towards the low polarizations of V<sub>BE</sub>. The simulated I<sub>c</sub> as a function of V<sub>CE</sub> at high temperatures is shown in Fig. 3b, the output characteristic was simulated for a fixed base current of 1  $\mu$ A, it can be seen that the output characteristics I<sub>C</sub> (V<sub>CE</sub>) change when the temperature rises, the maximum collector current density increases at high temperatures the heating can become very important.



Fig. 2 Current variation against  $V_{BE}$  for T = 300, 350, 400, 450 K **a** collector current  $I_C$ , **b** base current  $I_B$ 



Fig. 3 a Current gain, b output characteristic as a function of high temperature

**Dynamic characteristics at high temperatures**. The decrease at high temperatures of the static characteristics of the transistor (transconductance, access resistances) due to the decrease of the carrier's mobility and the band gap, this in turn generates a degradation of the HBT's dynamic performances. The transition frequency  $f_T$  decreases when the temperature rises by 150 K (Fig. 4a) due to a decrease in transconductance  $g_m$  that allows an increase in the loading time of the capacities  $C_{BE}$  and  $C_{BC}$ , as well as a decrease in mobility that leads to an increase in transit time  $\tau_T$ , which is inversely proportional to the transition frequency.

The maximum oscillation frequency  $f_{max}$  decreases as the transition frequency  $f_T$  reduces for high temperature, as shown in (Fig. 4b). Table 1 gives a summary of the dynamic results.



Fig. 4 Cut-off frequencies as function as temperature, **a** transition frequency, **b** maximum oscillation frequency

Temperature	300 K	350 K	400 K	450 K
f <sub>T</sub> (GHz)	334	316	288	268
F <sub>max</sub> (GHz)	397	382	360	343

Table 1 Frequency performances of BiCMOS55nm against the high temperature

# 3.2 The Effect of the Germanium Fraction Rate Introducing in the SiGe Base

Static characteristics. The development of static performances (I<sub>c</sub>, I<sub>b</sub> and  $\beta$ ) for germanium concentration of 10, 15, 20 and 25% is shown in Table 2. When the germanium rate is raised from 10 to 25%, the currents gradually increase with the V<sub>BE</sub> voltage. This increase in currents is mainly due to the reduction of the potential barrier experienced by electrons passing from the emitter to the base, this explains the increase in the electron injection efficiency. For low concentrations (10 and 20%) the current gain increases until it reaches the maximum value (2800), this is mainly due to the increase of I<sub>C</sub> with the germanium rate. For concentrations more than 20%, the maximum gain is smaller (2327), which is due to a considerable rise in the base current to the collector current.

**Dynamic characteristic.** The variation in cut-off frequencies ( $f_t$  and  $f_{max}$ ) for different germanium concentration in the Si<sub>1-x</sub>Ge<sub>x</sub> alloy is shown in Fig. 5a, b There is a slight increase in cut-off frequency when the germanium rate below 20% (for  $x_{Ge} = 20\%$ ,  $f_t/f_{max} = 334/397$  GHz), this is mainly attributable to a small rise in collector current. In the case where the rate of germanium becomes more than 20%, there is a decrease in the cut-off frequencies ( $ft/f_{max} = 325/395$  GHz). It is interesting to observe that when the germanium rate rises in the alloy, the physical properties of the material change and approach to those of germanium rather than silicon, thus modifying the electrical characteristics of the component studied (see Table 3). The obtained result can be merged with some techniques in control theory [19–22].

Germanium % 10% 15% 20% 25%  $6.23 \times 10^{-5}$  $9 \times 10^{-4}$  $3.81 \times 10^{-5}$  $1.3 \times 10^{-5}$  $I_{C}(A)$  $3.4 \times 10^{-8}$  $1.77 \times 10^{-8}$  $0.5 \times 10^{-8}$  $4 \times 10^{-7}$  $I_B(A)$ β 1833 2164 2600 2327

 Table 2
 Static performance according to the germanium rate introduced into the SiGe base



Fig. 5 Cut-off frequencies as a function of germanium fraction rate **a** transition frequency, **b** maximum oscillation frequency

Germanium %	10	15	20	25
f <sub>T</sub> (GHz)	330.65	332.37	334	325
f <sub>max</sub> (GHz)	396.3	396.8	397	395

 Table 3 Germanium fraction rate effect on frequency performances

#### 4 Conclusion

The electrical simulations of a SiGe Heterojunction Bipolar Transistor HBT integrated in BiCMOS55nm with DPSA-SEG (Double-Poly silicon, Self-Aligned, Selective Epitaxial Growth) architecture are the subject of this work. In order to examine the electrical features of HBT at high temperatures (T = 300, 350, 400, 450 K), we found that the HBT's electrical performances reduced significantly at high temperatures, when the temperature is 300 K, the cut-off frequencies (ft, fmax) drop from (334 GHz, 397 GHz) to (268 GHz, 343 GHz) respectively when the temperature rises to 450 K.

However, we have also simulated the impact of the germanium profile (10, 15, 20 and 25%) in the SiGe alloy on the HBT's electrical characteristics. As the germanium concentration of the  $Si_{1-x}Ge_x$  alloy increases the physical properties of the material change approaching those of germanium and moving away from those of silicon.

We would like to point out that for germanium rate less than 20%, static and dynamic performance improves but these performance deteriorates for germanium concentration over 20%.

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# **Environmental Protection** by the Adsorptive Elimination of Basic Violet 3 Dye from Water



K. Saadallah, C. Ad, M. Djedid, M. Benalia, and S. Saadallah

**Abstract** Various industries generate effluent that contains persistent pollutants, including dyes, which have detrimental impacts on the environment and human health. Underscore the need for eco-friendly materials to treat dve-containing wastewater and prevent adverse effects on water resources. This study focuses on the potential of using pine tree bark (PTB) as an adsorbent to remove hazardous basic violet 3 dye (BV3) from synthetic water. The study examines factors such as contact time, PTB mass, pH and initial BV3 concentration to understand their impact on batch-mode adsorption. The efficiency of PTB for BV3 dye removal is evaluated through a wide range of basic violet 3 dye (BV3) concentrations (15–150 mg/L), pH values (2-10), and temperatures (25-55 °C), with the kinetics and adsorption isotherms of dyes studied systematically. The kinetic and isotherm study shows that the pseudo-second-order kinetic and Freundlich isotherm models accurately describe the experimental data. Based on these findings, it can be concluded that pine tree bark (PTB) is a cost-effective, eco-friendly, and promising material for removing dye molecules from aqueous solutions. This material can effectively mitigate the adverse effects of dye-containing wastewater on the environment and water resources.

Keywords Adsorption • Pine tree bark • Basic violet 3 • Isotherm • Kinetics

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289

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#### **1** Introduction

Preserving the environment and securing the future of our planet and humanity has become imperative in the present times. With the advancement of industries and technology, the environment has faced numerous issues, such as pollution and degradation. The rampant industrialization and unregulated use of natural resources, particularly water, have caused a significant decline in water quality worldwide [1, 2]. The excessive use of synthetic dyes and toxic chemicals in industrial activities has further worsened the situation, increasing the influx of pollutants into water bodies [3]. synthetic dyes in industrial wastewater harm aquatic ecosystems by reducing light penetration, increasing biochemical oxygen demand, and ultimately affecting the photosynthetic process of aquatic ecosystem. Consequently, the availability of nutrients to aquatic organisms is significantly affected, leading to potential ecological impacts [4-7]. Dyes are classified into several categories, including acidic, basic, direct, dispersive, reactive, sulfur, and vat dyes [8]. Basic Violet 3 is classified as a cationic triphenylmethane dye, commonly called Gentian violet or Crystal violet. This dye has been utilized for various applications, including biological staining, dermatology, coloring textile fibres and paper printing. However, this dye has been found to possess mutagenic properties and acts as a mitotic poison [9]. This kind of dye is challenging to remove from wastewater due to its complex structures, making the efficient treatment of these pollutants a significant concern. The issue of effluents contaminated with dyes has led to the emergence of a wide range of physicochemical and biological approaches to combat the problem. Adsorption is known as a highly effective technique for decontaminating water from dyes, among other methods. It is favored for its high efficiency, ease of use, adaptability, and economic viability. As a result, it has become the go-to method for removing significant amounts of color from contaminated water sources [10, 11]. The most utilized adsorbent is Active carbon which known of its surface area and small-volume pores. However, the predominant use of coal-based activated carbon raises concerns due to its non-renewable nature and expected depletion of fossil fuels. Additionally, the high expense of activated carbon is a crucial factor to consider in the adsorption process [5, 12]. In light of these challenges, researchers are exploring the development of sustainable adsorbents that are not only cost-effective but also eco-friendly and easily regenerated using agricultural waste [13]. Therefore, this study aims to remove Basic violet 3 dye from water through adsorption using pine tree bark and analyze the kinetics and isotherms of the process.

#### 2 Experimental Procedure

#### 2.1 Materials

Pine tree bark (PTB) sourced from Laghouat, Algeria, was selected as the adsorbent. The bark was purified using tap and distilled water to eliminate any traces of dirt and dust. Afterwards, the sample was dried in an oven at 105 °C for 12 h. The dried sample was finely ground, sieved to achieve a uniform particle size and kept in a desiccator, ready for subsequent adsorption experiments. Basic Violet 3 (BV3), a cationic dye with a chemical formula of  $C_{25}N_3H_{30}Cl$  and a molar mass of 407.979 g/ mol, was selected as the adsorbate and obtained from Sigma Aldrich. To prepare a 1000 mg/L stock solution of BV3, 1 g of adsorbate was dissolved in 1000 mL of distilled water. The resulting solution was covered with aluminum foil and kept in a dark place to prevent UV degradation. BV3 solutions with desired concentrations were prepared by diluting the BV3 stock solution.

#### 2.2 Methodology

This research aimed to assess the adsorption process of Basic Violet 3 (BV3) dye by examining its isotherms and kinetics. In this regard, the batch system was utilized to perform the adsorption studies under different conditions. Including Pine tree bark (PTB) mass (0.1–1.00 g), initial basic violet 3 (BV3) concentration (25–150 ppm), pH (ranging from 2 to 10), contact time (1–180 min) at 25 °C. During each experiment, only one adsorption parameter was varied while the others were kept constant. The samples were agitated in a thermostatic water shaker at 150 rpm (rotations per minute) until equilibrium was achieved. Afterwards, the residual concentration of dye was analyzed using UV-Vis spectrophotometer at 588 nm. The formula for calculating the adsorbate uptake is provided in Eq. (1).

$$q_t = \frac{(C_i - C_f) \times V}{m} \tag{1}$$

The quantity of dye adsorbed on the adsorbent surface (mg/g) is represented by qt. The initial and final equilibrium concentrations of the dye (mg/L) are denoted by  $C_i$  and  $C_f$ , respectively. The mass of the adsorbent (g) is represented by m, and the volume of the solution sample (L) is represented by V) [6]. Following the batch equilibrium results, the study derived the dye adsorption isotherms.

#### **3** Results and Discussions

#### 3.1 Analysis of the Dye Adsorption Isotherms

Assessing the dye adsorption isotherms is important for comprehending the interplay between adsorbate and adsorbent, which could provide helpful insights for enhancing the utilization of adsorbents [13]. In this research, the adsorption isotherm analysis for the removal of basic violet 3 (BV3) onto pine tree bark (PTB). Freundlich and Langmuir isotherm equations were employed to validate the data's suitability.

Equation (2) provides the linear equation for Langmuir isotherm model [14].

$$\frac{1}{q_e} = \frac{1}{q_{\max}.K_L} \frac{1}{C_e} + \frac{1}{q_{\max}}$$
(2)

Equation (3) provides the linear equation for Freundlich isotherm model [15].

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3}$$

The equilibrium amount of dye adsorbed on the adsorbent surface (mg/g) is represented by qe, whereas Ce denotes the equilibrium dye concentration (mg/L) in the solution. The remaining parameters are the isotherms constants that the correlation coefficient of the experimental data can determine.

In the Langmuir equation, the monolayer dye uptake capacity of the adsorbent is represented by qmax (mg/g), whereas the Langmuir constant is represented by KL (dm<sup>3</sup> mg<sup>-1</sup>) [14].

While for the Freundlich equation incorporates a distribution coefficient,  $K_F$  (L  $g^{-1}$ ), which is indicative of the adsorption reliability. Along with this, the heterogeneity factor, n, is used to represent the degree of deviation from linearity of adsorption. If the value of n equals 1, the adsorption process is linear. Conversely, if n is less than 1, the adsorption process is chemical in nature and if n is greater than 1, the adsorption process is deemed favorable and physical in nature [16].

To assess the precision of experimental data fitting to isotherm models, the determination coefficients ( $R^2$ ) of the Langmuir and Freundlich models are taken into consideration. Additionally, the Langmuir isotherm is characterized by the  $R_L$  dimensionless separation parameter, which not only indicates the shape of the isotherm but also predicts the feasibility of the adsorption system.  $R_L$  is given by: Eq. (4)

$$R_L = \frac{1}{1 + (K_L . C_0)} \tag{4}$$

The  $R_L$  value obtained indicates the nature of the isotherm, which can be classified as unfavorable, linear, favorable, or irreversible. An  $R_L$  value greater than one suggests an unfavorable isotherm where chemisorption is the dominant process [15].



Fig. 1 Langmuir and Freundlich plots: mass of PTB = 0.6 g, initial BV3 dye concentration = 15-150 mg/l, temperature =  $25 \degree$ C, shaker speed = 150 rpm, time = 60 min

Adsorbate	Q <sub>0</sub> (mg/g)	Langmuir		Freundlich		
		KL	<b>R</b> <sup>2</sup>	n	K <sub>F</sub>	<b>R</b> <sup>2</sup>
BV3	6.7935	0.0396	0.9581	1.1680	0.0522	0.9938

 Table 1
 The isotherm parameters for BV3 dye adsorption onto pine tree bark (PTB)

If the  $R_L = 1$ , the isotherm is said to be linear, indicating that both chemisorption and physisorption occur at similar rates. If  $0 < R_L < 1$  implies a favorable isotherm where physisorption is the predominant process. If  $R_L = 0$ , it suggests an irreversible isotherm where the chemisorption process cannot be reversed [17].

Figure 1 shows the adsorption isotherms for BV3 dye, with the calculated parameters for each isotherm provided in Table 1. The results indicate that the Freundlich model ( $R^2 = 0.99375$ ) is a better fit for the data than the Langmuir model ( $R^2 = 0.95814$ ), suggesting that the adsorption process is heterogeneous and multi-layered [17]. The value of n > 1 suggests that physisorption is the predominant process and that adsorption is favorable. These results are consistent with previous research [17–19] which have successfully applied the Freundlich isotherm to the removal of the same adsorbate using different adsorbents. The Langmuir analysis showed a maximum dye uptake capacity ( $q_{max}$ ) of 6.7953 mg/g and a Langmuir constant of 0.03956 L/mg (refer to Table 1). The values of  $R_L$ , as depicted in Table 2, show that the dye uptake process was favorable, within the range of (0–1).

#### 3.2 Kinetics Study

To comprehend the involved control mechanisms in adsorption processes, kinetic models serve as an essential tool. Through kinetic studies, the dye uptake rate can be regulated, which consequently influences the residual time of the adsorbate at the

<b>Table 2</b> The R <sub>L</sub> values forthe BV3 dye onto (PTB)adsorbent		
	C <sub>o</sub> (mg/L)	R <sub>L</sub>
	15	0.58512
	30	0.41354
	50	0.2973
	75	0.22001
	100	0.17461
	150	0.12363

solution interface. Thus, this rate plays a crucial role in designing adsorption systems [20]. In this regard, two sorption kinetic models were applied, the pseudo first order (PFO) and pseudo second-order (PSO) equations, to evaluate the kinetics of BV3 dye uptake onto PTB adsorbent. Equations (5) and (6) provide the linear expressions for the PFO and PSO models, respectively.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2} \cdot \frac{1}{q_e^2} + \frac{t}{q_e}$$
(6)

The BV3 adsorption capacity (mg/g) at time t and at equilibrium is represented by  $q_t$  and  $q_e$ , respectively. The rate constants for the pseudo-first-order (L/min) and pseudo-second-order (g/mg min) models are denoted by  $k_1$  and  $k_2$ , respectively. The study evaluates the applicability of two kinetic models, pseudo-first-order and pseudo-second-order, to the adsorption process of basic violet 3 dye (BV3) onto pine bark adsorbent. The graphs of ln (qe – qt) against t and t/qt against t, respectively, are presented in Fig. 2. The kinetic constants are calculated from the slope and intercept of both models depicted in Table 3. The results reveal that the pseudo-second-order model is a suitable fit for the BV3 dye uptake onto the pine tree bark (PTB) adsorbent, with high  $R^2$  values of 0.99–1. Moreover, the calculated qe values are in agreement with the experimental values, further validating the viability of the pseudo-secondorder model for this process. These findings are consistent with previous research [19–23] that also reported the successful use of the pseudo-second-order model for adsorbing the same dye onto different adsorbents.



**Fig. 2** Plots adsorption Kinetic models: mass of PTB = 0.6 g, initial BV3 dye concentration = 15-150 mg/l, temperature = 25 °C, shaker speed = 150 rpm, time = 60 min

Dye	C <sub>0</sub> (mg/l)	Q <sub>exp</sub> (mg/ g)	First order kinetic model			Second order kinetic model		
			Q <sub>cal</sub> (mg/ g)	K <sub>1</sub>	R <sup>2</sup>	Q <sub>cal</sub> (mg/ g)	K <sub>2</sub>	R <sup>2</sup>
BV3	15	0.5512	0.4160	0.070	0.8916	0.4521	1.3340	0.9906
	30	1.8888	0.5901	0.043	0.771	1.7298	0.9891	0.9937
	50	3.5527	0.4161	0.163	0.8916	3.3168	0.7846	0.9979
	75	6.0276	1.4588	0.106	0.905	5.9595	0.6473	0.9999
	100	8.4814	1.5310	0.042	0.8394	8.5034	0.2147	1
	150	12.3114	1.995983	0.081	0.62	12.346	0.1014	0.9999

Table 3Comparative analysis of pseudo-first order and pseudo-second order models for adsorptionof BV3 dye

#### 4 Conclusion

The aim of this study was to investigate the potential of using Pine tree bark (PTB), a local eco-friendly adsorbent, for decontaminating synthetic water from basic violet 3 dye. The study relied on a combination of kinetic and isotherm analysis, which revealed that the experimental data was best, fitted to the Freundlich isotherm equation. At 25 °C, the maximum dye uptake capacity was determined to be 6.7935 mg/g using the Langmuir equation. Furthermore, the kinetics study showed that the pseudo-second-order kinetic model was the most appropriate for the adsorption process. These results indicate that PTB is a promising low-cost adsorbent for effectively removing toxic dye.
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## The Effect of Increasing the Thickness of an Annular Space Subjected to a Heat Flux Emitted by a Solar Panel on the Dynamic and Thermal Fields



Sofiane Touahri, Hassen Haithem, and Toufik Boufendi

Abstract The present work is a 3D numerical simulation, in an annular space between two horizontal concentric cylinders in which an incompressible fluid circulates. The wall of the inner cylinder is adiabatic while the wall of the outer cylinder is subjected to a constant thermal heat flux. The model equations of continuity, momenta and energy are numerically solved by the finite volume method with a second order spatiotemporal discretization. The used mesh is  $52 \times 44 \times 162$  nodes along the radial, angular and axial directions. The studied hydraulic diameters are: Dh = 0.75, 1.0, and 1.25 cm. The purpose of this work is to improve the heat transfer by increasing the thickness of the annular space, this allowed us to study the dynamic and thermal fields of the heat transfer fluid and make a comparison of average temperatures and Nusselt numbers for three different cases. The results obtained show that despite the qualitative similarity of thermal and dynamic fields for the three studied cases, the heat transfer increases when the thickness of the annular space is increased, this is justified by the increase in the Nusselt number.

Keywords Annular space · Mixed convection · 3D numerical simulation

## 1 Introduction

Laminar flows in horizontal annular spaces between two concentric cylinders are studied by several researchers, in this context, experimental and numerical works has been carried out for different types of annular space. In their numerical work, Nazrul et al. [1] studied heat transfer by laminar mixed convection of air in a annulus, the inner cylinder is subjected to a constant heat flux, while the outer cylinder is

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297

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adiabatic. The results obtained showed that the velocity and temperature fields are influenced by the transverse Archimedean thrust, the Nusselt number at  $Z^* = 0.1$  is higher by 30% and 110% for Ra = 10<sup>5</sup> and Ra = 10<sup>7</sup> respectively with respect to forced convection. In their numerical work, Touahri et al. [2, 3] studied The effect of variable fluid properties on mixed convection in horizontal pipe and in annular space between two horizontal cylinders, the outer cylinder is heated by an electric current passing its thickness and the inner cylinder is insulated. Thermal convection in the fluid domain is combined with thermal conduction in the solid thickness. The results obtained showed a considerable variation in viscosity and a moderate variation in thermal conductivity of the fluid. The Nusselt number of the mixed convection becomes higher than that of forced convection when the Grashof number increases. With the used parameters, the average Nusselt number is correlated as Nu<sub>A</sub> = 9.9130 Ri<sup>0.0816</sup>.

Gourari et al. [4] numerically studied the heat transfer by natural convection of laminar flow of water in inclined rings, the inner cylinder generates a constant heat source while the outer cylinder is cold, the upper and lower walls are insulated thermally, the results are obtained for the inclination angles: 0°, 45°, 90°, these results showed that the average Nusselt number increases with the increase in the Rayleigh number and that the heat transfer is maximum for  $\alpha = 90^{\circ}$ . Similar studies was also treated numerically by Basant et al. [5], Oni [6], Khemici et al. [7], Kotake et al. [8], Kumar [9], Chung et al. [10], Nouar [11] and Chaieb et al. [12]. The Heat transfer by forced and free convection of laminar air flow inside horizontal concentric pipes was studied experementally by Mohammed et al. [13], their results showed that the average Nusselt can be related with the different dimensionless numbers by the correlation: Nu<sub>A</sub> = 2.964(Gr·Pr/Re)<sup>0.0326</sup>. A similar study was also treated numerically and experimentally by Yuzhu et al. [14].

#### 2 Mathematical Model

We consider an annular space between two horizontal concentric cylinders having a length L = 1 m. The outer cylinder is subjected to a constant thermal heat flux transferred to laminar incompressible flow of distilled water (Pr = 8.082) which corresponds to the inlet fluid temperature (T = 15 °C), while the inner cylinder is considered adiabatic (Fig. 1).

The objective of our work is to study the effect of increasing the thickness of the annular space: e on improving heat transfer to the fluid, for this three geometries are studied:

- (1) First case: L = 100 cm,  $D_i = 0.75 \text{ cm}$ ,  $D_o = 2 \text{ cm}$ ,  $D_h = 1.25 \text{ cm}$ , e = 0.625 cm
- (2) Second case: L = 100 cm,  $D_i = 1.0 \text{ cm}$ ,  $D_o = 2 \text{ cm}$ ,  $D_h = 1.0 \text{ cm}$ , e = 0.5 cm
- (3) Third case: L = 100 cm,  $D_i = 1.25 \text{ cm}$ ,  $D_o = 2 \text{ cm}$ ,  $D_h = 0.75 \text{ cm}$ , e = 0.375 cm



Fig. 1 Geometry of the problem

For the three studied cases, the volume flow of the heat transfer fluid is considered constant and equal to  $1.343 \times 10^{-5} \text{ m}^3/\text{s}$  and the inlet temperature is equal to 15 °C. The thermal conductivity and kinematic viscosity of the fluid at the inlet are equal to:  $K_0 = 0.594725 \text{ W/m}^\circ\text{K}$  and  $v_0 = 1.14 \times 10^{-6} \text{ m}^2/\text{s}$  respectively.

To avoid the repetition, the geometry and mathematical modeling presented are those of the hydraulic diameter  $D_h = 1.25$  cm. For this case, at the entrance the fluid flows with an average speed equal to  $4.97 \times 10^{-2}$  m/s which gives a Reynolds number equal to 545. The Grashof number is considered equal to  $2.44 \times 10^5$ .

#### 2.1 Modelling Equations

The studied problem is well modeled by the following non-dimensional conservation partial differential equations with their initial and boundary conditions:

At 
$$(t^* = 0)$$
:  $V_r^* = V_{\theta}^* = V_{\tau}^* = T^* = 0$  (1)

• Mass conservation equation at  $(t^* > 0)$ 

$$\frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* V_r^*) + \frac{1}{r^*} \frac{\partial V_\theta^*}{\partial \theta} + \frac{\partial V_z^*}{\partial z^*} = 0$$
(2)

• Radial momentum conservation equation

$$\begin{aligned} \frac{\partial V_r^*}{\partial t^*} &+ \frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* V_r^* V_r^* \right) \\ &+ \frac{1}{r^*} \frac{\partial}{\partial \theta} \left( V_{\theta}^* V_r^* \right) + \frac{\partial}{\partial z^*} \left( V_z^* V_r^* \right) - \frac{V_{\theta}^{*2}}{r^*} \\ &= -\frac{\partial P^*}{\partial r^*} + \frac{Gr_0^*}{\text{Re}_0^2} \cos \theta T^* \end{aligned}$$

S. Touahri et al.

$$+\frac{1}{\operatorname{Re}_{0}}\left[\frac{1}{r^{*}}\frac{\partial}{\partial r^{*}}\left(r^{*}\tau_{rr}^{*}\right)+\frac{1}{r^{*}}\frac{\partial}{\partial \theta}\left(\tau_{r\theta}^{*}\right)-\frac{\tau_{\theta\theta}^{*}}{r^{*}}+\frac{\partial}{\partial z^{*}}\left(\tau_{rz}^{*}\right)\right]$$
(3)

• Angular momentum conservation equation

$$\frac{\partial V_{\theta}^{*}}{\partial t^{*}} + \frac{1}{r^{*}} \frac{\partial}{\partial r^{*}} \left( r^{*} V_{r}^{*} V_{\theta}^{*} \right) + \frac{1}{r^{*}} \frac{\partial}{\partial \theta} \left( V_{\theta}^{*} V_{\theta}^{*} \right) + \frac{\partial}{\partial z^{*}} \left( V_{z}^{*} V_{\theta}^{*} \right) + \frac{V_{r}^{*} V_{\theta}^{*}}{r^{*}} \\ = -\frac{1}{r^{*}} \frac{\partial P^{*}}{\partial \theta} - \frac{G r_{0}^{*}}{\operatorname{Re}_{0}^{2}} \sin \theta T^{*} + \frac{1}{\operatorname{Re}_{0}} \left[ \frac{1}{r^{*2}} \frac{\partial}{\partial r^{*}} \left( r^{*2} \tau_{\theta r}^{*} \right) \\ + \frac{1}{r^{*}} \frac{\partial}{\partial \theta} \left( \tau_{\theta \theta}^{*} \right) + \frac{\partial}{\partial z^{*}} \left( \tau_{\theta z}^{*} \right) \right]$$
(4)

• Axial momentum conservation equation

$$\frac{\partial V_z^*}{\partial t^*} + \frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* V_r^* V_z^* \right) + \frac{1}{r^*} \frac{\partial}{\partial \theta} \left( V_\theta^* V_z^* \right) + \frac{\partial}{\partial z^*} \left( V_z^* V_z^* \right) \\ = -\frac{\partial P^*}{\partial z^*} + \frac{1}{\operatorname{Re}_0} \left[ \frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* \tau_{rz}^* \right) + \frac{1}{r^*} \frac{\partial}{\partial \theta} \left( \tau_{\theta z}^* \right) + \frac{\partial}{\partial z^*} \left( \tau_{zz}^* \right) \right]$$
(5)

• Energy conservation equation

$$\frac{\partial T^{*}}{\partial t^{*}} + \frac{1}{r^{*}} \frac{\partial}{\partial r^{*}} (r^{*} V_{r}^{*} T^{*}) + \frac{1}{r^{*}} \frac{\partial}{\partial \theta} (V_{\theta}^{*} T^{*}) + \frac{\partial}{\partial z^{*}} (V_{z}^{*} T^{*})$$

$$= G^{*} - \frac{1}{\operatorname{Re}_{0} \operatorname{Pr}_{0}} \left[ \frac{1}{r^{*}} \frac{\partial}{\partial r^{*}} (r^{*} q_{r}^{*}) + \frac{1}{r^{*}} \frac{\partial}{\partial \theta} (q_{\theta}^{*}) + \frac{\partial}{\partial z^{*}} (q_{z}^{*}) \right]$$
(6)

## 2.2 The Boundary Conditions

The previous differential equations are solved with the following boundary conditions:

• At the entrance:  $(z^* = 0)$ 

$$V_r^* = V_\theta^* = T^* = 0, V_z^* = 1$$
(7)

• At the exit:  $(z^* = 100)$ 

$$\frac{\partial V_r^*}{\partial z^*} = \frac{\partial V_\theta^*}{\partial z^*} = \frac{\partial V_z^*}{\partial z^*} = \frac{\partial}{\partial z^*} \left( K^* \frac{\partial T^*}{\partial z^*} \right) = 0$$
(8)

• At the internal pipe:  $(r^* = 0.5)$ 

300

The Effect of Increasing the Thickness of an Annular Space Subjected ...

$$V_r^* = V_\theta^* = V_z^* = 0, and\left(\frac{\partial T^*}{\partial r^*}\right) = 0$$
<sup>(9)</sup>

• At the external pipe:  $(r^* = 1)$ 

$$V_r^* = V_\theta^* = V_z^* = 0, and\left(\frac{\partial T^*}{\partial r^*}\right) = 1$$
<sup>(10)</sup>

#### 2.3 Nusselt Numbers

At the solid–fluid interface  $(r^* = 1)$  the local Nusselt number is defined as:

$$Nu(\theta, z^{*}) = \frac{h(\theta, z^{*})D_{i}}{K_{0}} = \left[\frac{\left(K^{*}\partial T^{*} / \partial r^{*}\right)\Big|_{r^{*}=1}}{T^{*}(1, \theta, z^{*}) - \partial T^{*}_{A}(z^{*})}\right]$$
(11)

#### **3** Numerical Procedure

The finite volume method described by Patankar [15] is used for the numerical solution of the previous modeling equations. The convective and nonlinear terms were discretized according to the Adams–Bashforth numerical scheme, the spatiotemporal numerical discretization is second order, so the order of temporel numerical error is  $(\Delta t^*)^2$  and  $(\Delta r^*)^2$ ,  $(\Delta z^*)^2$ ,  $(\Delta \theta)^2$  for radial, axial and azimithal direction respectively. A Fortran code based on the SIMPLER algorithm is used to process the pressure–velocity coupling, the tri-diagonal matrix algorithm (TDMA) is used to obtain the iterative solution of the equations of the discretized model. The meshes used in this work are:  $26 \times 44 \times 162$  and  $52 \times 88 \times 162$  in the radial, azimuthal and axial directions respectively and the results presented are those of the second mesh. The proposed time step is  $(\Delta t^* = 5.10^{-4})$  and the time march is continued until the steady state is obtained which is controlled by the stabilization of the temporal evolution of the hydrodynamic and thermal fields.

The used numerical code has been validated by the comparison of our results with those of Nazrul et al. [1] who studied the laminar mixed convection heat transfer in a horizontal concentric annulus with adiabatic outer wall and a uniform heat flux at the inner wall. The controlling parameters are:  $D_2/D_1 = 2$ , Re = 200, Pr = 0.7 and Gr = 0, The axial evolution of the circumferentially averaged Nusselt number is illustrated in Fig. 2, it is seen that there is a good agreement between the two results.

301





### 4 Results and Discussions

Qualitatively the results of the three studied cases are similar but quantitatively there are differences. To avoid repetition, we will present in this section the results of the case  $D_h = 1$  cm. The other results are used in the quantitative comparisons of the different studied cases. For this case, the Reynolds number is equal at 545, the Prandtl number equal to 8.082 and the Grashof number is equal to  $2.44 \times 10^5$ . The dynamic field is characterized by a main flow in the axial direction and a transverse flow influenced by the density variation with temperature.

#### 4.1 Transverse Flow

At the entrance (Z = 0 cm), the transverse flow is nonexistent because the fluid temperature is constant. Just after, the heat transferred to the fluid through a constant heat flux at the wall of the external cylinder creates a temperature gradient oriented inward. This situation induces a transverse movement explained as follows: the fluid moves along the hot wall of the external cylinder from the bottom towards the up and then descends from the top to the bottom near the wall of the internal cylinder (Fig. 3).

#### 4.2 Axial Flow

At the entrance to the annulus, the fluid presents itself with a constant speed  $V_0$ . At this section, the axial component is constant while the angular and radial components





Z=100 cm



are zero. After; the axial speed field enters a continuous variation such that the low speeds are located near the walls of the cylinders and the maximum is at the heart of the annular space (Fig. 4).

## 4.3 Temperature Field and Heat Transfer

At the inlet, the fluid has a constant temperature, after in the presence of the secondary flow, an angular variation of the temperature is imposed. This variation is explained as follows: at a given axial section, the hot fluid near from the outer wall of the

annulus is transported by the transverse movement upwards under the effect of the thermal thrust force, the relatively cold fluid descends near from the internal wall (Fig. 5).

#### Axial variation of the average fluid temperature (see Fig. 6)

#### Local Nusselt number

The heat transfer phenomenon is quantified by the local Nusselt number. On the wall of the inner cylinder, the local Nusselt number is zero but on the wall of the outer





Fig. 6 Axial evolution of the average fluid temperature



cylinder, there is an axial and angular variation in the local Nusselt number from the inlet to the outlet, this variation is shown in Fig. 7.

#### Axial Nusselt number

The axial Nusselt number is shown in Fig. 8 for all cases studied. Qualitatively there is a similarity in the variation of the axial Nusselt number as a function of Z, in the short entry zone of the annular space, the axial Nusselt number undergoes a very significant decrease followed by an increase up to the exit from the annular space. It is very clear that the axial Nusselt for the case  $D_h = 1.25$  cm is the most superior followed by the case  $D_h = 1.0$  cm and finally the case  $D_h = 1.25$  cm. This is justified as follows: the local Nusselt number defined by Eq. (11) is the ratio between the incident heat flux which is constant and the difference between the local temperature at the wall and the average temperature for the same axial section.





## 5 Conclusion

In this work, we have numerically studied the heat transfer by mixed convection in a horizontal annulus, the external pipe is heated by a constant thermal flux while the internal pipe is isolated. The objective of this work is to study the effect of increasing the thickness of the annulus on improving heat transfer for the same fluid flow rate.

The obtained results show that the increase in the thickness of the annular space is accompanied by an increase in the Nusselt number and automatically an improvement in heat transfer to the working fluid. The use of a thickness e equal to 0.625 cm improves the heat transfer by 37.66% and 95.69% compared with thickness equal to 0.5 and 0.375 cm respectively.

## Abbreviations

## Nomenclature

- D Diameter, m
- k Thermal Conductivity, W/m°C
- L Length, m
- Nu Nusselt number
- P Pressure, N/m<sup>2</sup>
- Pr Prandtl number
- r Radial Coordinate, m
- Re Reynolds number

- t Time, s
- T Temperature, °K
- U Radial Velocity Component, m/s
- V Axial Velocity Component, m/s
- W Angular Velocity Component, m/s
- z Axial Coordinate, m

#### **Greek Letters**

- μ Dynamic viscosity, kg m/s
- $\theta$  Angular coordinate, rad
- $\tau$  Viscous stress, N/m<sup>2</sup>
- ρ Density, kg/m<sup>3</sup>

## **Subscripts**

- *A* Average at given section
- r,  $\theta$ , z Reference to the radial, angular and axial direction, respectively

## **Superscripts**

\* Non dimensional

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# Control Systems for Renewable Energy Production

## Wind Turbine Energy Production Based on Event-Triggered Speed Control



311

Abdelmalek Zahaf, Abdelhamid Bounemeur, and Sofiane Bououden

**Abstract** An improved strategy for energy production is introduced based model predictive control, with a precise control instance using event triggered mechanism. Aiming to optimize the wind turbine speed for energy production while accounting for uncertainties and sensor malfunctions. The proposed strategy leverages model predictive control, a powerful control technique known for its ability to optimize system performance by considering future predictions of power generation. In this context, MPC is utilized to formulate an optimal control sequence for wind turbine operation, accounting for various factors such as wind speed fluctuations, turbine dynamics, and power output constraints. Unlike traditional time-triggered control updates are triggered only when specific events or significant changes occur in the system, thereby optimal control demands and improving efficiency.

Keywords Wind turbine · Speed control · Sensor fault · Event-triggered

## 1 Introduction

Clean energy production has been experiencing significant growth in last decades. As known, the wind turbine has a challenging operational conditions, due to the complexity of wind turbine structure several scenarios can have encountered. Usually, occurring faults on actuators/sensors of the system during the processing is often happening. That can result disgrace the performances of the main components. To

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avoid system breakdown due to the control components failures, the diagnosis tasks are significant steps during the working of process [1]. To manage the occurred faults, fault tolerant control (FTC) approach is involved in many applications. To maintain high properties such as stability and performances, FTC based model predictive control is investigated and analyzed by [2-9] to ensure and enhance the stability and the efficient control strategy. Meanwhile, FTC based adaptive control is proposed in [10-19] to improve the effectiveness of the controller. Applying these control strategies on various clean energy sources aims to target the maximum quantity of energy. Thorough that, the nonlinear dynamic state feedback controller is proposed as multivariable control strategy in [20]. To improve the variable speed control, a multimodel optimal control scheme given by [21]. For more precision and reliability of the controlled multimodel based multivariable control strategy, the predictive theory has employed in [22]. To this end, authors in [23] analyses the case of occurring faults for wind turbine during the processing based on fault tolerant predictive control. The using the wind power generation for Load Frequency of Hybrid Power System has discussed by [24] based Model Predictive Control.

In this paper, to improve the wind turbine speed for energy production, uncertainties and sensor malfunctions are taking into consideration for an efficient controller, that employs an observer based predictive control scheme. After given new sight of wind-turbine modeling with uncertainties, a new reformulation of the original system to QP is introduced, which have been used for minimizing the evaluation function to compute the predictive control inputs. The control updates are triggered only when specific events or significant changes occur in the system. As result, the event-triggered based predictive control mechanism improve precise control instance using obtained optimal control. finally, simulation results of wind-turbine are given.

The rest of this paper is presented as next: a new sight for the modelling of windturbine systems is given. Control scheme for wind-turbine, and discussions of the simulation results.

#### 2 Model Plant and Modelling of Wind-Turbine

In this work, wind-turbine system is analyzed. Considering the different ways of modelling as [20-22], the wind turbine can be described by the following differential equations:

$$\begin{cases} \dot{\Omega}_{T}(t) = \overset{\sim}{\mathbf{T}_{aero}} - \overset{\sim}{\mathbf{T}_{mec}} \\ \dot{\Omega}_{g-ls}(t) = \overset{\sim}{\mathbf{T}_{mec}} - \overset{\sim}{\mathbf{T}_{em}} \\ \dot{\mathbf{T}}_{me}(t) = \kappa \left(\Omega_{T} - \Omega_{g-ls}\right) + \beta \left(\dot{\Omega}_{T}(t) - \dot{\Omega}_{g-ls}(t)\right) \end{cases}$$
(1)

where,  $\widetilde{T}_{em} = T_{em}G_g/J_{g-ls}$ ,  $\widetilde{T}_{aero} = T_{aero}/J_T$  and  $\widetilde{T}_{mec} = T_{mec}/J_T$  are the generator torque, the torque caught by the wind turbine and the low-speed shaft torque resulting from the torsion and frictions effects, respectively; while  $J_{g-ls}$  and  $J_T$  are respectively the generator and the turbine inertia.  $\Omega_{g-ls}$  is the generator rotational speed reported to the low speed shaft.

Let us define

$$\dot{z}(t) = \begin{bmatrix} \dot{\Omega}_T(t) & \dot{\Omega}_{g-ls}(t) & \dot{T}_{me}(t) \end{bmatrix}^{l}$$
(2)

$$\dot{z}(t) = \begin{bmatrix} 0 & 0 & 1/J_T \\ 0 & 0 & 1/J_T \\ \kappa & -\kappa & 0 \end{bmatrix} z(t) + \begin{bmatrix} 1/J_T \\ -G_g/J_{g-ls} \\ 0 \end{bmatrix} u(t_k) + \begin{bmatrix} \beta \\ -\beta \\ 0 \end{bmatrix} \dot{z}(t)$$
(3)

Then, we get

$$\dot{z}(t) = \overline{\mathcal{A}}z(t) + \overline{\mathcal{B}}u(t_k) \tag{4}$$

where, A, and B are represented the matrix state and matrix of signal control.

 $\beta$  is the event-triggered matrix.  $u(t_k) = [T_{aero}T_{em}0]$  represent the event-triggered input.

The defining matrices of (4) are describing as follows:

$$\overline{\mathcal{A}} = \tilde{\beta}^{-1} \mathcal{A}, \overline{\mathcal{B}} = \tilde{\beta}^{-1} \mathcal{B} \text{ and } \tilde{\beta} = \begin{bmatrix} 1 + \beta \ 1 - \beta \ 1 \end{bmatrix},$$
$$\mathcal{A} = \begin{bmatrix} 0 & 0 & 1/J_T \\ 0 & 0 & 1/J_T \\ \kappa - \kappa & 0 \end{bmatrix}, \mathcal{B} = \begin{bmatrix} 1/J_T \\ -G_g/J_{g-ls} \\ 0 \end{bmatrix}$$

To convert the uncertain non-linear problem (4) to an uncertain linear problem, we use LFT (Fractional Linear Transformation) representations as formalisms.

With appropriate sampling time for the system (4) we get the following discretetime uncertain system as next:

$$\Psi(k+1) = A\Psi(k) + Bu(k) \tag{5}$$

## 3 Efficient Dynamic Control Strategy

From Eq. (5) we consider the next closed loop discrete-time system is employed an observer, which is designed as:

$$\widehat{\Psi}(k+1) = (A+B)\widehat{\Psi}(k) + LCe(k)$$
(6)

where *A*, *B* and *C* are state matrices, *K* are the controller gains matrix and *L* is the observer gain matrix

The previous uncertain wind-turbine system occurring sensors faults can be written as:

$$\Psi(k+1) = \tilde{A}(k) \Psi(k) + \tilde{B}\tilde{u}(k)$$
(7)

where,  $\tilde{A}_p = \begin{bmatrix} A & LC \\ C & F_s FC \end{bmatrix}$ ,  $\tilde{B}_p = \begin{bmatrix} B \\ 0_n \end{bmatrix}$ ,

The matrix  $\tilde{A}$  and  $\tilde{B}$  represent the system and the input matrices, respectively.

Taking into account results in [1], the  $\tilde{y}$  is the output of the augmented wind-turbine system, and the control input u(k) represents the desired energy of the current step k. The performance of optimization quadratic function J is given as follows:

$$\begin{cases} \min_{u} J_{h}(k) = \sum_{j=0}^{h} \left( \| \widetilde{\Psi}(k+j/k) \|_{Q}^{2} + \| u(k++j/k) \|_{R}^{2} \right) + \rho \widehat{\Psi}^{T}(k/k) P_{0} \widehat{\Psi}(k/k) \\ Subject to \begin{cases} \widetilde{\Psi}(k+1) \\ Wu \leq Z \end{cases} \end{cases}$$
(8)

where

$$\begin{cases} \tilde{y}(k) = [y(k+1)y(k+2)\dots y(k+N)]^T\\ \tilde{u}(k) = [u(k)u(k+1)\dots u(k+N)]^T\\ \rho = [01] \text{ is the triggering threshold} \end{cases}$$
(9)

The *h* and  $\lambda$  represents the prediction step and weighting factor for input, respectively. The term  $[\tilde{y}(k+j/k) - y_d(k+j/k)]^2$  represents the weighting of future error, and  $\lambda [\tilde{u}(k+j/k)]^2$  represents the energy of input control.

The predictive model  $\tilde{y}(k)$  is described as next:

$$\tilde{y}(k+1) = H(k)\tilde{x}(k) + M\vec{u}(k) + G\tilde{u}(k)$$
(10)

where, G, H and F are respectively the augmented state matrix system, input control and Event-triggered matrices

$$H = \begin{bmatrix} \tilde{C}\tilde{A}\tilde{C}\tilde{A}^{2}\dots\tilde{C}\tilde{A}^{N} \end{bmatrix}^{T},$$

$$G = \begin{bmatrix} \tilde{C}\tilde{B}\tilde{C}\tilde{A}\tilde{B}\dots\tilde{C}\tilde{A}^{N-1}\tilde{B} \end{bmatrix}^{T},$$

$$M = \begin{bmatrix} 0_{n} & 0_{n}\dots & 0_{n} \\ \tilde{C}\tilde{B} & 0_{n}\dots & 0_{n} \\ \vdots & \vdots & \ddots & \vdots \\ \tilde{C}\tilde{A}^{N-1}\tilde{B} & 0_{n}\dots & 0_{n0} \end{bmatrix}$$

Furthermore, in this paper the  $\vec{u}$  term indicates the desired energy for the speed control of *h* step prediction horizon for wind-turbine. for relaxation conditions of the online optimization, we hold the (10) in (8), then, the cost function can be arranged as (11), taking into consideration the constrains of the control input. The performance index *J* defined to calculate the optimal solution.

$$\min_{\vec{u}, i>0} \frac{1}{2} \vec{u}^T P \tilde{u} + R^T \vec{u} \quad \text{Subject to} \quad \mathcal{W}u \le \mathcal{Z}$$
(11)

Where W and Z are representing the lower and upper energy limits, respectively.

To deal with actuators and sensors failures the P and R matrices in (11) are defined as follows:

$$P = \lambda \mathcal{V}^T \mathcal{V} + M^T M \tag{12}$$

$$R = M^{T}(H(k)\tilde{x}(k) + Gu(k))$$
(13)

where  $\mathcal{W}, \mathcal{V}$  and  $\mathcal{Z}$  are appropriate matrices

In this stage to test the convexity and feasibility of (11) for the FDMPC, the definiteness of Matrix *P* has been evaluated. To compute the optimal control input based on the Quadratic Programming optimization. The necessary condition is that the quadratic function defined in (11) is strictly convex if and only if matrix *P* is positive definite.

### 4 Simulation Results

To test and evaluated the effectiveness of the presented approach, the model (6) that reflected the wind –turbine system (1) after modelling and reformulation. The simulation parameters used in this paper are as next (Table 1).

Parameters	Description	Numerical value
$J_T$	Turbine inertia	$4.75 \times 10^6 \text{ N m s}^2$
$J_g$	Generator inertia	$0.85 \times 10^6 \text{ N m s}^2$
Gg	Gearbox gain	91.3
$\Omega_{T-nom}$	Nominal speed	2.05 MW
Pnom	Nominal power	17.75 rpm
β	Mechanical coupling damping coefficient	$3.2 \times 10^5 \text{ N m}^{-1} \text{ s}$
κ	Mechanical coupling stiffness coefficient	$109 \times 10^{6} \text{ N m}^{-1} \text{ s}$
ρ	Air density	1.225 kg/m <sup>3</sup>

Table 1Wind-turbine physical parameters.



Fig. 1 The estimated generator speed of wind-turbine

The weighting matrices are:  $Q_0 = I_n$ ,  $R_0 = 0.5$ .

Figure 1 shows the variation of the predicted generator speed in presence of event-triggered for the scenario of low wind speed. The estimated generator speed is controlled around the desired value (i.e. 171 rad/s), meanwhile, the generator speed has changing between 156 and 184 rad/s, that consider as an acceptable deviation, since it's around of 10% as ratio.

## 5 Conclusion

The event-triggered based predictive control strategy is studied in this paper. To improve precise control instance using obtained optimal control, an augmented system is reformulated using a state observer based predictive control scheme as a constrained QP. This approach employs event-triggered sampling, mainly, the control updates are triggered only when specific events or significant changes occur in the wind-turbine. The simulations results show good performances for the generator speed of wind-turbine.

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## PID Controller for Precise Voltage Output of Solid Oxide Fuel Cell



#### Abdelhamid Bounemeur, Abdelmalek Zahaf, and Mohamed Chemachema

Abstract In this paper, we introduce a novel methodology for precise control of Solid Oxide Fuel Cell (SOFC) systems, aiming to optimize power generation while accounting for uncertainties, disturbances, sensor malfunctions, and nonlinear actuator issues. Our approach leverages PID controller as the main components in our control strategy. PID is known as a powerful tool in control theory due to its ability to handle uncertainties and ensure a precise tracking to any given references. Voltage control is a critical aspect of SOFC operation, directly influencing the cell's efficiency and stability. PID controllers play a pivotal role in maintaining a steady and controlled voltage output by dynamically adjusting operating parameters based on real-time feedback. By employing PID control in voltage regulation, SOFCs can maintain a stable electrical output, preventing overvoltage or underperformance issues. Precise tuning of PID parameters tailored to the specific characteristics of SOFCs is crucial to achieving optimal voltage control. Simulation study will show the advantages behind integrating PID controller on voltage control of a SOFC system.

Keywords Solid oxide fuel cell · PID controller · Voltage control

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#### **1** Introduction

In the last decade, researchers have been widely focused on the study of Solid Oxide Fuel Cell, Solid Oxide Fuel Cells (SOFCs) are innovative energy conversion devices that produce electricity through an electrochemical process. They operate at high temperatures, utilizing a solid ceramic electrolyte that conducts oxygen ions from the cathode to the anode. This unique design allows them to efficiently convert the chemical energy of fuels, such as hydrogen, natural gas, or methane, directly into electricity. Controlling SOFCs is crucial to optimize their performance and ensure their efficiency and durability. Among the various control techniques used, PID (Proportional-Integral-Derivative) control is often employed to regulate and stabilize different aspects of SOFC operation. The PID control system consists of three main components [1–10]. Proportional (P) Control: This component responds proportionally to the error between the desired and actual values. In the context of SOFCs, P control can be used to regulate parameters like temperature, fuel flow rate, or oxygen flow rate. For instance, if the temperature deviates from the setpoint, the P component adjusts the control signal in proportion to the error to bring the temperature back to the desired level. Integral (I) Control: The integral component accumulates the error over time and uses this accumulated error to eliminate any steady-state error [10–15]. In SOFCs, I control can help mitigate long-term deviations from setpoints. For example, it can compensate for slow changes in operating conditions or help maintain consistent fuel or air flow rates. Derivative (D) Control: The derivative component predicts the future trend of the error based on its rate of change. In SOFC applications, D control can anticipate rapid changes in operating conditions and provide preemptive adjustments to prevent overshoots or instability in parameters like temperature or voltage.

In a SOFC system, PID control can be applied to various aspects [7, 16–19]: Temperature Control: PID controllers can regulate the temperature within the SOFC to maintain optimal operating conditions, preventing thermal stresses and ensuring efficient performance. Fuel and Air Flow Control: By utilizing PID control on flow control valves, the flow rates of fuel and air entering the SOFC can be adjusted dynamically to maintain the required stoichiometry and prevent issues like fuel starvation or oxygen depletion.

Compared to adaptive and predictive control scheme, the PID controller has a superiority against modern control theory, due to its cost and execution time [1-24].

Voltage and Current Control: PID control can be employed to regulate the output voltage and current of the SOFC to prevent overvoltage, underperformance, or fluctuations in power output.

In our study, we will focus on the control of the voltage of the SOFC to prevent any overvoltage and fluctuations in the output to the systems. Moreover, PID controller will be integrated in the feed forward path a s a main controller to further enhance the performances in case of faults or uncertainties.

The emphasize of this paper is organized as follows:

Mathematical model of a SOFC; Linear Model; Controller strategy; Simulation; Conclusion.

## 2 Model Plant and Control Dynamic

The mathematical model of the SOFC plant is defined with the following state-space representation:

$$\begin{cases} \dot{x}_{1}(t) = \frac{1}{\tau_{f}} [u(t) - x_{1}(t)] \\ \dot{x}_{2}(t) = \frac{1}{\tau_{H_{2}}} \left[ \frac{1}{K_{H_{2}}} (x_{1}(t) - 2K_{r}i(t)) - x_{2}(t) \right] \\ \dot{x}_{3}(t) = \frac{1}{\tau_{H_{2}0}} \left[ \frac{2K_{r}i(t)}{K_{H_{2}0}} - x_{3}(t) \right] \\ \dot{x}_{4}(t) = \frac{1}{\tau_{O_{2}}} \left[ \frac{1}{K_{O_{2}}} \left( \frac{x_{1}(t)}{r_{H_{-}0}} - 2K_{r}i(t) \right) - x_{4}(t) \right] \\ y(t) = N \cdot \left[ E^{0} + \frac{RT}{2F} \left( \frac{x_{2}(x_{4})^{\frac{1}{2}}}{x_{3}} \right) \right] - R_{\text{ohmic}} i(t) \end{cases}$$
(1)

where the output is considered as the battery voltage V;  $P_{H_2}$ ,  $P_{H_2o}$ ,  $P_{o_2}$  are respectively the partial pressure of the hydrogen, water, and oxygen. This equation is defined based on the Nernst equation regarding the ohmic losses.

## 3 Linear Model of SOFC

To make the controller easy to build, a linearization model around an equilibrium point is presented below, with four state matrix A, B, C, D:

$$\begin{cases} \dot{X} = A + Bu\\ Y = CX + Du \end{cases}$$
(2)

where

$$V = N \cdot \left[ E^{0} + \frac{RT}{2F} \ln \left( \frac{P_{H_{2}}(P_{O_{2}})^{\frac{1}{2}}}{P_{H_{2}O}} \right) \right] - R_{\text{ohmic}} \cdot I$$
(3)

$$\mathbf{x}(\mathbf{t}) = \begin{pmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \\ x_4(t) \end{pmatrix} = \begin{pmatrix} q_{\mathrm{H}_2} \\ P_{\mathrm{H}_2} \\ P_{\mathrm{H}_2\mathrm{O}} \\ P_{\mathrm{O}_2} \end{pmatrix}, \mathbf{y}(\mathbf{t}) = V$$
(4)

$$\mathbf{A} = \begin{bmatrix} \frac{\partial f_{1}}{\partial x_{1}} & \frac{\partial f_{1}}{\partial x_{2}} & \frac{\partial f_{1}}{\partial x_{3}} & \frac{\partial f_{1}}{\partial x_{4}} \\ \frac{\partial f_{2}}{\partial x_{1}} & \frac{\partial f_{2}}{\partial x_{2}} & \frac{\partial f_{2}}{\partial x_{3}} & \frac{\partial f_{3}}{\partial x_{4}} \\ \frac{\partial f_{4}}{\partial x_{1}} & \frac{\partial f_{4}}{\partial x_{2}} & \frac{\partial f_{4}}{\partial x_{3}} & \frac{\partial f_{4}}{\partial x_{4}} \end{bmatrix}_{X=X_{eq}} = \begin{bmatrix} -\frac{1}{\tau_{f}} & 0 & 0 & 0 \\ \frac{1}{\tau_{H_{2}} K_{H_{2}}} & -\frac{1}{\tau_{H_{2}}} & 0 & 0 \\ 0 & 0 & -\frac{1}{\tau_{H_{2}}} & 0 \\ \frac{1}{\tau_{0_{2}} K_{0_{2}} r_{H-0}} & 0 & 0 & -\frac{1}{\tau_{0_{2}}} \end{bmatrix}$$
(5)  
$$\mathbf{B} = \begin{bmatrix} -\frac{1}{\tau_{f}} \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

 $x_{20}$ ,  $x_{40}$ : represents the equiliburm points.

$$\mathbf{C} = \left[ 0 \ \frac{NRT}{2Fx_{20}} - \frac{NRT}{2F} \ \frac{NRT}{4F(x_{40})^2} \right], \mathbf{D} = 0$$
(6)

The real parameters of the SOFC are presented in Table 1.

Parameters	Values	Unity	Representation					
Т	1273	К	Absolute temperature					
F	$96.487 \times 10^{6}$	C/kmol	Faraday constant					
R	8314	J/(kmol K)	Universal gas constant					
E <sup>0</sup>	1.18	V	Ideal standard voltage					
N	450	-	Cellule numbers in the «stack»					
Rohmic	$3.2813 \times 10^{-4}$	Ω	Ohmic losses					
K <sub>r</sub>	$0.996 \times 10^{-6}$	kmol/(s A)	Constant					
K <sub>H2</sub>	$8.43 \times 10^{-4}$	kmol/(s atm)	Hydrogen constant					
K <sub>H2O</sub>	$2.81 \times 10^{-4}$	kmol/(s atm)	Water constant					
K <sub>O2</sub>	$2.52e \times 10^{-3}$	kmol/(s atm)	Oxygen constant					
$ au_{ m H_2}$	26.1	s	Response time of hydrogen flux					
$ au_{ m H_2O}$	78.3	s	Response time of water flux					
τ <sub>O2</sub>	2.91	8	Response time of oxygen flux					
$\tau_f$	5	s	Time-constante for combustion					
r <sub>H-O</sub>	1.145	-	Ratio between H <sub>2</sub> et O <sub>2</sub>					
i <sub>L</sub>	800	A/cm <sup>2</sup>	Density of the limited current					
a	0.05	-	Constant of Tafel					
b	0.11	-	Slope of Tafel					

 Table 1
 SOFC real parameters



Fig. 1 PID controller scheme

## 4 Controller Strategy

In this part, a PID controller has been proposed in order to meet the desired performances and deal with parameters uncertainties and disturbances.

PID controller has three actions, the past action (integral), the present action (proportional), and the future action (derivative), the block diagram of this controller in shown Fig. 1.

The process in our case is the SOFC system.

## 5 Results and Simulation

In this part, simulation result will be presented for the output voltage of the SOFC along with the different pressure and the control input signal (Fig. 2).

The first test is the step input, so that we can assess the behavior of the system for a step testing input.

After choosing the PID gains with tunning, we can further obtain a good result as shown in Figs. 3 and 4.



Fig. 2 Step response of the open-loop





## 6 Conclusion

We can conclude in this paper that the PID controller is a powerful toll for controlling any process with the presence of disturbances and uncertainties. Thus, the SOFC process should have a precise voltage control during its operating mode and also, in other works, authors tried to control also the temperature of the SOFC, which will be our next study. Furthermore, the used PID controller proves the efficiency and the accuracy of the output voltage.

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## Finite-Control-Set Model Predictive Control (FCS-MPC) and Fuzzy Self-Adaptive PI Controller (FSA-PIC) for Wind Turbine System Based on DFIG



Amira Aggoune, Farid Berrezzek, and Khaled Khelil

**Abstract** This paper aims at conducting a comparative analysis between two control strategies, namely the finite-control-set model predictive control (FCS-MPC) and the fuzzy self-adaptive proportional-integral controller (FSA-PIC), for regulating the rotor side converter (RSC) in a wind turbine system (WTS) based on a doubly-fed induction generator (DFIG). This study seeks to assess the performance of these strategies with regard to precision and stability when faced with random variations in wind speed and changes in system parameters. To achieve this objective, numerous numerical tests have been carried out within the MATLAB/Simulink environment, employing a 1.5 MW WTS model. The results obtained from these tests consistently demonstrate that the FCS-MPC outperforms the FSA-PIC in terms of accuracy, robustness, and the minimization of power fluctuations across all operational scenarios.

**Keywords** Wind turbine system • Doubly-fed induction generator • Fuzzy self-adaptive PI controller • Finite-control-set model predictive control

## 1 Introduction

In the last decade, wind energy conversion systems (WECS) equipped with doublyfed induction generator (DFIG) are becoming the most competitive renewable energy alternative for delivering clean energy to the power grid [1]. Thanks to its primary features of power transmission controllability, operational flexibility at different operation modes and low voltage ride-through capability [2, 3]. However, one of the main issues in WECS based on DFIG is often to lack stability due to the intrinsic randomness of wind energy and the non-linear nature of the DFIG [1]. As a result, many control strategies have been developed including the decoupled vector control with

327

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standard PI regulator, which have the perfect capability of controlling independently the stator active and reactive power supplied to the power grid [2]. However, this control method still unsuitable for non-linear and uncertain systems, and suffers from poor transient performance resulting from the conventional method of adjusting the PI parameters [4].

Therefore, adopting an adaptive control algorithm is one potential solution to overcome the drawbacks of the PI controllers [3]. The most common adaptive technique presented in the literature is fuzzy self-adaptive PI controller (FSA-PIC) [1]. In this technique the PI gains are updated in real-time according to the system operating conditions [2, 3]. This method exhibits optimal performance addressed to the model uncertainties and external disturbances [1]. However, the major shortcoming of the fuzzy logic control (FLC) resides in the need for expert knowledge of the process.

Recently, the finite-set-control model predictive control (FCS-MPC) has been introduced as an alternative control strategy able to ensure optimal and robust control performance to the WECS [5]. The FCS-MPC is an optimization technique based on the dynamical model of the system [6]. In this technique, the switching states that trigger the rotor side converter (RSC) are generated with respect to the system plant and a cost function. The key feature of the FSC-MPC lies in removing current regulation loop and the modulation block [4]. The control signals are obtained by minimizing a cost function that evaluate the error between the set point and its own prediction value for each possible switching state of the RSC [6].

In this paper, we will conduct a comparative analysis between the FCS-MPC and the FSA-PIC, with the goal of evaluating the introduced control strategies in terms of precision and stability with respect to parametric variations and different operating modes that the DFIG can handle. This paper is intended to be an additional contribution to comparative performance analysis of FSA-PIC and FCS-MPC to control WTS based on DFIG. The rest of the paper is organized as follows: Mathematical description of the major parts of the WECS is presented in Sect. 2. FSA-PIC design is the subject of Sect. 3. The FCS-MBPC description is given in Sect. 4. The comparative analysis between the FSA-PIC and FCS-MPC is conducted in Sect. 5. Finally, Sect. 6 concludes the article.

#### 2 DFIG Based WTS Modeling

#### 2.1 DFIG Modeling

The current state representation of the DFIG in the synchronous d-q reference frame in terms of the stator and rotor resistances  $R_s$ ,  $R_r$ , stator, rotor and mutual inductances  $L_s$ ,  $L_r$ ,  $L_m$  respectively, the stator angular speed  $\omega_s$  and generator slip g can be expressed as follows [5, 7]: Finite-Control-Set Model Predictive Control (FCS-MPC) and Fuzzy ...

$$\frac{d}{dt} \begin{pmatrix} i_{sd} \\ i_{sq} \\ i_{rd} \\ i_{rq} \end{pmatrix} = \frac{L_m}{\sigma} \begin{pmatrix} -\frac{1}{\tau_s L_m} & \omega_s \kappa_m & \frac{1}{\tau_r L_s} & \frac{\omega_s \kappa_s}{L_s} \\ -\omega_s \kappa_m & -\frac{1}{\tau_s L_m} & -\frac{\omega_s \kappa_s}{L_s} & \frac{1}{\tau_r L_s} \\ \frac{1}{\tau_s L_r} & -\frac{\omega_s \kappa_s}{L_r} & -\frac{1}{\tau_r L_m} & \omega_s \kappa_g \\ \frac{\omega_s \kappa_s}{L_r} & \frac{1}{\tau_s L_r} & -\omega_s \kappa_g & -\frac{1}{\tau_r L_m} \end{pmatrix} \begin{pmatrix} i_{sd} \\ i_{sq} \\ i_{rd} \\ i_{rq} \end{pmatrix} \\
+ \frac{L_m}{\sigma} \begin{pmatrix} \frac{1}{L_s L_m} & 0 & \frac{-1}{L_s L_r} & 0 \\ 0 & \frac{1}{L_s L_m} & 0 & \frac{-1}{L_s L_r} \\ -\frac{1}{L_s L_r} & 0 & \frac{1}{L_r L_m} & 0 \\ 0 & \frac{-1}{L_r L_m} & 0 \\ \frac{1}{L_r L_m} & 0 & \frac{1}{L_r L_m} \end{pmatrix} \begin{pmatrix} V_{sd} \\ V_{rq} \\ V_{rq} \end{pmatrix} \tag{1}$$

With:  $\kappa_m = \left(\frac{1}{L_m} - \frac{L_m g}{L_s L_r}\right), \kappa_g = \left(\frac{g}{L_m} - \frac{L_m}{L_s L_r}\right), \kappa_s = (1 - g), \tau_s = \frac{L_s}{R_s}, \tau_r = \frac{L_r}{R_r}$ The stator active and reactive powers of the DFIG are given by [8]:

$$\{P_s, Q_s\} = \left\{\frac{3}{2} \left( V_{sd} i_{sd} + V_{sq} i_{sq} \right), \frac{3}{2} \left( V_{sq} i_{sd} - V_{sd} i_{sq} \right) \right\}$$
(2)

#### 2.2 RSC Modeling

The output voltage of a two-level RSC is defined as [4]:

$$\begin{bmatrix} V_{An} \\ V_{Bn} \\ V_{Cn} \end{bmatrix} = \frac{V_{dc}}{3} \begin{bmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{bmatrix} \begin{bmatrix} S_a \\ S_b \\ S_c \end{bmatrix}$$
(3)

With  $V_{An}$ ,  $V_{Bn}$ ,  $V_{Cn}$  are the phase voltages,  $V_{dc}$  is the DC -link voltage and  $S_a$ ,  $S_b$ ,  $S_c$  are the RSC switching states. Note that for a two-level RSC the number of switching states is equal to eight. Therefore, eight vector voltages can be obtained (see Fig. 1).





#### **3** Desing of FSA-PIC for DFIG Based WTS

The decoupled d-q vector control is the most frequent control scheme applied to the WECS; however, it suffers from suboptimal performance resulting from the design of the PI regulator gains which is achieved by linearizing the system model at single operating point [3]. Therefore, adopting an intelligent method to adjust PI controller gains is a brilliant solution. For that reason, this section is devoted to the design of a fuzzy self-adaptive PI controller (FSA-PIC) (see Fig. 2).

#### 3.1 Fundamentals on the Decoupled Vector Control

Generally, the stator active and reactive powers of the DFIG are controlled by means of the RSC using the decoupled d-q vector control strategy. In this technique, the d-axis component of the synchronous reference frame is aligned with the stator flux vector as described in (4) [3]:

$$\left\{\varphi_{sd},\varphi_{sq}\right\} = \left\{L_s i_{sd} + L_m i_{rd}, L_s i_{sq} + L_m i_{rq} = 0\right\}$$
(4)

From (4), the relationship between the DFIG stator and rotor currents is [9]:



 $\left\{i_{sq}, i_{sq}\right\} = \left\{\frac{\varphi_{sd}}{L_s} - \frac{L_m}{L_s}i_{rd}, -\frac{L_m}{L_s}i_{rq}\right\}$ (5)

Fig. 2 Decoupled vector control-based FSA-PIC structure

 $\omega_s L_s$ 

Generally, we assumption that for medium and large-scale wind power generators the stator resistance is neglected, so the stator voltages expression can be written as follows [2]:

$$\left\{V_{sd}, V_{sq}\right\} = \left\{0, \omega_s \varphi_{sd}\right\} \tag{6}$$

As a result, the rotor voltage components can be deduced as [2, 3]:

$$\left\{V_{rd}, V_{rq}\right\} = \left\{R_r i_{rd} + \sigma L_r \frac{di_{rd}}{dt} - \sigma L_r g\omega_s i_{rq}, R_r i_{rq} + \sigma L_r \frac{di_{rq}}{dt} - \sigma L_r g\omega_s i_{rd} + \frac{gL_m V_s}{L_s}\right\}$$
(7)

Furthermore, the stator active and reactive powers expressions can be deduced by replacing (4) in (2) as:

$$\{P_{s}, Q_{s}\} = \left\{-\frac{3}{2} \frac{V_{sq}L_{m}}{L_{s}} i_{rq}, -\frac{3}{2} \left(\frac{V_{sq}L_{m}}{L_{s}} i_{rd} - \frac{V_{sq}^{2}}{\omega_{s}L_{s}}\right)\right\}$$
(8)

#### 3.2 FSA-PIC Design

In this study the fuzzy logic control has been used as a supervisory system that adjusts online the parameters of the PI regulator  $k_p(t)$  and  $k_i(t)$  as represented in Fig. 3. Consequently, the parameters of the PI can be expressed in function of the PI controller's initial gains  $k_{p0}$ ,  $k_{i0}$  and  $\Delta k_p(t)$ ,  $\Delta k_i(t)$  the output variables of the fuzzy inference as follows:

$$\{k_p(t), k_i(t)\} = \{k_{p0} + \Delta k_p(t), k_{i0} + \Delta k_i(t)\}$$
(9)

Finally, the expression of the output control system is given by equation:



System output

Fig. 3 FSA-PIC structure

A. Aggoune et al.

$$u(t) = (k_{p0} + \Delta k_p(t))e(t) + (k_{i0} + \Delta k_i(t))\int_0^t e(t)dt$$
(10)

As explained previously, the fuzzy logic technique is used to update in real-time the parameters of the PI regulator in terms of the error e(t) and change of error  $\Delta e(t)$ , which will serve as inputs for the FSA-PI controller. Each controller variable is labelled.

Each controller variable is labelled with five triangular membership functions (MFs) denoted as follows: NB/NS (negative big/small), ZE (Zero), PS/PB (positive small/big) (see Fig. 4). Additionally, the rule base is composed of 50 rules used to allow the Mamdani fuzzy inference system to proceed the decision-making process, as represented in Table 1. The output signal is generated by applying the centre of gravity (COG) defuzzification technique.



Fig. 4 MFs distribution of inputs and outputs of the FLC

$\Delta k_p(t)/\Delta k_i(t)$		$\Delta e(t)$					
		NB	NS	ZE	PS	PB	
<i>e</i> ( <i>t</i> )	NB	PB/NB	PB/NB	PS/NS	PS/NS	ZE/ZE	
	NS	PB/NB	PB/NB	PS/NS	ZE/ZE	NS/PS	
	ZE	PB/NB	PS/NS	ZE/ZE	NS/PS	NS/PS	
	PS	PS/NS	ZE/ZE	NS/PS	NS/PS	NB/PB	
	PB	ZE/ZE	NS/PS	NS/PS	NB/PB	NB/PB	

Table 1 Fuzzy rules of the PI controller's gains
## 4 FCS-MPC for the Control of DFIG

The FCS-MPC is a control technique that makes an explicit use of the dynamical model of the process to predict its future evolution over a short period of time and choose the optimal control action by minimizing a cost function [6]. In this study, the rotor current regulation loop and the modulation block are replaced by a predictive rotor current control that uses the finite number of switching states that trigger the RSC and the system model to forecast the rotor currents of the DFIG, for each switching state, on a sampling period  $T_s$ . For each prediction, the optimization process is repeated using a cost function and the switching state yielding the least error between the predicted variable and the reference is chosen to be implemented during the next sampling period (Fig. 5).

#### 4.1 Predictive Current Rotor Control

Based on the current state representation developed in (1), one can define the DFIG's rotor currents equations as follows:

$$\frac{di_{rd}}{dt} = \frac{L_m}{\sigma} \left( \frac{1}{\tau_s L_r} i_{sd} - \frac{\omega_s \kappa_s}{L_r} i_{sq} - \frac{1}{\tau_r L_m} i_{rd} + \omega_s \kappa_g i_{rq} - \frac{1}{L_s L_r} V_{sd} + \frac{1}{L_m L_r} V_{rd} \right)$$
(11)  
$$\frac{di_{rq}}{dt} = \frac{L_m}{\sigma} \left( \frac{\omega_s \kappa_s}{L_r} i_{sd} + \frac{1}{\tau_s L_r} i_{sq} - \omega_s \kappa_g i_{rd} - \frac{1}{\tau_r L_m} i_{rq} - \frac{1}{L_s L_r} V_{sq} + \frac{1}{L_m L_r} V_{rq} \right)$$
(12)



Fig. 5 FCS-MBPC structure

In order to derive the discrete model of the predicted rotor currents, we will adopt the forward difference Euler method as in (13) [10]:

$$\frac{dx}{dt} = \frac{x(k+1) - x(k)}{T_s}$$
(13)

Therefore, the discrete model of the predicted rotor currents corresponding to instant time k + 1 can be written as following:

$$i_{rd}^{k+1} = \frac{L_m T_s}{\sigma} \left( \left( 1 - \frac{1}{\tau_r L_m} \right) i_{rd}^k + \omega_s \kappa_g i_{rq}^k + \frac{i_{sd}^k}{\tau_s L_r} - \frac{\omega_s \kappa_s}{L_r} i_{sq}^k - \frac{1}{L_s L_r} V_{sd}^k + \frac{1}{L_m L_r} V_{rd}^k \right)$$
(14)  
$$i_{rq}^{k+1} = \frac{L_m T_s}{\sigma} \left( \left( 1 - \frac{1}{\tau_r L_m} \right) i_{rq}^k - \omega_s \kappa_g i_{rd}^k + \frac{\omega_s \kappa_s}{L_r} i_{sd}^k + \frac{1}{\tau_s L_r} i_{sq}^k - \frac{1}{L_s L_r} V_{sq}^k + \frac{1}{L_m L_r} V_{rq}^k \right)$$
(15)

The cost function can be calculated as follows [11]:

$$g = \left(i_{rdref}^{k+1} - i_{rd}^{k}\right)^{2} + \left(i_{rqref}^{k+1} - i_{rq}^{k+1}\right)^{2}$$
(16)

where  $i_{rdref}^{k+1}$  and  $i_{rqref}^{k+1}$  are the reference rotor currents at time (k + 1). They can be calculated by utilizing the 2nd order Lagrange extrapolation as following:

$$i_{rd,rqref}^{k+1}(k+1) = 3i_{rd,rqref}^{k} - 3i_{rd,rqref}^{k-1} + i_{rd,rqref}^{k-2}$$
(17)

## 5 Results and Discussion

This section is devoted to compare the FSA-PIC controller to the FCS-MPC performances under the same operation conditions. For that reason, a simulation study of a 1.5 MW DFIG based WTS has been carried out using MATLAB/Simulink software. The operation conditions applied to the WECS are as following: the stator active power is set to the maximum power generated by the wind turbine, whilst the stator reactive power reference is set to zero value in order to maintain the power factor at unity. The wind profile adopted during this simulation test is depicted in Fig. 6.

### 5.1 Reference Test Track

Figure 7 presents the simulation results of the DFIG based WTS using the introduced strategies. The stator active power tracks perfectly its reference value. Meanwhile, the stator reactive power is kept at zero value during the simulation study. It can be



Fig. 6 Applied wind speed profile

clearly seen that the d-q axis rotor currents are the images of the stator reactive and active powers respectively and they follow their imposed references. The comparative analysis of the obtained results shows that the decoupled control is ensured for both control strategies. However, the FCS-MPC shows a faster and more precise system response compared to the FSA-PIC. Moreover, the controlled variables ripples are considerably reduced using the FCS-MPC.



Fig. 7 Reference track test response



Fig. 8 Robustness test response

## 5.2 Robustness Test

In this section, the FSA-PIC is compared to the FCS-MPC considering an intermittent wind speed profile and the following parametric variations: 130% of the mutual inductance within the range of [0–10 s]. In the range of [10–20 s]: 200% of stator and rotor resistances. Figure 8 depicts the simulation results of the FSA-PIC and FCS-MPC. It is obviously observed that the FCS-MPC is insensitive to parametric changes when compared to the FSA-PIC whose performances are considerably degraded when the mutual inductance varies. Moreover, The obtained result can be merged with adaptive and predictive techniques in control theory [12–34].

## 6 Conclusion

This work offers a comprehensive examination of the performance comparison between FSA-PIC and FCS-MPC, both applied to control RSC of a wind turbine system based on a DFIG. The analysis of the obtained results from both experiments consistently demonstrates that FCS-MPC exhibits robustness superior to that of FSA-PI, ensuring stable operation even in the presence of random wind power fluctuations and parametric variations. Furthermore, FCS-MPC outperforms FSA-PI in terms of reference tracking, precision, accuracy, and the minimization of power ripples. In conclusion, this study suggests that the FCS-MPC strategy holds significant promise for the control of WECS.

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