IMPEDANCE SPECTROSCOPY ANALYSIS OF THE $[(NA_{0.535}\ K_{0.480})_{0.966}\ LI_{0.058}](NB_{0.90}TA_{0.10})O_3$ BASED LEAD-FREE CERAMICS

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RÉSUMÉ

Polycrystalline samples of $[(Na_{0.535}\ K_{0.480})_{0.966}\ Li_{0.058}](Nb_{0.90}Ta_{0.10})O_3$ were prepared using the high-temperature solid-state reaction technique. XRD analysis indicated the formation of a single-phase with orthorhombic structure. AC impedance plots were used as tool to analyse the electrical behaviour of the sample as a function of frequency at different temperature. The AC impedance studies revealed the presence of grain effect, from 425°C onward. Complex impedance analysis indicated non-Debye type dielectric relaxation. The Nyquist plot showed the negative temperature coefficient of resistance (NTCR) characteristic of NKLNT.

Mots Clés: *Impedance spectroscopy, Dielectric relaxation, perovskite structure, Conductivity*

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NOMENCLATURE

Symboles :
T temperature (°C)
Z* complex impedance
Z ′real part
Z″ imaginary part
f frequency(Hz)
R_g grain resistance
C_g grain capacitance
W frequence

Lettres grecques :
Ɛ permitivity

1. INTRODUCTION

Actually, $PbZr_{(1-x)}Ti_xO_3$ (PZT) and lead-based compounds constitute the best family of piezoelectric and ferroelectric materials suitable for integration in devices, such as actuators, sensors and ultrasonic transducers. However, at the present time, there are some restrictions based upon European directives and thus lead-based piezoelectric materials are only tolerated for piezoelectric devices [1]. As a consequence, new lead-free materials

are the aim of studies and several recent papers made an inventory of the compounds actually considered as potential candidates for the replacement of PZT [2-3].

Among lead-free piezoelectric systems, the niobate-based ceramics are the most promising [4–5]. For pure $(Na,K)NbO_3$ (NKN) ceramics prepared by normal sintering, the highest piezoelectric coefficient was no more than 100 pC/N [2]. However, their piezoelectric properties could be enhanced by introducing Li and Ta, respectively, into the A and B sites of perovskite-structured NKN ceramics [4, 6–7]. On the other hand, the $[(Na_{0.535}K_{0.480})_{0.966}Li_{0.058}](Nb_{0.90}Ta_{0.10})O_3$ system has been paid considerable attention on account of the existence of a orthorhombic and tetragonal morphotropic phase boundary (MPB) [8] .

In addition, it is well known that defects such as A-site vacancies, space charge electrons or oxygen vacancies have great influence on ferroelectric fatigue or ionic conductivity of the material [14]. Considering that the solid defects play a decisive role in all of these applications, it is very important to gain a fundamental understanding of their conductivity mechanisms of materials. Various kinds of defects are always suggested as being responsible for the dielectric relaxations at high temperature range. The Ac impedance analysis is a powerful mean to distinguish effects between the grain boundary, the grain, and the electrodes, which are usually the traps for defects. It is also useful to establish its relaxation mechanism by appropriately assigning different values of resistance and capacitance to the grains and grain boundaries effects.

In this paper, we focused our research on the $[(Na_{0.535}K_{0.480})_{0.966}Li_{0.058}](Nb_{0.90}Ta_{0.10})O_3$ material (named NKLNT) which exhibits quite good properties with excellent piezoelectric characteristics [8]. In this work a detailed analysis by ac impedance spectroscopy was carried out to characterize the dielectric relaxation. The Ac conductivity data were used to estimate the apparent activation energy, the density of states at Fermi level, and the minimum hopping length.

2. METHODE EXPERIMENTALE

The raw materials of $[(Na_{0.535}K_{0.480})_{0.966}Li_{0.058}](Nb_{0.90}Ta_{0.10})O_3$ (named NKNLT) samples processed by solid state reaction method were pure reagent K_2CO_3, Na_2CO_3, Nb_2O_5, Li_2O_3 and Ta_2O_5. They were weighed and milled for 2h using a zirconia ball media in a teflon jar and isopropanol.They were then dried .The powders were calcined at 850 °C for 2h.

To manufacture pellets, an organic binder (Polyvinyl alcohol, 5 w_t%) was manually added to the powder and disks (7 and 13 mm in diameter, 1mm and 1.5mm thickness, respectively) were shaped by uni-axial pressing under 100MPa. The green samples were finally sintered in air at 1100°C for 2 hours, with heating and cooling rates of 150°C/h. The crystallised phase composition has been identified by X-ray diffraction (XRD) technique using the Cu kα X-ray radiation (Philips X' Pert) and the microstructures were observed using a Scanning Electron Microscopy (SEM Philips XL'30). The specimens were polished and electroded with a silver paste. The electric properties were determined using HP4284A meter versus temperature (from 20°C to 500°C), and the frequency range from 100 Hz to 1 MHz.

3. RESULTATS

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Fig. 1 shows the X-ray diffraction (XRD) patterns of NKNLT sintered samples. The patterns reveals a single perovskite structure without any secondary phases suggesting that homogeneous solid solutions of $[(Na_{0.535}K_{0.480})_{0.966}Li_{0.058}](Nb_{0.90}Ta_{0.10})O_3$ are formed. The NKNLT system exhibits an orthorhombic structure which has been indexed according to the data of Kumada et al. ($KNbO_3$ with lattice constants: a = 3.976 Å; b = 5.695 Å; and c = 5.717 Å with space group *Amm*2) [15]. The unit-cell parameters for the NKNLT composition were

determined by fitting the XRD patterns of the samples. The obtained lattice parameters are: $a = 4.0009$ Å; $b = 5.7075$ Å; and $c = 5.7075$ Å. The slight variation of lattice parameters is due to the formation of NKNLT solid solution. In this solid solution, Na^{+}, K^{+}, and Li+ should occupy A^{1+} sites, while Nb^{5+} and Ta^{5+} should occupy B^{5+} sites due to their valence and ionic radii.

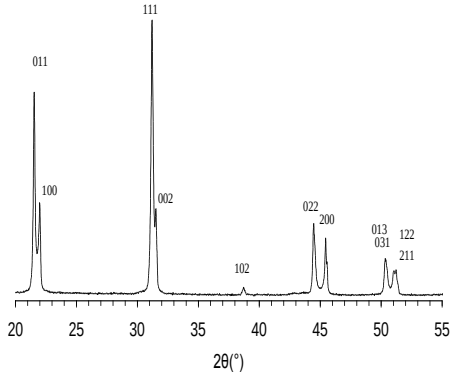

Figure 1: X-ray diffraction patterns of NKNLT composition sintered at 1100°C for 2 hours.

Figure. 2 shows SEM micrographs of sintered ceramic sample. It shows a quasi-cubic morphology with clear grain boundaries. It can also be seen that the ceramics with relatively homogenous microstructure and low porosity can be obtained, the average grain size being about 1 to 4 μm.

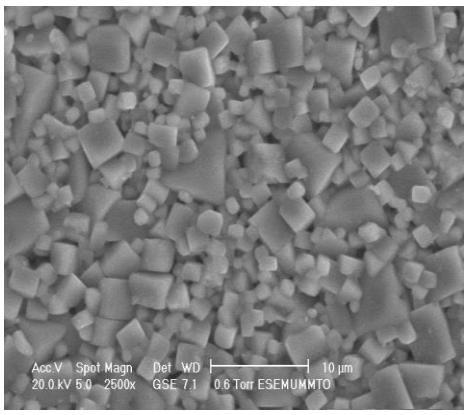

Figure 2: Scanning electron micrographs of fracture for the sintered ceramic.

Figure. 3 shows the temperature dependence of the dielectric constant (ε_r) and dielectric losses tangent (tan δ) of NKNLT ceramics at the frequencies of 1, 10, and 100 kHz respectively.

There are two anomalisms within the measured temperature range from room temperature to 400◦C. These anomalisms are considered to correspond to the following phase transitions from orthorhombic phase to tetragonal phase at lower temperature. (O-T) and from tetragonal phase to cubic phase at higher temperature (T_C). The dielectric loss (tanδ) was lower, and the dielectric constant (ε_r) varied from 800 to 7000 at room temperature and at T_C, respectively. The dielectric loss increases rapidly at higher temperature due to the rapid increase of conductance loss.

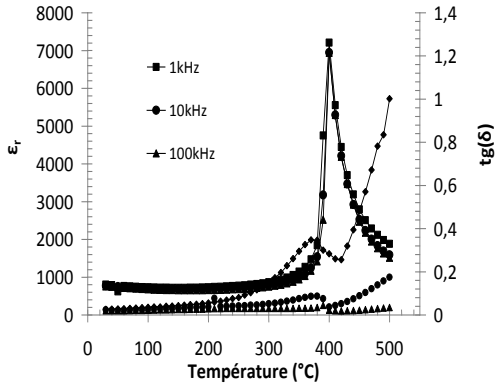

Figure 3: Temperature dependence of permittivity and dielectric loss at different frequency of NKNLT.

Fig. 4(a) and Fig. 4(b)**:** shows the variation of imaginary part (Z") with frequency and temperature. As the temperature increases, the peaks are more and more flattened in this specimen indicating relaxation is stronger at higher temperatures (Fig. 4(b). It can be seen that the curves display broad and low intensity peaks with asymmetrical shape. The broadening of the peak and half widths of the peaks indicate multiple relaxations and deviations from Debye behaviour.

In order to study the impedance spectrum corresponding to different effects such as grain boundaries, grains (bulk or intrinsic properties of material) and electrode contribution, Cole–Cole analysis has been performed.

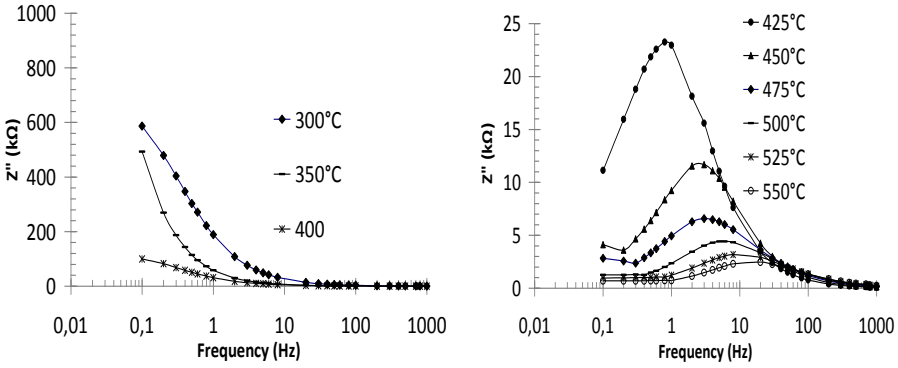

Figure 4: Variation of real part Z′ and imaginary Z" of impedance of NKNLT with frequency at different temperature

Fig. 5(a) and 5(b) shows Cole–Cole plots: (a plot drawn between Z" (imaginary part) vs Z' (real part) of the impedance) at various temperatures. For temperature measurements above 400°C, there is no semicircle formation (Fig.4 (a)). By increasing temperature, the behavior of Z'' vs Z' changes and semicircles appear indicating an increase of the materials conductivity (Fig.5(b)).

The presence of a single semicircular arc passing through the origin in the entire frequency region for all the temperatures indicates that the relaxation mechanism in NKNLT may be only a grain effect. Hence it is appropriate to fit the Z-plot to a single R_gC_g parallel circuit due to the fact that the response peaks of the grain boundaries are not present. The expression for Z* is given by:

$$Z^* = R_g / (1+j\omega R_g C_g) \quad (1)$$

Where R_g and C_g are the grain resistance and grain capacitance respectively. Unfortunately, for Debye type relaxation, one expects semicircular plots with the centre located on the Z'-axis, whereas for a non-Debye type relaxation these Argand plane plots are close to semicircular arcs with end-points on the real axis and the centre lies below this axis. The complex impedance in such a case can be described as [16]:

$$Z^*(\omega) = Z' + iZ'' = R/(1+(i\omega/\omega_0)^{1-\alpha} \quad (2)$$

Where α represents the magnitude of the departure of the electrical response from an ideal condition and this can be determined from the location of the centre of the semicircles. Further, it is known that when α approaches to zero, i.e. {(1-α) =1}, Eq. (2) gives rise to classical Debye's formalism. It can be seen from the impedance plots (Fig.4(b)) that the curves are not full semicircle: they are depressed one, i.e. centre of semicircles lie little below the abscissa (Z') axis (α > 0), which increases with the rise in temperature suggesting the dielectric relaxation to be of non-Debye type in NKNLT composition.

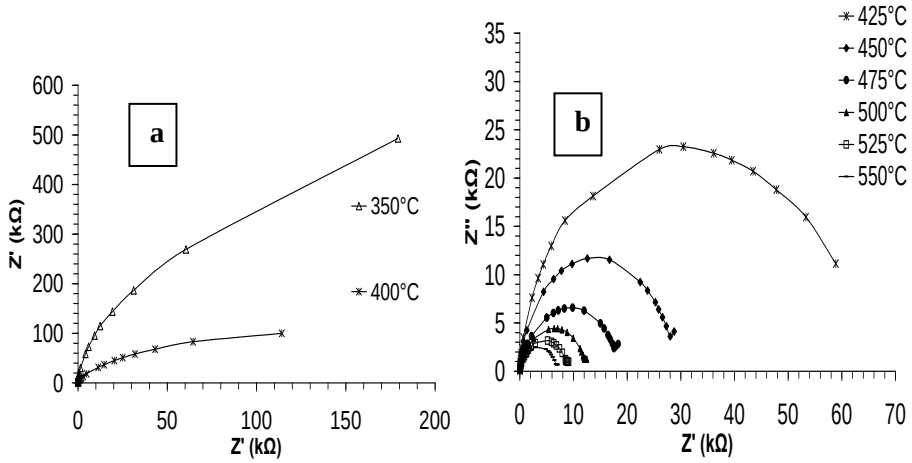

Figure 5 Complex impedance plots (Z″ vs. Z′) of NKNLT at different temperatures.

4. CONCLUSIONS

Polycrystalline $[(Na_{0.535}K_{0.480})_{0.966}Li_{0.058}](Nb_{0.90}Ta_{0.10})O_3$ perovskite, prepared through a high-temperature solid-state reaction technique, was found to be a single-phased perovskite-type. Impedance analyses indicated the presence of grain effect in NKNLT ceramics. The dielectric relaxation was found to be of non-Debye type and the relaxation frequency shifted to higher values with the increase of temperature.

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