Third International Conference on Energy, Materials, Applied Energetics and Pollution
ICEMAEP2016, October 30-31, 2016, Constantine,Algeria
M.KADJA, A.ZAATRI, Z.NEMOUCHI, R.BESSAIH, S.BENISSAAD and K. TALBI (Eds.)

FIRST-PRINCIPLES STUDY OF THE STRUCTURAL AND THERODYNAMIC PROPERTIES OF THE COMPLEXES K_2PtCl_6- STRUCTURE HYDRIDES Ca_2OsH_6.

O.BOUDRIFA [1], A. BOUHEMADOU [2]

[1] Research Center In Industrial Technologics CRTI, P.O. Box 64, Cheraga 16014, Algiers – Algeria,
o.boudhrifa@crti.dz
[1,2] Laboratory for Developing New Materials and their Characterization, University of Setif 1, 19000 Setif,
Algeria, a_bouhemadou@yahoo.fr
.

ABSTRACT

We report the results of an ab initio study of the structural and thermodynamic properties of the Ca_2OsH_6 compounds using the pseudopotential plane-wave method within the framework of the density functional theory with the GGA-PBEsol. The calculated equilibrium structural parameters are in good agreement with the available experimental data ones when the latter are available. We have investigated the thermodynamic properties of the Ca_2OsH_6 system in the temperature range from 0 to 1000 K and the pressure range from 0 to 12 GPa using the quasi-harmonic Debye model as implemented in the Gibbs program. We have successfully obtained the temperature and pressure dependence of the lattice constant, bulk modulus, thermal expansion, the constant volume heat capacity and constant pressure heat capacity as these are essential for crystal growth.

Key words: *Structural, Ab Initio Calculations, Ternary Hydrides, Mechanical Properties, Bulk Modulus and* Thermal effect.

NOMENCLATURE

Symboles :	
E	energie,eV
T	température, K
P	Pression, GPa
X_H	internal parameter, Å
B	bulk modulus, GPa
B'	bulk modulus pressure derivative
C_v	constant volume heat capacity, J mole-1 K-1
C_P	constant pressure heat capacity, J mole-1 K-1
θ_D	Debye temperature, K
Indices / Exposants :	
D	Debye
p	pressure
v	volume

---

1. INTRODUCTION

In the last five years, the study of metal hydrides has expended enormously due to the potential technology importance of these class materials in hydrogen based energy conversion schemes. All hydrides are obtained by sintering the metallic powders at moderate temperature (460-500°C) under high-pressure hydrogen atmosphere (70-130 bar) [1]. The hydrides have attracted enormous research effort owing to their wide range of applications such the hydrogen solid-state storage [2-3], rechargeable batteries [3], smart windows [4-5], switchable mirrors [6-7], etc. Among the most important application is the storage of hydrogen, for this it is necessary that these hydrides mentioned have well defined properties as the rapid kinetics of the hydrogenation and dehydrogenation operation without deterioration of materials, base temperature at which the hydrogenation and dehydrogenation take place, a high hydrogen concentration, and low total weight of hydrides [8-9]. The search of compounds which have a high volume density of hydrogen has included complex transition metals hydrides (CTMHs) such as the A_2TH_6, where *A*=Mg, Ca, Sr, Ba, Eu, Sm; *T*=Fe, Ru, Os, but the disadvantage is the high stability, which makes them disregarded at ambient temperature, such us hydrogen solid-state storage in fuel cell vehicles [10], but they attract much attention for high temperature applications, such as the thermochemical storage of heat for solar thermal plants or excess industrial heat for which hydrogen discharge temperature exceeding 700K are desired [10-11-12]. In addition, this class of hydrides has been suggested as a source of important applications in semiconductor electronics, such as transparent conducting materials [13-14].photovoltaics [15], and optoelectronics [16]. Studied on novel technological application of hydrides have been classified into in new scientific field knowns as “hydrides electronic” [16-17], which is at the intersection of ‘physics of semi-conductors’ and ‘hydrogen storage materials’. Metals hydrides have been of steadily increasing importance for a long time due to their important applications, which urges us to study the structural, elastic, thermodynamic and vibrational properties of Ca_2OsH_6 by methods ab initio. Experimentally, Ca_2OsH_6 has been subject of some works, there is numerous experiment have been to done synthetize the ternary ruthenium based hydrides Ca_2OsH_6 [18-19], and their structural properties [18-19]**,** spectroscopic properties (IR- and Raman-spectra) [18-19] have been investigated. On the theoretical side, several first principal calculations based on the DFT within generalized gradient approximation (GGA) and local density approximation have been performed to understand the structural [20-21-22-23], electronic [22-23] and properties optical [20] of these complex transition metal hydrides. From above, it is clear that experimental and theoretical information about thermodynamic properties are scare.

2. COMPUTATIONAL METHODES

We used an ab initio calculation with the self-consistent field (SCF) method as implemented in the CASTEP code [24] in MS Modeling software. The Khon-Sham equations are solved within the framework of density functional theory [24] by expanding the wave functions of valance electrons in a basis set of plane waves with kinetic energy smaller than a specified cut-off energy, E_{cut}. The electronic exchange–correlation interactions were treated within the recent developed generalized gradient approximation of Perdew et al. (GGA96) [19]. Interactions of electrons with ion cores were presented by the norm conserving pseudopotential for Ca, Os and H atoms [25]. The Mg, Ca, Sr, Ba $3s^2$, Os $4d^7 5s^1$ and H $1s^1$ electron states are explicitly treated as valance electron states. The plane-wave cutoff energy of 990 eV was used for all the calculations. The special points sampling integration over the Brillouin zone was employed by using the Monkhhorst-Pack method a 10x10x10 special k-point mesh [26]. These parameters were sufficient in leading to well converged total energy, geometrical configurations and elastics moduli. The structural parameter were determined using the Broyden– Fletcher–Goldfarb–Shanno (BFGS) minimization technique [27], with the following thresholds for converged structures: energy change per atom less than $5x10^{-6}$, residual force less than 0.01 eV/ Å, stress below 0.02 GPa and the displacement of atoms during the geometry optimization less than $5x10^{-4}$ Å. Knowledge of the behaviors of solids when they are under severe constraints such as high-pressure and high-temperature environment are of a great interest and importance for both the fundamental research and technological applications. To address this interest in the present work, pressure and temperature dependences of the unit-cell volume, bulk modulus, volume expansion coefficient, isochoric heat capacity and Debye temperature of both considered phases were explored using the PP-PW method [28] combined with the quasi-harmonic Debye model as implemented in Gibbs program [29]. Theoretical details about the quasi-harmonic Debye model are available in Blanco et al. [29].

3. RESULTS

3.1. STRUCTURAL PROPERTIES

The hydrides Ca_2OsH_6 have a NaCl structure with faced centered cubic (FCC) structure belonging to the space group Fm-3m. The primitive cell consists of nine atoms, with the Ca atoms are located at 8c (1/4, 1/4, 1/4), Os atoms at 4a (0, 0, 0), and H atoms occupying the 24*e* (x_H , 0, 0) Wyckoff sites [24].The determination of the equilibrium structure is the first step and essential in any calculation, the care which is taken to him will strongly condition the quality of the ulterior analysis. For this, we first calculated the structural properties of Ca_2OsH_6 compounds and we started our calculations with experimental parameter, reported in references [19] and [26]. The obtained structural parameters, the available experimental and theoretical data were summarized in table1. We note that our calculated results by GGA96 are slightly smaller than the experimental values; this means that the experimental data are measured at room temperature whereas our calculated results are predicted at zero temperature. The deviation between our calculated lattice parameter and the measured ones $d\left(\%\right)$ $\left(d\left(\%\right)=\left(Calculated\ value-Measured\ value\right)\times 100\right)/\left(Measured\ value\right))$ is 0.3%.

Under hydrostatic pressure effect, the H atom positional parameter has a linear variation with upward bowing. The calculated unit cell volumes at fixed values of applied hydrostatic pressure in the range 0–15GPa were fitted by the fourth equations of state of Birch Murnaghan, Birch, Murnaghan and Vinet. The obtained bulk modulus B and its pressure derivative B' from this fitting are listed in Table 1. To the best of the authors' knowledge, no experimental and theoretical data on the bulk modulus of the herein investigated materials.

To ensure the thermodynamic stability of Ca_2OsH_6 in its cubic structure, we calculated its formation energy and the cohesive energy with GGA PBE. The formation energy is the energy necessary to form Ca_2OsH_6 compound in this structure. If the formation energy of Ca_2OsH_6 in a cubic structure is negative, it means that the structure is energetically favorable and will occur. The formation enthalpy for Ca_2OsH_6 compound was calculated by following equation [30]:

$$\Delta H_f(\mathrm{Ca}_2 OsH_6) = E_{Tot}^{Ca_2OsH_6} - (2E_{Tot}^{\mathrm{Ca}(solid)} + E_{Tot}^{Os(solid)} + E_{Tot}^{H(gaz)}).$$

Where $\mathrm{E}_{\mathrm{Tot}}^{Ca_2\mathrm{OsH}_6}$, $\mathrm{E}_{\mathrm{Tot}}^{\mathrm{Ca(solid)}}$, $\mathrm{E}_{\mathrm{Tot}}^{\mathrm{Os(solid)}}$ and $\mathrm{E}_{\mathrm{Tot}}^{\mathrm{H(gaz}}$ stand to the total energy of the primitive cell of Ca_2OsH_6 compound and the total energies per atom of the solid states of the pure elements Ca, Os and H, respectively.
The cohesive energy E_{coh} is the energy that is required for the crystal to decompose into free atoms. The cohesive energy E_{coh} of Ca_2OsH_6 was calculated using the following expression [30]:

$$E_{coh}(\mathrm{Ca}_2 OsH_6) = E_{Tot}^{\mathrm{Ca}_2 OsH_6} - (2E_{Tot}^{\mathrm{Ca}(atom)} + E_{Tot}^{Os(atom)} + 6E_{Tot}^{H(atom)})$$

The obtained cohesive energy and formation enthalpy are listed in Table 1. From Table 1, we can see that the cohesive energy and the formation enthalpy of the investigated cubic hydrides phases are negative, which means that this material is energetically stable.

In order to fully characterize the pressure dependence of the structural parameters, we turn our attention to the pressure dependence of the interatomic distances. The bond lengths at zero pressure of the considered bonds are listed in Table 1. Analysis of the relative variations of the considered bond-lengths shown in Figure.1 allows us to draw some conclusions: (i) $H-Ca$, $Ca-Os$ bonds are more compressible than $H-Os$ bonds, so they are the softest ones; (ii) $H-A$ and $Ca-Os$ bonds are compressing with the same manner; and (iii) variations of all chemical bonds can be well approximated by a second-order polynomial: $d/d_0 = 1 + BP + CP^2$, where d stands to the bond-length at a pressure P and d_0 its corresponding value at zero pressure.

$$(d/d_0)_{(H-Os)}^{(Ca_2OsH_6)} = 1 - 5.80949\times10^{-4}P + 6.12421\times10^{-6}P^2$$

$$(d/d_0)_{(H-Ca)}^{(Ca_2OsH_6)} = 1 - 0.00516P + 8.89318\times10^{-5}P^2$$

$$(d/d_0)_{(Ca-Os)}^{(Ca_2OsH_6)} = 1 - 0.00525P + 9.26645\times10^{-5}P^2$$

3.2 THERMODYNAMIC PROPERTIES

The thermal properties of a crystal determine the suitable conditions for initiating and maintaining the quality of crystal growth. Through the quasi-harmonic Debye model, we have investigated the thermodynamic properties of the Ca_2OsH_6 over a range of pressures from 0 to12GPa.

Fig.1 presents the lattice constant-temperature diagram at several pressures and Fig.1 shows the relationship between the lattice constant and pressure at different temperatures for Ca_2OsH_6 compounds. The lattice constant increases with increasing temperature at a given pressure. On the other side, as the pressure P increases the lattice constant decreases at a given temperature. The calculated lattice constants values at room temperature and zero pressure is 8.73 Å.

The temperature and pressure dependences of the bulk modulus for Ca_2OsH_6 compound are plotted in Fig. 1. Fig. 1demonstrates that the bulk modulus B is nearly constant for temperatures lower than 100K and it decreases linearly with increasing temperatures higher than 100K. It can be seen that the bulk modulus B decreases with temperature T increasing at a given pressure, while it increases with pressure P increasing at a given temperature. It also shows that the effect of increasing pressure on Ca_2OsH_6 compound is the same as that of decreasing temperature. However, the effect of the pressure on the bulk modulus is more important than that of the temperature. At zero pressure and ambient temperature, B is approximately equal to 50.34 GPa.

	a	B	B'	x_H	d_{H-Os}	d_{Ca-Os}	d_{H-Ca}	ΔH	E_{coh}
Present	7.2343	59.29^{2}, 59.72^{2}	3.90^{1}, 3.63^{2}	0.2375	1.7171	3.1313	2.5583	7.21	22.56
		59.47^{3}, 59.69^{4}	3.83^{3}, 3.81^{4}						
Expt.	7.253[19] 7.2530 [26]								
Others	7.26471[19] 7.1785[22]			0.23789 [19] 0.2405[22]					

TABLEAU 1.Optimized lattice parameters (a , in Å), internal coordinates (x_H), Calculated bond-length ($H-Os$ $Ca-Os$ and $H-Ca$, in Å), bulk modulus (B , in GPa) and bulk modulus pressure derivative (B') at zero pressure for the Ca_2OsH_6 material. Existing experimental and theoretical data are shown for comparison. B and B' were obtained from the Birch, Murnaghan, Birch-Murnaghan and Vinet EOS_S .

(1) From EOS Birch, (2) from EOS Murnaghan, (3) from EOS Birch-Murnaghan, (4) from EOS Vinet

Within the quasi-harmonic approximation, the anharmonicity is restricted to the thermal expansion. The temperature and pressure dependences of the volume thermal expansion coefficient α of Ca_2OsH_6 compound is plotted in Fig.1. It can be seen that the volume thermal expansion coefficient increases quickly at a given temperature, especially at zero pressure below the temperature of 200K, whereas it gradually tends to a linear increase at higher temperature. However, it is noted from Fig. 1 that, as the pressure increases, the volume thermal expansion coefficient decreases strongly. These results indicate that the anharmonic effects are important at low temperatures and high pressures for Ca_2OsH_6 compound. At zero pressure and room temperature α is approximately equal to 12.81 x 10^{-5} K^{-1} for Ca_2OsH_6.

The variations of the heat capacities C_V and C_P versus temperature at various pressures are shown in Fig.1. It can be found that the constant pressure C_P and constant volume C_V are proportional to T^3 at lower temperature T [31], and that the difference between C_P and C_v is very slight, while with the increase of temperature T , C_P takes on the linear increase and C_V follows the Debye model and approaches the Dulong–Petit limit, indicating that the thermal energy at high temperature excites all phonon modes. According to the thermal formula $C_{p,\,vib} = C_{v,\,vib}\left(1\alpha\gamma T\right)$ [32], the difference between C_P and C_V is due to the thermal expansion caused by anharmonic effect. Fig. 1 also indicates that temperature and pressure have opposite influences on the heat capacity and the effect of temperature on the heat capacity is more significant than that of pressure. It is worth mentioning that, in our work, the value of C_V at 300K and zero pressure is 203.47 J mol^{-1} K^{-1}.

The Debye temperature is another essential fundamental parameter, which is directly related to many physical properties of solids like melting temperature, specific heat, etc. The variation of the Debye temperature θ_D as a function of pressure and temperature illustrated by our results is displayed in Fig. 1. It can be seen that θ_D is nearly constant from 0 to 100 K and decreases linearly with increasing temperature from $T > 200\ K$. It is also shown that when the temperature is constant, the Debye temperature increases almost linearly with applied pressure. Our calculated θ_D at zero pressure and zero temperature is equal to 425 K which is in good agreement with the value of 457 K computed accurately in terms of the elastic constants.

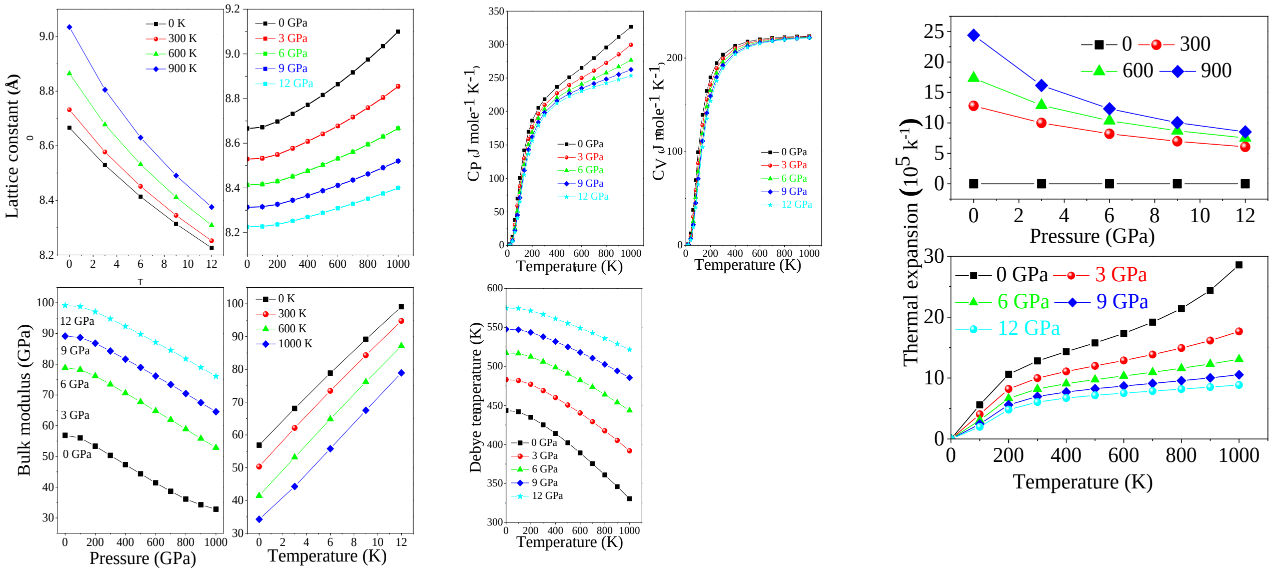

FIGURE 1. Lattice constant, bulk modulus, the constant pressure heat capacity, volume thermal expansion coefficient, the constant volume heat capacity, he constant pressure heat capacity and Debye temperature dependence versus temperature at different pressures and versus pressures at different temperature for Ca_2OsH_6 compound.

4. CONCLUSIONS

In this paper, we have presented a full first-principles study of the structural and thermodynamic properties for Ca_2OsH_6 compound at the GGA-PBE level. The calculations are performed using the plane-wave pseudopotential method, density functional perturbation theory implemented in the CASTEP code and the quasi-harmonic Debye model as implemented in the Gibbs program

(1) First, the optimized structural parameters are obtained and compared with the available data in the scientific literature. The good agreement between our calculated structural parameters and their corresponding measured ones confirms the reliability of the used calculation approaches.

(2)The obtained results through the quasi-harmonic Debye model show that at a fixed pressure the increase of temperature leads to an increase in the unit-cell volume, heat capacity and volume thermal expansion coefficient, but it leads to a decrease in the bulk modulus and Debye temperature. At a fixed temperature, the increase of pressure leads to the increase of the bulk modulus and Debye temperature whereas it leads to the decrease of the unit-cell volume, volume

REFERENCES

[1] B. Huang, F. Bonhomme, P. Selvam, and K. Yvon, New ternary and quaternary metal hydrides with K2PtCl6,-type structures, *J. Less Common Met*. 171,301–311, 1991.

[2] P. Chen, Z.T. Xiong, J.Z. Luo, J.Y. Lin, and K.L. Tan, Interaction of hydrogen with metal nitrides and imides, *Nature*, 420, 302–304, 2002.

[3] L. Schlapbach and A. Zuttel, Hydrogen-storage materials for mobile applications, *Nature*, 414, 353–358, 2001.

[4] J.N. Huiberts, R. Griessen, J.H. Rector, J.H. Recor, R.J. Wijngaarden, J.P. Dekker, D.G. de Groort, and N.J. Koeman, Yttrium and lanthanum hydride films with switchable optical properties, *Nature* 380, 231–234, 1996.

[5] J.L.M. van Mechelen, B. Noheda, W. Lohstroh, R.J. Westerwaal, J.H. Rector, B. Dam, and R. Griessen, Mg–Ni–H films as selective coatings: Tunable reflectance by layered hydrogenation, *Appl. Phys. Lett*, 84, 3651–36523, 2004.

[6] T.J. Richardson, J.L. Slack, R.D. Armitage, R. Farangis, and M.D. Rubin, Switchable mirrors based on nickel–magnesium films, *Appl. Phys. Lett*. 78, 3047–3049, 2001.

[7] G. Kresse and J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B*, 54, 11169–11186, 1996.

[8] S.Z. Karazhanov, U. Sheripov, and A.G. Ulyashin, Classification of hydrides according to features of band structure, *Philos. Mag*, 89, 1111–1120, 2009.

[9] S.Z. Karazhanov and A.G. Ulyashin, Similarity of optical properties of hydrides and semiconductors for antireflection coatings, *Philos. Mag*, 90, 2925–2937, 2010.

[10] K.M. Nicholson and D.S. Sholl, First-principles prediction of new complex transition metal hydrides for high temperature applications, *Inorg. Chem*, 53, 11849–11860, 2014.

[11] K.M. Nicholson and D.S. Sholl, First-principles screening of complex transition metal hydrides for high temperature applications, *Inorg. Chem*, 53, 11833–11848, 2014.

[12] B. Bogdanovic, A. Reiser, K. Schlichte, B. Spliethoff, and B. Tesche, Thermodynamics and dynamics of the Mg–Fe–H system and its potential for thermochemical thermal energy storage, *J. Alloys Compd*, 345, 77–89, 2002.

[13] S.Z. Karazhanov, A.G. Ulyashin, P. Ravindran, and P. Vajeeston, Semiconducting hydrides, 82, *Phys. Lett*, 1–5, 17006, 2008.

[14] S.Z. Karazhanov, P. Ravindran, P. Vajeeston, and A.G. Ulyashin, Hydrides as materials for semiconductor electronics, *Philos. Mag*, 88, 2461–2476, 2008.

[15] S.Z. Karazhanov and A.G. Ulyashin, Similarity of electronic structure and optical properties of Mg_2NiH_4 and Si, *Phys. Lett*, 82, 1–6, 2008.

[16] S.Z. Karazhanov, A.G. Ulyashin, P. Ravindran, and P. Vajeeston, Hydride electronics, *Phys. Status Solidi (a)*, 204, 3538–3544, 2007.

[17] S. Bouras, B. Ghebouli, M. Benkerri, M.A. Ghebouli, H. Choutri, L. Louail, T. Chihi, M. Fatmi, A. Bouhemadou, R. Khenata, and H. Khachai, Theoretical characterization of quaternary iridium based hydrides NaAeIrH6 (Ae = Ca, Ba and Sr), *Mater. Chem, Phys*. 149–150, 87–93, 2015.

[18] M. Kritikos and D. Noreus, Synthesis and characterization of ternary alkaline-earth transition metal hydrides containing octahedral $[Ru(II)H6]^{-4}$ and $[Os(II)H6]^{-4}$ complexes, *J. Solid State Chem*, 93, 256–262, 1991.

[19] K. Kadir, D. Moser, M. Munzel, and D. Noreus, Investigation of Counterion Influence on an octahedral IrH6- complex in the solid state hydrides AAeIrH6 (A = Na, K and Ae = Ca, Sr, Ba, and Eu) with a new structure type, *Inorg. Chem*, 50, 11890–11895, 2011.

[20] S.Z. Karazhanov and A.G. Ulyashin, Similarity of optical properties of hydrides and semiconductors for antireflection coatings, *Philos. Mag*, 90, 2925–2937, 2010.

[21] S.V. Halilov, D.J. Singh, M. Gupta, and R. Gupta, Stability and electronic structure of the complex K2PtCl6-structure hydrides DMH6 (D = Mg, Ca, Sr; M = Fe, Ru, Os), *Phys. Rev*. B, 70, 1–6 2004.

[22] E. Orgaz and A. Aburto, Electronic structure of ternary ruthenium-based hydrides, *J. Phys. Chem*. C 112, 15586–15594, 2008.

[23] E. Orgaz and M. Gupta, The electronic properties of intermetallic hydrides with the K2PtC16 structure, *J. Phys. : Condens. Matter*, 5, 6697-6718, 1993.
[24] R.O. Moyer Jr., C. Stanitski, and J. Tanaka, Ternary hydrides of calcium and strontium with iridium, rhodium and ruthenium, *J. Solid State Chem*, 3, 541–549, 1971.
[25] M. Kritikos, D. Noreus, B. Bogdanović, and U. Wilczok, Mg2OsH6, a new ternary hydride with the K2PtCI6, - Type structure, *J. Less Common Met*, 161, 337–340, 1990.
[26] J. J. Reilly, and R. H. Wiswall, Reaction of hydrogen with alloys of magnesium and nickel and the formation of Mg2NiH4, *Inorg. Chem*, 7, 2254–2256 (1968).
[27] D. Noreus, K. W. Tarnroos, A, Borje, T. Szabo, W. Bronger, H. Spittank, G. Auffermann,and P.Muller, Na_2PdH_2, a hydride with a novel linear $[PdH_2]$ complex, *J. Less-Common Met*, 139, 233-239, 1988.
[28] M. Kritikos and D. Noreus, Synthesis and characterization of ternary alkaline-earth transition metal hydrides containing octahedral [Ru(II)H6]−4 and [Os(II)H6]−4 complexes, *J. Solid State Chem*, 93, 256–262, 1991.
[29] S.V. Halilov, D.J. Singh, M. Gupta, and R. Gupta, Stability and electronic structure of the complex K2PtCl6-structure hydrides DMH6 (D = Mg, Ca, Sr; M = Fe, Ru, Os), *Phys. Rev. B*, 70, 1–6, 2004.
[30] J. haines, J. Leger and G. Bocquillon. Annu, Synthesis and Design of Superhard, *Materials Rev. Mater. Res*. 31, 1-23, 2001.
[31] P. Debye, Zur Theorie der spezifischen Wärmen, *Ann. Phys*, 39,789-839, 1912.
[32] M.A.Blanco, E.Francisco and V.Luaña, GIBBS: isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model, *Comput.Phys.Commu*, 158, 57–72, 2004.