Vibrational and thermodynamic properties of monazite-type $LnPO_4$ (Ln=La, Ce): A first Principles study

L Motsomone*[1], R G Diale[2], P E Ngoepe[1], R Koen[3] and H R Chauke[1]

[1] Materials Modelling Centre, University of Limpopo, Private Bag X 1106, Sovenga, 0727, South Africa

[2] Advanced Materials Division, MINTEK, Private bag X 3015, Randburg, 2125, South Africa

[3] The South African Nuclear Energy Corporation Ltd. (Necsa), P.O. Box 582, Pretoria, 0001, South Africa

E-mail: `lmotsomone@gmail.com*`

Abstract. Monazite is an ore mineral consisting of various rare earth elements (REEs), thorium (Th), and uranium (U). These components are utilized in numerous modern areas of technology, including metallurgy, catalysis, and magnetic fields. This monazite mineral has a notoriously stable structural conformation, making the conventional cracking process extremely inefficient. However, new innovative technologies (e.g. thermal cracking) have been proposed for improving the extraction of REEs (such as La, Ce, Nd), Th and U. In this study, we use the first-principles calculation based on density functional theory to investigate vibrational and thermodynamic properties of monazite systems. It was found that the lattice parameters of $LaPO_4$ and $CePO_4$ monazite correlate well with experimental values to within 5% error. The heats of formation value for $LaPO_4$ (-0.766 eV/atom) is more negative than for $CePO_4$ (-0.729 eV/atom), suggesting the most stable structure. The phonon dispersion curves revealed that $LaPO_4$ and $CePO_4$ systems are vibrationally not stable. Furthermore, monazite systems were found to exhibit structural transitions at 500 K. The findings assisted in understanding the stability and thermodynamic structure of monazite as the temperature increases.

1. Introduction

Monazite is a radioactive phosphate mineral containing the light rare earth metals [Ce, La, Nd, Pr and Y], thorium and uranium [1]. The mineral is mined mainly for its rare elements and thorium content, which are critical to modern technology (such as the screen of a smartphone or computer) and nuclear power production [2]. Monazite is a mineral formed by a variety of rock types and conditions. The formation of these conformations occurs under a variety of pressure and temperature conditions in sedimentary, metamorphic, and igneous rocks [3]. Previously, monazite was reported to contain about 60 percent of rare-earth elements with cerium oxide (up to 32 %), thorium as ThO_2 (up to 10 %) and uranium as (U_3O_8) (up to 0.4 %) being the most industrially relevant constituents [4].

In contrast, conventional chemical processes have become highly complicated and costly to use for extracting REE, thorium, and uranium from monazite [5]. Hence, a new process (thermal plasma) is being developed to improve the extraction efficiency of monazite [1]. In that regard, a theoretical study of monazite's structural and mechanical properties could assist in reinforcing experimental screening parameters and optimizing this specialized extraction process. We investigated the vibrational properties of $LaPO_4$ and $CePO_4$ using first-principle calculations based on density functional theory (DFT) to explore how the monazite molecules move when thermally cracked to gain insight into the best way to extract these REEs.

2. Methodology

All calculations were carried out using the first-principles method within the framework of density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP) code [6]. The influence of the different k-point samplings and plane-wave cut-off energy was explored in a series of test calculations, leading to the calculations for the electronic properties being performed with 12x11x13 k-point sampling and a cut-off energy of 600 eV containing 24 atoms. The geometry optimization is accomplished by employing the generalized gradient approximation (GGA) [7] of the Perdew-Burke-Ernzerhof (PBE) [8]. The positions of atoms in the simulation cell, the lattice parameters, and the corresponding angles are fully optimized using the conjugate gradient method until the atomic force is smaller than 0.01 eV/Å. A precision was set at ″accurate″ to make errors of the calculation into a reasonable scale. A strain value of 0.006 was chosen for the deformation of the lattice when calculating elastic properties. A PHONON code [9] was used to evaluate the vibrational stability from phonon dispersion curves.

3. Results and Discussion

3.1. *Structural and thermodynamic Properties*

The experimental unit cell parameters for $LaPO_4$ structure were found to be a=6.841 Å, b=7.078 Å and c= 6.515 Å [10], also for $CePO_4$ experimental observed unit cell parameters are a=6.777 Å, b=7.993 Å, c=6.445 Å [11]. In addition, Table 1 lists the calculated and experimental lattice parameters, as well as the heats of formation for the optimised structures of various monazite systems. The thermodynamic stability of these systems can be deduced from the heats of formation (ΔH_f). For a structure to be confirmed as the most stable structure, the ΔH_f must have the lowest possible value (generally ΔH_f <0), whereas for ΔH_f >0 implies thermodynamic instability of a structure.

The following expression is used to estimate the heats of formation (ΔH_f):

$$\Delta H_f = E_c - \sum_i x_i E_i \tag{1}$$

where E_c is the calculated total energy of the compound and E_i is the calculated total energy of each element in the compound. The predicted ΔH_f values of $LnPO_4$ shows that the $LaPO_4$ has the lowest heat of formation (-0.766 eV/atom), while $CePO_4$ has the highest heat of formation (-0.729 eV/atom). These values suggest that $LaPO_4$ is the most stable structure compared to $CePO_4$ structure.

Table 1. The lattice parameters and the heats of formation (ΔH_f) for monazite type $LnPO_4$ (Ln = La, Ce).

Structure (P21/n)		Lattice parameters			ΔH_f (eV/atom)
		a	b	c	
$LaPO_4$	Cal.	6.841	7.078	6.515	-0.766
	Exp. [10]	6.841	7.078	6.513	
$CePO_4$	Cal.	6.770	6.990	6.450	-0.729
	Exp. [11]	6.777	7.993	6.445	

3.2. *Elastic moduli*

Elastic moduli are determined using the following expressions: the Bulk Modulus (B), Shear modulus (G), Young‘s modulus (E), Poisson ratio (σ) and the Pugh ratio (B/G). The bulk modulus is a measure of resistance to volume change under pressure, it is used to measure the hardness/strength of the material. Shear modulus describes the resistance to shape change caused by shearing force, in this case it is used to check the material rigidity where the high value indicates that the material is highly rigid otherwise flexible. Young's modulus describes the relative stiffness of a material. Furthermore, we determined the ratio of bulk modulus to shear modulus (B/G) to investigate the extent of fracture range in these structures. Pugh proposed that materials are considered ductile if the value of Pugh's criterion (B/G) > 1.75 [12]. In addition to substantiate this even further, the Poisson ratio (σ) was determined and considered as ductile if (σ) > 0.26 [13].

The calculated Bulk, Shear and Young modulus, as well as Pugh and Poisson ratio, are shown in figure 2 and 3, respectively. From the calculated results, it is indicated that $LaPO_4$ structure has high value of Bulk, Shear and Young 's modulus suggesting that it is hard and has a high degree of free stiffness also not easily compressed than $CePO_4$. The Pugh and Poisson 's ratio is greater than 1.75 and 0.26, respectively for $LaPO_4$ and $CePO_4$ structures. The results suggest ductility behaviour in these systems at 0 K

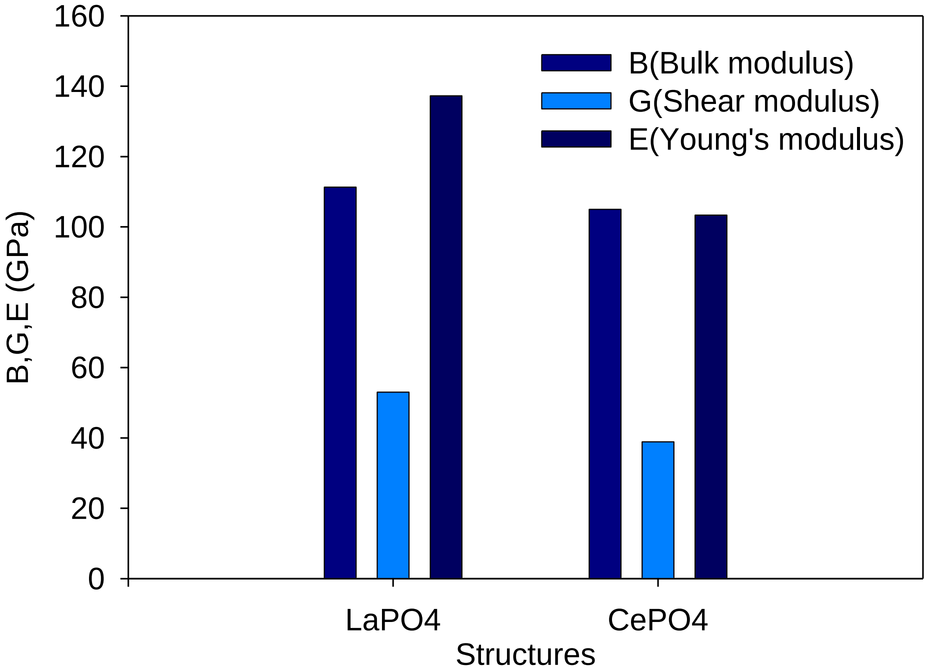

Figure 2. Calculated Bulk (B), Shear (G) and Young's (E) modulus of monazite systems $LnPO_4$ (Ln = La, Ce)

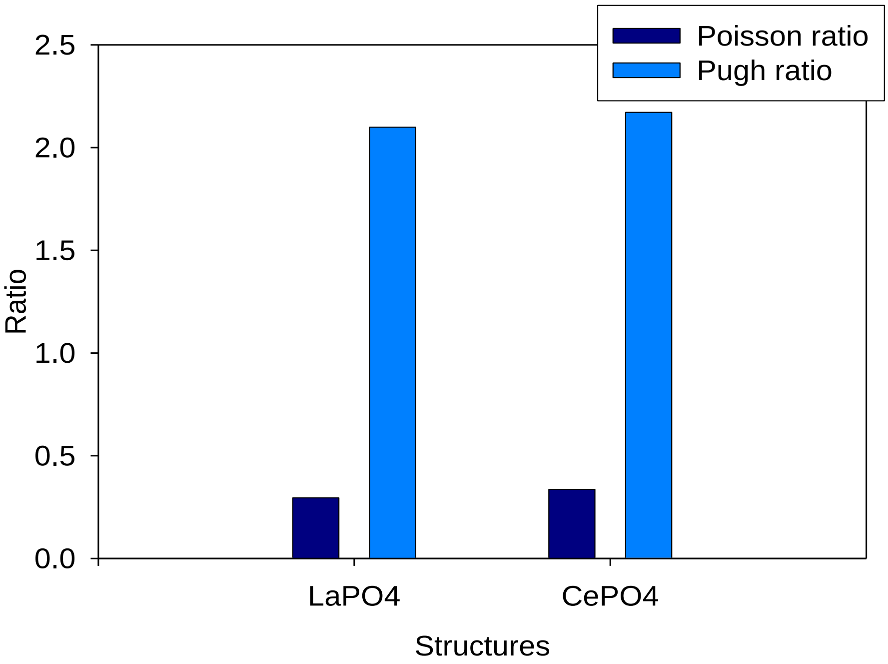

Figure 3 Calculated Poisson (σ) and Pugh (B/G) ratio of monazite systems $LnPO_4$ (Ln = La, Ce)

3.3. Phonon dispersion curves

Phonon dispersion curves are used to investigate the vibrational stability of the structures. The structure is considered stable if all the phonon frequencies are positive, however if some of the phonon frequencies are negative the system is considered unstable. Figure 4 shows the calculated phonon dispersion curves of monazite type $LnPO_4$ at 0 GPa pressure along different symmetry directions. The dispersion curves show the presence of negative phonon frequencies on both structures that suggests that they are vibrationally unstable.

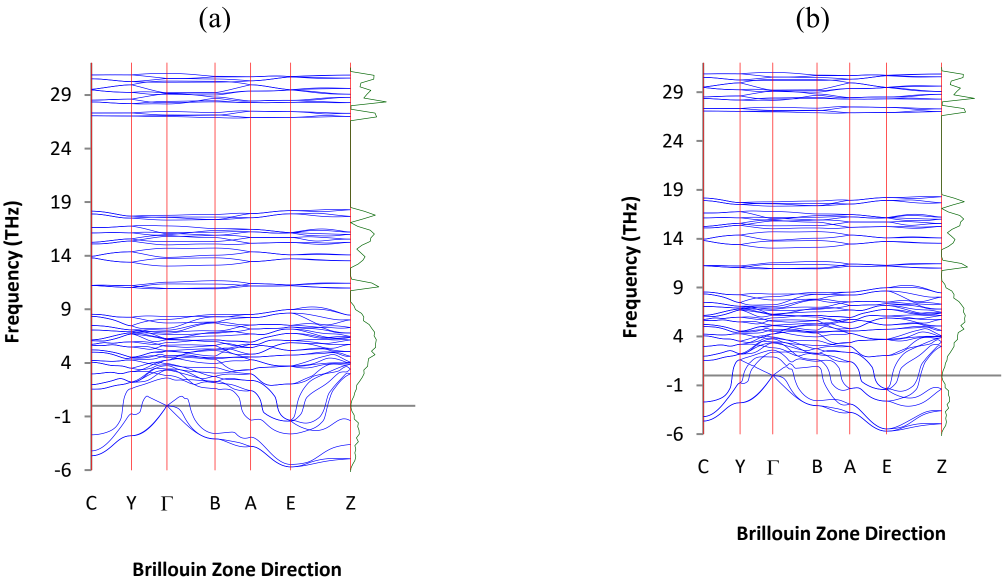

Figure 4. Phonon dispersion curves of (a) $LaPO_4$ and (b) $CePO_4$ monazite structures.

3.4. Thermal Properties

An understanding of thermodynamic properties of materials is of great importance in order to extend our knowledge about their specific behaviours when exposed to severe constraints such as high pressure and high temperature environments. Heat capacity (Cv) gives information about lattice vibration, phase transition and motion of molecules. In figure 5, the specific heat capacity increases in the temperature range from 0 K to 500 K before it starts to be constant.

Our computed results of the specific heat capacity of the monazite systems indicate that Cv has obeyed the Dulong-Petit law at the high-temperature limit [14] which is reasonable to all solids at high temperatures. For all the studied materials, the Cv functions flatten out as the temperature increases above 500 K, thus suggesting that structural transition occurs at a very low temperature below 500 K for all monazite systems. Furthermore, the results suggest that weaker bond state is reached due to bigger thermal vibrations above 500 K.

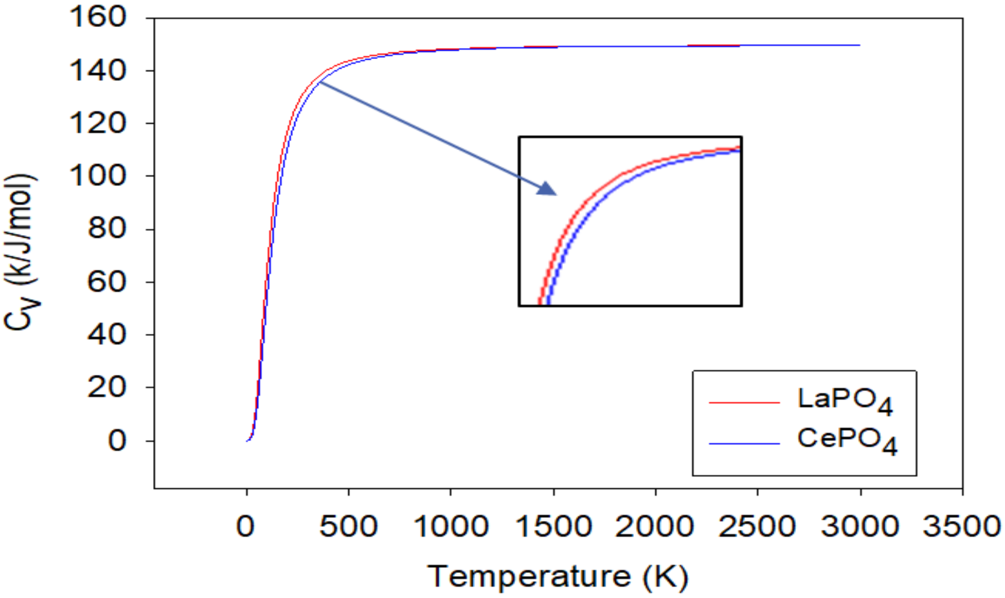

Figure 5. The heat capacity at the constant volume (Cv) as a function of temperature for the monazite systems.

4. Conclusion

The first-principle calculations were used to study the equilibrium lattice parameters, heats of formation, elastic properties and phonons of monazite systems. The results of lattice parameters were found to be in good agreement with the experimental values for both monazite-type structures (within 5%). From calculated heats of formation, it was found that $LaPO_4$ is the most stable structure. Furthermore, monazite structures indicated ductility behaviour at 0 K. The results also revealed that the monazite systems are vibrationally unstable, also that there is no phase transition above 500 K.

Acknowledgement

The work was carried at the Materials Modelling Centre, University of Limpopo. The authors would like to acknowledge the financial support of the Department of Science and Innovation (DSI), through the Nuclear Materials Development Network (at Necsa) of the Advanced Materials Initiative (AMI). The support of South African Research Chair initiative of Department of Science and Innovations is highly appreciated.

References

[1] Kemp , D; Cilliers, A C;, "High-temperature thermal plasma treatment of monazite followed by aqueous digestion," *Journal of the Southern African Institute of Mining and Metallurgy,,* vol. 10, pp. 901-906, 2016.

[2] Catlos, E J; Baker, C B; Çemen, I; Ozerdem, C;, "Whole rock major element influences on monazite growth: examples from igneous and metamorphic rocks in the Menderes Massif, western Turkey," *Mineralogia,* vol. 39, pp. 7-30, 2008.

[3] Hoshino, M; Sanematsu , K; Watanabe, Y;, "Chapter 279-REE mineralogy and resources," *in Handbook on the physics and chemistry of rare earth,* vol. 49, pp. 129-291, 2016.

[4] Udayakumar, S; Mohd-Noor, A; Sheik, A;, "Teuku , A; Anderson, G; Rama, P;, "Chemical and Mineralogical Characterization of Malaysian Monazite Concentrate," *Mining,Metallurgy and Exploration,* vol. 37, pp. 415-431, 2020.

[5] Hurst, C;, "China's Rare Earth Elements Industry: What Can the West Learn?," Institute for the Analysis of Global Security (IAGS), Potomac, MD, 2010.

[6] Kresse, G; Hafner, J;, "Ab initio molecular dynamics for liquid metals," *Physical Review B,* vol. 47, p. 558, 1993.

[7] Perdew, J P; Yue, W;, "Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling," *Physical Review B,* vol. 24, p. 13298., 1991.

[8] Perdew, J P; Burke K, K; Ernzerhof , M;, "Generalized Gradient Approximation Made Simple," *Physical Review Letters,* vol. 77, p. 3865, 1996.

[9] Parlinski, K; Li, Z Q; Kawazoe, Y;, "First-Principles Determination of the Soft Mode in Cubic ZrO2," *Physical Review. Letter,* vol. 78, p. 4063 , 1997.

[10] Callejas, G; Blanco, M; Cabrera, S; Prieto, O; Luna, I; Choque, V; Crespo , P;, "Simulation of the crystal structure of low temperature monazite LaPO4 phase from x-ray diffraction diffusion pattern," *Bolivian scientific journal in chemistry,* vol. 17, p. 22–7, 2000.

[11] Keller, G; Walter, K;, "Representation, lattice constants and chemical properties of some ternary oxides of plutonium, americium and curium of type MeIIIXVO4," *journal inorganic nuclear chemistry ,,* vol. 27, p. 1253–1260, 1965.

[12] Pugh, S F;, "XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals," *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science,* vol. 367, pp. 823-843, 1954.

[13] Greaves, G N; Greer, A L; Lakes, R S; Rouxel, T;, "Poissons Ratio and Modern Material," *Nature Materials,* vol. 10, pp. 823-837, 2011.

[14] Hofmeister, A M;, "Thermal diffusivity of garnets at high temperature," *Physics and Chemistry of Minerals,* vol. 1, pp. 45-62, 2006.

[15] Du, A; Wan, C; Qu, Z; Pan, W;, "Thermal Conductivity of Monazite-Type REPO4 (RE= La, Ce, Nd, Sm, Eu, Gd)," *Journal of the American Ceramic Society,* vol. 11, pp. 2687-2692., 2009.