Mechanical and thermal properties of monazite $LaPO_4$ under pressure

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Abstract. Monazite-La (LaPO4) is considered the first constituent of the rare-earth orthophosphate group and has received a considerable scientific interest owing to its notable physical characteristics, such as its optical emissivity and its ability to withstand radiation damage and corrosion when exposed to molten glass. This material is deemed suitable for the extended-term containment of radioactive nuclear waste. This study investigates the influence of pressure on the mechanical and thermal properties of Monazite-La within the pressure range of 0 to 100 gigapascals (GPa) through the utilization of the density functional theory (DFT) approach. At 0 GPa, it was shown that the lattice parameters exhibited a significant level of concurrence with experimental findings to within 3%. Furthermore, it has been observed that the structure exhibits mechanical stability up to a pressure of 100 GPa. Additionally, this paper will also address the concepts of heat capacity, and thermal expansion. The findings provide enhanced insights into the mechanical and thermal properties of Monazite-La when subjected to pressure.

1 Introduction

The prevalence of natural lanthanide orthophosphates on earth is well studied, making them the most often found minerals containing rare earth elements [1]. The compounds exhibit structural similarities to orthosilicates, orthovanadates, and orthoarsenates, as indicated by reference [2]. The $LnPO_4$ compounds show two distinct crystal structures: a monazite-type monoclinic structure and tetragonal xenotime-type structure associated with rare earth elements (REEs) [3]. Monazite mineral exhibits monoclinic symmetry when it crystallizes, as determined by its space group $P2_1/n$ [1]. In this particular structure, the lanthanide element is coordinated by a total of nine oxygen atoms. It should be noted that the Ln-O bond lengths are not exactly comparable.

Over the last few decades, rare-earth orthophosphates, such as $LaPO_4$, have received large attention as a result of its intriguing physical and chemical properties. Some

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of these properties are a high fusion temperature, a high optical emissivity, and resistance to damage from radiation or molten glass corrosion [4, 5, 6]. Furthermore, it is important to highlight that the aforementioned materials exhibit noteworthy attributes, such as strong chemical resistance, the capacity to absorb significant quantities of uranium and thorium, and resilience against geological events [6]. These characteristics make them well-suited for the long-term storage of radioactive nuclear waste. As a result, it is imperative to comprehend the high-pressure (HP) characteristics of monazite, as they hold great significance in the areas of mineral physics, chemistry, and petrological investigation. The acquired knowledge derived from research conducted under high pressure conditions holds significant relevance in the context of the practical application of $LaPO_4$, which is an extremely promising host material for the purpose of effectively immobilizing high-level nuclear waste [7].

Investigation of monazite-type phosphate ($LaPO_4$) under high pressure conditions has been the focus of numerous experimental and theoretical studies. Notably, Ghosh et al. (2018) [6] conducted one of such study. The investigation involved the examination of phase-transformation utilizing Density functional theory (DFT). Their study revealed the transition pressure between the monazite-type crystal structure ($P2_1/n$) and the post barite-type crystal structure ($P2_12_12_1$) could take place at approximately 28 GPa. In addition, Ruiz-Fuertes et al. (2016) [8] have demonstrated that phase induced by pressure transitions are possible in monazite-type $LaPO_4$ at pressures exceeding 26 GPa. Furthermore, the study suggested that as the size of the trivalent cation decreases, the maximum pressure required to stabilize the monazite phase shifts towards higher pressures. It is important to acknowledge that research on monazites previously, under high pressure have not just concentrated on the observation of pressure-induced phase changes but have also examined their structural and vibrational characteristics [9], elastic properties [7], mechanical behaviour [10], and other related aspects. Despite the previously mentioned attempts, a complete understanding of monazite characteristics under varying pressure conditions has yet to be attained. Therefore, the present work utilizes DFT based on ab initio simulations to examine how pressure affects the mechanical and thermal properties of monazite $LaPO_4$.

2 Methodology

An ab initio method was employed to investigate the pressure-dependent behaviour of the $LaPO_4$ system. The calculations were conducted utilizing the DFT, a highly effective methodology for exploring the characteristics of materials at the electronic level. The Vienna Ab initio Simulation Package (VASP) code [11] was employed to execute these calculations. The convergence of 1 meV per formula unit in the total energy is sufficient. For the purpose of integrating within the Brillouin zone, we used a Monkhorst-Pack grid with 12x13x11 k-points to make sure the calculations were accurate. The employed grid facilitated a comprehensive exploration of the reciprocal space, effectively capturing the fundamental characteristics of the system being examined. Furthermore, a cutoff energy of 700 electron volts (eV) was selected to guarantee the utilization of a large basis set in the calculations. The exchange correlation interaction was evaluated with functional Generalized Gradient Approximation (GGA) [12] of the Perdew, Burke, and Ernzerhof (PBE) [13]. The elastic properties were computed using 0.006 strain as the strain value for lattice deformation.

3 Results and discussion

3.1 Structural properties

The table (Table 1) below presents a comparison between equilibrium lattice constant obtained in this study and previous experimental findings for the $LaPO_4$ monazite system at 0 GPa. In order to determine equilibrium lattice parameters, relaxed structures were optimized for their equilibrium characteristics. The $LaPO_4$ monazite structure exhibited lattice parameters that closely matched the experimental values [14] within a 5% margin of error. This discovery suggests that the use of DFT calculation methodologies yields precise predictions of lattice parameters in comparison to experimental data.

Table 1. Comparisons of the equilibrium lattice constant of this work to other theoretical and experimental results for the $LaPO_4$ monazite system.

Lattice parameters	This work (Å)	Experimental (Å)	Theoretical (Å)
		[9]	[14]
a	6.841	6.829	6.841
b	7.078	7.058	7.078
c	6.515	6.469	6.513

The investigation also involved determining the changes in the structural parameters as a function of pressure, as depicted in Figure 1. It is observed that there is a decrease in the lattice parameters as the pressure is increased. Furthermore, it should be noted that the a-axis exhibits a higher degree of compressibility compared to the b and c-axis. This suggests that the specific arrangement of atoms along the a-axis allows easier compression or expansion in response to changes in pressure. Moreover, it is also observed that the unit-cell parameter "*a*" tends to converge towards the value of "*c*". This might indicate a tendency towards a more symmetrical crystal structure, possibly suggesting a shift towards a higher symmetry space group.

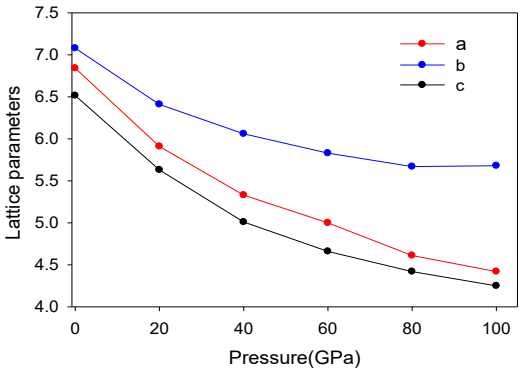

Fig. 1. Lattice parameters against pressure for the $LaPO_4$ structure.

The calculations of lattice parameters have been previously compared with experimental data from sources [2, 8], revealing a remarkable level of agreement up to a pressure of 27 GPa. According to the findings of the current study, it is important to note that beyond 100 GPa, the lattice parameter may undergo a phase change due to the contraction of a and c. However, the experimental results do indicate the occurrence of a notable phase change at approximately 27 GPa (from monazite to postmonazite structure) by an abrupt collapse of a lattice parameter while *b* and *c* parameters slightly expand [2, 8].

3.2 Pressure dependence on elastic properties

The calculation of elastic characteristics was conducted to evaluate the mechanical stability of monazite systems under high pressure conditions. The values of parameters such as elastic constants and moduli were determined.

3.2.1 Elastic constants

The determination of the elastic constant serves as a crucial factor in the prediction of the elastic strength exhibited by Monazite-La when subjected to varying levels of pressure. The data presented in Figure 2 depicts the computed elastic constant against pressure for the $LaPO_4$ structure. In order to determine the stability of a structure, it is imperative that the stability criterion for the elastic constants be met.

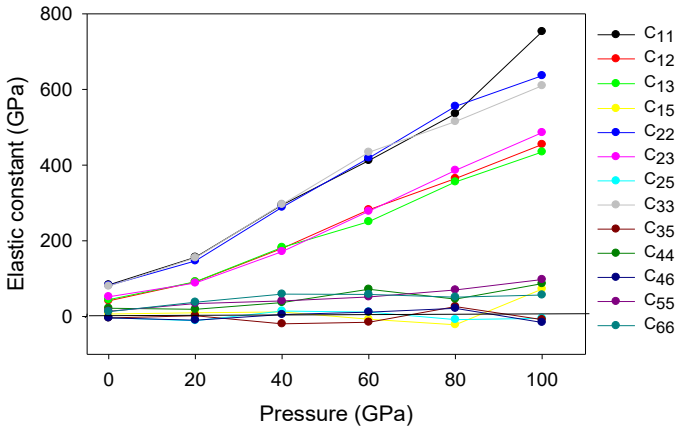

Fig. 2. Elastic constant against pressure for the $LaPO_4$ structure.

For a monoclinic system, the mechanical stability criterion is defined as [15]:

$$c_{ij} > 0\ (i = 1,2,3,4,5,6),\ \ (c_{44}c_{66} - c_{46}^2) > 0\ ,(c_{33}c_{55} - c_{35}^2) > 0\ ,\ (c_{22} + c_{33} - 2c_{23}) > 0\ ,\ [c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{13} + c_{23})] > 0\ ,[c_{22}\ (c_{33}c_{55} - c_{35}^2) + 2c_{23}c_{25}c_{35} - c_{23}^2c_{55} - c_{25}^2c_{33}\ ] > 0\ ,\{\ 2[c_{15}c_{25}(c_{33}c_{12} - c_{13}c_{23}) + c_{15}c_{35}\ (c_{22}c_{13} - c_{12}c_{23}) + c_{25}c_{35}\ (c_{11}c_{23} - c_{12}c_{13})]\ [\ c_{15}^2(c_{22}c_{33} - c_{23}^2c_{11}\ ) + c_{25}^2\ (c_{11}c_{22} - c_{12}^2\ ) + c_{55}\ g\} > 0 \quad (1)$$

but $(g = c_{11}c_{22}c_{33} - c_{11}c_{23}^2 - c_{22}c_{13}^2 - c_{33}c_{12}^2 + 2c_{12}c_{13}c_{23})$.

It is observed that the elastic constants exhibit a positive correlation with the applied pressure, resulting in an increase in their values. Moreover, it is evident that the mechanical stability criteria are met up to 100 GPa, indicating that the structure exhibits mechanical stability within the investigated pressure range. The observed behaviour of c_{15}, c_{35}, and c_{46} reveals a transition to negative values upon surpassing a pressure threshold of 20 GPa. Nevertheless, it is crucial to acknowledge that these negative magnitudes are sufficiently small so as to not significantly impact the monoclinic criteria. Consequently, the structural integrity of the system remains intact even beyond the 20 GPa mark, thereby affirming its stability. The high values of c_{11} reaching beyond 700 GPa indicate a strong resistance to compression in the system. It is also noted that when the pressure increases, it causes the atoms in the material to rearrange into a more tightly packed crystal structure. This

rearrangement leads to stronger interatomic bonds and increased stiffness, resulting in the observed rise in c_{15} beyond 80 GPa.

3.2.2 Elastic modulus

One crucial aspect of investigating mechanical properties relates to the modulus of the material. A higher modulus signifies a higher capacity of the material to withstand deformations, such as Bulk (B), elastic, and Shear (G) deformation. Figure 3 illustrates graphically the relationship between the Bulk modulus, Young's modulus (E), and Shear modulus (G) and the applied pressure. It is noteworthy that with an increase in applied pressure, there is a corresponding rise in the value of bulk modulus.

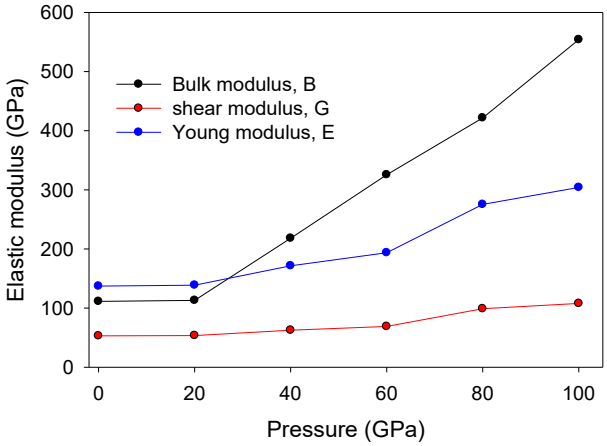

Fig. 3. The bulk (B), shear (G), and Young's (E) modulus against pressure for the LaPO4 structure.

This observation implies that the material's capacity to withstand uniform compression also increases with an increase in pressure. Furthermore, it is observed noting that the highest value attained is 553.9 GPa when the pressure (P) is set at 100 GPa. B can also reveal the average value of the atomic bond strength. Henceforth, it is evident that the atomic bond strength of the $LaPO_4$ structure demonstrates an increase in accordance with an increase in pressure. In addition, the values of G for $LaPO_4$ exhibit an increasing pattern as pressure increases which suggests that the material's resistance to shear deformation becomes stronger at higher pressure conditions. A higher shear modulus clearly indicates significantly more pronounced directional interatomic bonding [16]. Hence, the bonding behaviours of $LaPO_4$ exhibit improved directionality as pressure is increased. Furthermore, E exhibits a monotonically increasing trend in response to changes in pressure. This implies that the material's resistance to uniform stretching becomes stronger as the pressure is elevated.

Figure 4 illustrates the fluctuation pattern of the Poisson ratio (σ) and the modulus ratio (B/G) in relation to the applied pressure. It is noted that when the σ value decreases, the magnitude of the volume change increases. The values of σ exhibit a positive correlation with pressure, suggesting a reduced magnitude of volume change during uniaxial deformation. In order to evaluate the ductile or brittle characteristics of materials, Pugh has presented a straightforward correlation, where a higher B/G number indicates malleability, while a lower value indicates brittleness [17]. In the case where the ratio of B/G exceeds 1.75, the material exhibits ductile behaviour. At 0 GPa, the research findings indicate that the B/G ratio has a value of 2.098, which, illustrates that the system is ductile. Furthermore, when the pressure

is increased, the values of B/G increases. Thus, the $LaPO_4$ structure maintains its ductility properties as the pressure is increased.

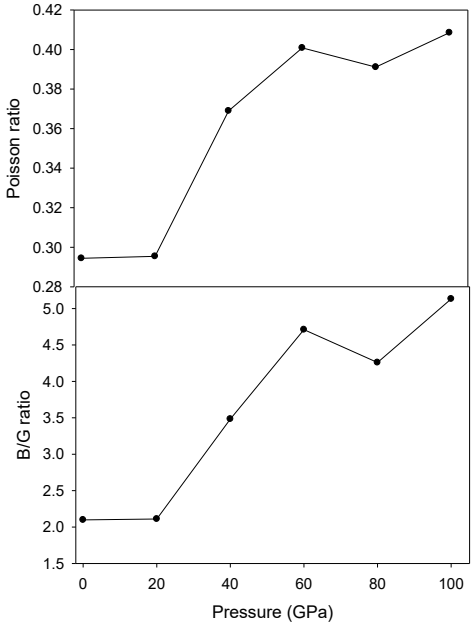

Fig. 4. Poisson and Pugh ratio against pressure for the LaPO4 structure.

3.3 Pressure dependence on thermal properties

The investigation of thermodynamics yields detailed insights into how a material responds to changes in temperature and pressure. This is crucial for understanding the material's performance under specific conditions. Parameters such as heat capacity and thermal expansion offer valuable evidence regarding important material characteristics such as inter-atomic interaction and thermodynamic stability. For this study, we will be varying the temperature from 0 to 3000 K and the pressure from 0 to 100 GPa to examine the heat capacity and thermal expansion of $LaPO_4$.

3.3.1 Heat capacity

The heat capacity (C_v) is a fundamental thermodynamic quantity that provides insights into the nature of lattice vibrations and phase transitions within a given structure. However, due to the absence of f electrons in La, the heat capacity of $LaPO_4$ is merely attributed to lattice vibrations. The impact on the (C_v) under varying temperature and pressure conditions is illustrated in Figure 5. At a temperature of 290 K and absolute zero pressure, Monazite-La exhibited a molar heat capacity of 130.512 J/mol/K. The (C_v) exhibits a positive correlation with temperature, while it demonstrates an inverse relationship with pressure. Nevertheless, when exposed to high temperatures, the (C_v) tends to converge towards constant values and exhibits a monotonous decrease as the pressure is increased. This finding is in accordance with the well-known Dulong-Petit law [18], which is applicable to all solid materials. According to the law, the constant value of an element's product of specific heat and atomic mass, also known as gram atomic capacity, remains unchanged. The $LaPO_4$ lattice heat capacity at constant volume, as described by the Dulong-Petit high temperature limit, may

be expressed as cv = 3nR = 18R = 149.661 J/mol/K. In this equation, n represents the number of atoms per unit cell, which in this case is n = 6, and R is the gas constant. This number is also in proximity to the measurement obtained at a temperature below ambient conditions. The obtained findings exhibit a strong correlation with the Debye model, demonstrating its efficacy throughout a wide range of temperatures, including both low and high temperatures. At low temperatures ($T << \theta_D$), the theory posits a T^3 dependence for the cv. Conversely, at temperatures considerably higher than the Debye temperature ($T >> \theta_D$), the theory yields the Dulong-Petit limit.

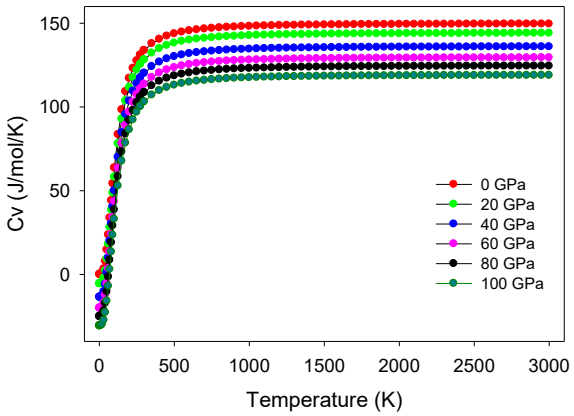

Fig. 5. Heat capacity (C_v) against pressure for the $LaPO_4$ structure.

3.3.2 Thermal coefficient expansion

Thermal expansion is a notable characteristic exhibited by materials, which explains their response to changes in temperature and pressure.

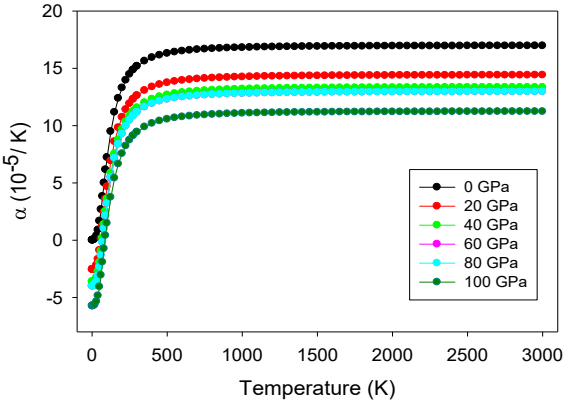

Fig. 6. Thermal coefficient expansion (α) against pressure for the $LaPO_4$ structure.

Figure 6 illustrates the relationship between the thermal expansion coefficient (α) and temperature and pressure for the $LaPO_4$ structure. The findings indicate a notable augmentation in thermal expansion as temperatures decrease, particularly up to 500 K. This suggest that as pressure increases from 0 to 20 GPa, the structure is able to expand in response to temperature also increases proportionally. Subsequently, a state of near-constant behaviour is observed as temperatures rise to higher levels (> 500 K). Conversely, it is noteworthy that pressure induces an inverse impact, wherein a rise in pressure yields a reduction in the

thermal expansion coefficient. This observation implies that the expansion of the $LaPO_4$ structure is noticeable or significant at lower pressure conditions compared to higher pressure conditions. The result also shows that the system have clustered around 40, 60, and 80 GPa, indicating that it may have reaching critical points, where significant changes in its physical properties occur. Furthermore, the drop in thermal coefficient expansion at 100 GPa could be attributed to a change in the material's behaviour under extremely high pressure. Further research would be needed to fully understand the reasons behind this sudden decrease.

4 Conclusion

The present investigation used a first-principles approach to examine the mechanical and thermal properties of $LaPO_4$ under conditions of elevated pressure. The lattice parameters were seen to exhibit a close correspondence with the experimental findings, with a deviation of no more than 5% at a pressure of 0 GPa. Following the discovery of elastic constant, it was confirmed that the $LaPO_4$ structure is mechanically stable across the entire pressure range, from 0 to 100 GPa. The analysis of the elastic shear moduli further supports this finding. Monazite-La exhibits a greater capacity to withstand various types of deformations, due to the higher value of B, G, and E as pressure increases. Additionally, it has been shown that the material exhibits ductile behaviour. It has been shown that the structural expansion is more pronounced at lower pressure conditions. In conclusion, these findings hold great significance for the development of new materials that possess enhanced properties.

This research was carried out at the Materials Modelling Centre, University of Limpopo. The authors would like to express their gratitude to the Department of Science and Innovation (DSI) for their financial support through the Nuclear Materials Development Network (at Necsa) of the Advanced Materials Initiative (AMI). They also extend their appreciation to the Centre for High Performance Computing (CHPC) for providing computational resources, and to the South African Research Chair Initiative of the Department of Science and Innovation for their support.

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