Structural and mechanical properties of monazite type LnPO$_4$ (Ln = La, Ce, Pr and Nd)

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Abstract. Monazite, as a source of raw materials, plays a significant role in the development and applications of green technologies, including medicine and energy production. It contains nuclear materials, which are challenging to extract by convectional cracking processes. However, a new method (thermal plasma cracking) has been proposed for processing monazite. The first principles calculation approach was used to investigate the theoretical structure and mechanical properties of monazite-systems to gain deeper understanding of monazite's thermodynamics and mechanical structure. The calculated lattice parameters were found to correlate well with obtained experimental values and that these monazite type systems are exceptionally mechanically stable. The results also show that there are imaginary soft modes in dispersion curves which may correspond to negative elastic constant $C_{35}$ indicating vibrational instability.

1 Introduction

Monazite is widely considered a potential source of fissile feedstock for nuclear power generation, as it generally contains significant quantities of thorium (Th), uranium (U) and rare earth elements (REEs) within the mineral ore structure. The mineral exists in three common forms; Monazite-Ce, Monazite-La and Monazite-Nd and also it is chemically very stable and highly inert [1]. Monazite is a useful geochrometer due to its crystal structure being able to withstand high α dosage and recoil damage because of the presence of thorium and uranium [2]. The basic constituent elements (REEs, Th and U) are used in a wide variety of niche applications, for example, Nd being an essential component in permanent magnets which are used in wind turbines to produce electricity, while other REEs play a crucial role in smartphones, computer hard disk and other high end electronic components efficacy [3].

However, the main interest in monazite lies in the possibility of extracting a large amount of REEs (thorium and uranium) because these elements are also significant for various nuclear application. Currently, it is very difficult to extract these fissile materials from the monazite in its natural state [4]. Furthermore, a fundamental understanding of the structural,
thermodynamic, and mechanical properties of monazite have not been robustly contextualized. Hence, this study aims to explore the quantum behaviour of the monazite molecules movement induced by thermal cracking to gain insight into how these REEs could be best extracted. This study employs density functional theory (DFT) were used to investigate the mechanical stability of monazite systems, LnPO$_4$ (Ln = La, Ce, Pr and Nd).

2 Methodology

The simulation in this study was performed using the Vienna ab initio simulation package (VASP) code [5] based on the density functional theory (DFT). The exchange correlation functional was treated with the generalized gradient approximation (GGA) [6] of Perdew-Burke-Ernzerhof (PBE) [7]. A plane wave cutoff energy of 600 eV and k-point mesh of 12x11x13 for the monazite systems were used to converge the total energy of the structures. Optimization of structural parameters was obtained by minimization of forces and stress tensors. Before the determination of heats of formation, elastic constants and phonon dispersion curves, the structure was fully relaxed with respect to the volume, shape, and internal atomic positions until the atomic forces were less than 0.01 eV/Å for the unit cell. 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 [8] as implemented in Materials Design within the MedeA software platform was used to evaluate the phonon dispersion curves, with the interaction range of 7 Å.

3 Results and Discussion

3.1 Structural and thermodynamic Properties

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 calculated equilibrium lattice parameters were in good agreement with available experimental values (to within 5%). The thermodynamic stability of these systems can be deduced from the heats of formation ($\Delta H_f$) calculations. For a structure to be confirmed as the most stable structure, the $\Delta H_f$ must have the lowest possible value (generally $\Delta H_f$ <0), whereas for $\Delta H_f$ >0 implies thermodynamic instability of a structure. The following expression is used to estimate the heats of formation ($\Delta H_f$):

$$\Delta H_f = E_c - \sum_i x_i E_i$$  \hspace{1cm} (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 $\Delta H_f$ values of LnPO$_4$ shows that the PrPO$_4$ has the lowest heat of formation (-1.024 eV/atom), while CePO$_4$ has the highest heat of formation (-0.729 eV/atom). These values suggest that PrPO$_4$ is the most stable structure followed by CePO$_4$, configuration in comparison with LaPO$_4$ and NdPO$_4$ structures.
3.2 Elastic Properties

The elastic constants can be used to deduce the mechanical stability of the material with each structural orientation having its specific criteria. The stability criterion for the elastic constants must be satisfied for the structure to be defined as stable.

The mechanical stability condition for a monoclinic system can be defined by [12]:

$$[c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{13} + c_{23})] > 0; \quad (c_{33}c_{55} - c_{35}^2) > 0; \quad (c_{44}c_{66} - c_{46}^2) > 0; \quad (c_{22} + c_{33} - 2c_{23}) > 0; \quad [c_{22} (c_{33}c_{55} - c_{35}^2) + 2c_{23}c_{25}c_{35} - c_{23}^2c_{55} - c_{25}^2c_{33}] > 0;$$

$$\{ 2[c_{15}c_{25}(c_{33}c_{12} - c_{13}c_{23}) + c_{15}c_{35} (c_{22}c_{13} - c_{12}c_{23}) + c_{25}c_{35} (c_{11}c_{23} - c_{12}c_{13})] - [c_{15}^2(c_{22}c_{33} - c_{23}^2c_{11}) + c_{25}^2 (c_{11}c_{22} - c_{12}^2) + c_{55}g] > 0 \text{ but } \quad (g = c_{11}c_{22}c_{33} - c_{11}c_{23}^2 - c_{22}c_{23}^2 - c_{33}c_{12}^2 + 2c_{12}c_{13}c_{23})$$

The stability criterion for the elastic constant must be satisfied for the structure to be stable. Table 2 shows the elastic constants ($C_{ij}$), elastic shear moduli ($C'$) and anisotropy of monazite type LnPO$_4$ (Ln=La, Ce, Pr and Nd) structures. It is noted that elastic constants of monazite type structures display negative $c_{35}$ as defined in equation 2. More importantly, the LaPO$_4$, PrPO$_4$ and NdPO$_4$ monazite structures are mechanically stable as the monoclinic stability conditions are satisfied. However, the CePO$_4$ structure appears to have negative elastic constant $C_{46}$ and $C_{66}$ which indicates mechanical instability.

The elastic anisotropic factors of Monazite systems were calculated; this is due to the potential anisotropic nature of these crystals, which is correlated with the high possibility to induce microcracks in the materials. For a monoclinic structure the elastic anisotropy is indicated by A1, A2 and A3 values in Table 2. For an isotropic crystal, the anisotropy factors A1, A2, and A3 must be 1, while any value smaller or larger than unity is a measure of the degree of elastic anisotropy. Therefore, the results indicate that LaPO$_4$, PrPO$_4$ and NdPO$_4$ show an isotropic behaviour while CePO$_4$ was noted to be anisotropic. This may suggest that there is a low possibility of microcrack formation in LaPO$_4$, PrPO$_4$ and NdPO$_4$ systems. However, in the case of CePO$_4$, microcracks might be visible during heating.
Table 2. Calculated elastic constants ($C_{ij}$), elastic shear modulus ($C'$) and anisotropy of monazite-type structures LnPO$_4$ (Ln = La, Ce, Pr and Nd).

<table>
<thead>
<tr>
<th>Elastic constants (GPa)</th>
<th>LaPO$_4$</th>
<th>CePO$_4$</th>
<th>PrPO$_4$</th>
<th>NdPO$_4$</th>
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<tr>
<td>$c_{11}$</td>
<td>147.35</td>
<td>129.19</td>
<td>166.67</td>
<td>172.18</td>
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<tr>
<td>$c_{12}$</td>
<td>61.71</td>
<td>55.56</td>
<td>69.60</td>
<td>71.60</td>
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<tr>
<td>$c_{13}$</td>
<td>80.04</td>
<td>80.75</td>
<td>81.55</td>
<td>84.69</td>
</tr>
<tr>
<td>$c_{15}$</td>
<td>4.99</td>
<td>2.52</td>
<td>7.52</td>
<td>6.67</td>
</tr>
<tr>
<td>$c_{22}$</td>
<td>189.56</td>
<td>174.15</td>
<td>219.38</td>
<td>224.82</td>
</tr>
<tr>
<td>$c_{23}$</td>
<td>76.38</td>
<td>74.62</td>
<td>75.99</td>
<td>78.25</td>
</tr>
<tr>
<td>$c_{25}$</td>
<td>5.17</td>
<td>6.20</td>
<td>8.30</td>
<td>11.37</td>
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<tr>
<td>$c_{33}$</td>
<td>228.33</td>
<td>220.59</td>
<td>237.56</td>
<td>242.20</td>
</tr>
<tr>
<td>$c_{35}$</td>
<td>-15.00</td>
<td>-13.30</td>
<td>-19.17</td>
<td>-15.09</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>49.15</td>
<td>48.36</td>
<td>55.44</td>
<td>57.50</td>
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<tr>
<td>$c_{46}$</td>
<td>5.80</td>
<td>-63.76</td>
<td>5.01</td>
<td>6.06</td>
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<tr>
<td>$c_{55}$</td>
<td>55.49</td>
<td>57.14</td>
<td>67.40</td>
<td>64.46</td>
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<tr>
<td>$c_{66}$</td>
<td>44.70</td>
<td>-16.46</td>
<td>48.50</td>
<td>49.43</td>
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<tr>
<td>$C'$</td>
<td>85.64</td>
<td>36.82</td>
<td>48.54</td>
<td>50.29</td>
</tr>
</tbody>
</table>

To determine the strength, compressibility, and stiffness of the monazite systems, various moduli are calculated. The calculated Bulk (B), Shear (G) and Young’s (E) moduli, are shown in Figure 1. The Bulk modulus showed that NdPO$_4$ is slightly harder as compared to LaPO$_4$, CePO$_4$ and PrPO$_4$ due to high value of B. Furthermore, the highest value of Young’s modulus is observed for NdPO$_4$ which indicates that the structure is stiffer. It is also observed that NdPO$_4$ is less compressible due to the highest value of Shear modulus. A lower value of G and E is observed for CePO$_4$ which suggests that this structure is more compressible and less stiff.

![Fig. 1. Calculated Bulk modulus (B), Shear modulus (G) and Young’s modulus (E) of monazite systems LnPO$_4$ (Ln = La, Ce, Pr and Nd) (4)](https://doi.org/10.1051/matecconf/202237009008)
Pugh B/G and Poisson ratios $\sigma$ were also calculated to check the ductility and brittleness characteristics of the monazite systems. Pugh [13] proposed that materials are predicted to be ductile if the value of Pugh’s criterion $(B/G) > 1.75$ while for Poisson [14] $\sigma > 0.26$ otherwise brittle. It is clearly seen that monazite structures satisfy the ductile conditions since their values of $B/G > 1.75$ and $\sigma > 0.26$ (see Figure 2). Therefore, this suggests that monazite shows ductile behaviour, with the order of ductility being as follows:

$$\text{CePO}_4 > \text{LaPO}_4 > \text{NdPO}_4 > \text{PrPO}_4$$

![Graph showing Pugh and Poisson ratios](image)

**Fig. 2.** Calculated Poisson ($\sigma$) and Pugh (B/G) ratio of monazite systems $\text{LnPO}_4$ ($\text{Ln} = \text{La, Ce, Pr and Nd}$)

### 3.3 Phonon dispersion curves and density of states (DOS)

To investigate the vibrational stability of monazite structures, phonon dispersion curves and its density of state were calculated and are shown in Figure 3 and 4, respectively. The structure is considered stable if there are no soft modes along high symmetry directions, otherwise, it is unstable (presence of soft modes). In Figure 3 (a), the phonon dispersion curve displays soft modes along all the high symmetry directions. Similar behaviour was observed with other structures ($\text{CePO}_4$, $\text{PrPO}_4$ and $\text{NdPO}_4$). The presence of soft modes in the negative frequency suggests the vibrational instability of the structures. Furthermore, the presence of soft modes corresponds with the negative $c_{35}$ of the elastic constants.

Figure 4 shows the phonon density of states for monazite systems. Recall that there were negative vibrations observed in these systems. So, it is of great importance to understand which of the atoms are responsible for the soft modes. In Figure 4 (a) and (b), there is a small sharp peak along -6 and -3 THz which indicate the contribution of La and Ce, respectively. This suggests that La and Ce vibrations are responsible for the instability of the monazite systems. Furthermore, it is observed that P atoms are dominant at 29 THz while the O states are dominant throughout the frequency range of 0 THz to 30 THz. This indicates that P and O atoms vibrate in modes of high frequencies at those frequencies. Now, considering the phonon DOS of $\text{PrPO}_4$ and $\text{NdPO}_4$. It is noted that there is the vibrational sharp peak at approximately -0.8 and -0.5 THz which are the contribution of Pr and Nd with a very minimal
contribution of P and O. This suggests that Pr and Nd vibrations are responsible for the instability of the monazite systems.

Fig. 3. Phonon dispersion curves of (a) LaPO₄, (b) CePO₄, (c) PrPO₄ and (d) NdPO₄
Fig. 4. Phonon density of states for (a) LaPO₄, (b) CePO₄, (c) PrPO₄ and (d) NdPO₄
4 Conclusion

Using a first principle theoretical approach, we studied the equilibrium lattice parameters, elastic properties, and phonon dispersion curves of LaPO$_4$, CePO$_4$, PrPO$_4$ and NdPO$_4$. It was noted that lattice parameters agree well with experimental values to within 5%. From calculated elastic constants, it was found that LaPO$_4$, PrPO$_4$ and NdPO$_4$ monazite systems are mechanically stable, while CePO$_4$ is mechanically unstable. NdPO$_4$ was found to be the hardest structure as compared to other structures. It was found that monazite systems showed ductile behaviour. Furthermore, the results from phonon dispersion curves, predicted that all monazite systems are vibrationally unstable.

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References