Structural, electronic and mechanical stability study of olivine LiMPO$_4$ (M: Mn, Fe, Co)

NL Lethole, HR Chauke and PE Ngoepe
Materials Modelling Centre, University of Limpopo, Private Bag x1106, Sovenga, 0727, South Africa
E-mail: Lesley.lethole@ul.ac.za

Abstract. First-principle calculations to investigate the structural, thermodynamic, electronic and mechanical stabilities of LiMPO$_4$ crystal structures have been performed. The structural lattice parameters are in good agreement with the available experimental data within 3%. The independent elastic properties suggested mechanical stability of LiMPO$_4$ crystal structures. Lastly, the electronic density of states suggests that LiMPO$_4$ crystal structures are metallic.

1. Introduction
Previous studies have shown that olivine lithium iron phosphate, LiFePO$_4$ is a promising cathode material candidate for new generation of lithium rechargeable batteries. The following characteristics: low cost, non-toxicity, remarkable thermal stability, good electrochemical properties and environmental benign make this material a competitive candidate [1,2]. Consequently, attention has also been shifted to other olivine lithium transition metal phosphates such as LiMnPO$_4$ and LiCoPO$_4$. It is known that LiFePO$_4$ has an operating voltage of 3.45 V which is twice more that of a standard AA alkaline battery. Moreover, its theoretical capacity is relatively high (170 mAh/g) [2]. On the other hand LiMnPO$_4$ and LiCoPO$_4$ show an operating voltage of 4.1 V and 4.5 V, and theoretical capacity of 171 mAh/g and 70 mAh/ respectively [3,4,5].

LiMPO$_4$ (M: Mn, Fe, Co) is an ordered olivine orthorhombic system with space group $Pnma$ where M and P atoms occupy half of octahedral sites and quota of the tetrahedral sites in a hexagonal close-packed array of oxygen atoms, respectively (fig. 1). In this work, we present first principles stability study on LiMPO$_4$ structures, particularly the thermodynamic, electronic and mechanical stability. The equilibrium lattice parameters, heats of formation, phonon dispersion curves and elastic properties will be investigated to mimic the stability trends between LiMPO$_4$ structures.
Figure 1: Schematic representation of olivine LiMPO₄ structure.

2. Methodology
We have performed first-principle calculations using the density functional theory (DFT+U) method as implemented in the Vienna ab initio simulation package (VASP) [6]. The Projector augmented wave (PAW) potential sets were used with the exchange and correlation energies approximated in the local density approximation with the Hubbard parameter correction (LDA+U) following the rotationally invariant. A plane wave basis set cut-off of 500 eV and k-mesh of 4x6x6 was chosen since they are sufficient to converge the total energy of the systems. Optimization of structural parameters was achieved by minimization of forces and stress tensors. Finally, the densities of states (DOS) were calculated using a smearing width of 0.05 eV using a Methfessel–Paxton smearing approach [7].

3. Results and discussion
Table 1. Structural lattice parameters, cell volumes, heats of formation, elastic constants and moduli of LiMPO₄ polymorphs; the experimental data are in parenthesis.

<table>
<thead>
<tr>
<th>Structure</th>
<th>LiMnPO₄</th>
<th>LiFePO₄</th>
<th>LiCoPO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>10.52</td>
<td>10.38</td>
<td>10.42</td>
</tr>
<tr>
<td></td>
<td>(10.4)</td>
<td>(10.30)</td>
<td>(10.2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>6.118</td>
<td>6.055</td>
<td>5.886</td>
</tr>
<tr>
<td></td>
<td>(6.09)</td>
<td>(5.99)</td>
<td>(5.92)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.777</td>
<td>4.707</td>
<td>4.734</td>
</tr>
<tr>
<td></td>
<td>(4.74)</td>
<td>(4.69)</td>
<td>(4.69)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>307.3</td>
<td>295.0</td>
<td>290.29</td>
</tr>
<tr>
<td></td>
<td>(301.1)</td>
<td>(289.8)</td>
<td>(283.2)</td>
</tr>
<tr>
<td>Hf, kJ/mol</td>
<td>-1340.45</td>
<td>-1184.49</td>
<td>-1097.25</td>
</tr>
<tr>
<td>C₁₁</td>
<td>167.61</td>
<td>209.56</td>
<td>152.17</td>
</tr>
<tr>
<td>C₁₂</td>
<td>82.33</td>
<td>117.29</td>
<td>68.83</td>
</tr>
<tr>
<td>C₁₃</td>
<td>79.07</td>
<td>99.83</td>
<td>61.75</td>
</tr>
<tr>
<td>C₂₂</td>
<td>199.84</td>
<td>270.49</td>
<td>192.50</td>
</tr>
<tr>
<td>C₂₃</td>
<td>63.41</td>
<td>80.53</td>
<td>51.42</td>
</tr>
<tr>
<td>C₃₃</td>
<td>200.78</td>
<td>249.58</td>
<td>199.33</td>
</tr>
</tbody>
</table>
3.1 Structural and thermodynamic properties

The structural lattice parameters, cell volumes and formation energies have been calculated by performing full geometric optimization and are presented in table 1. We note that our calculated lattice parameters and cell volumes are in good agreement with the experimental values to within 3% which is reasonable for DFT transition metal phosphates calculations \[11\]. It is also observed that our calculated values slightly overestimate the experimental data except for the LiCoPO\(_4\) lattice parameter \(b\); however, the volume is overestimated as expected from DFT calculations.

The structural formation energies were calculated using the expression:

\[ \Delta H_f(\text{LiMPO}_4) = \frac{1}{N} \left[ E - (E_{\text{Li}} + E_{\text{M}} + E_{\text{P}} + 4E_{\text{O}}) \right] \]  \hspace{1cm} (1)

According to this expression, it was found that the LiMPO\(_4\) structures show relatively low formation energy values, with the LiMnPO\(_4\) (-1340.45 kJ/mol) displaying the lowest energy value. This suggests that the structure is the most stable over LiFePO\(_4\) (-1184.49 kJ/mol) and LiCoPO\(_4\) (-1097.25 kJ/mol), respectively.

![Heats of formation for LiMPO\(_4\) structures as a function of the average number of valence electrons per atom (e/a).](image)

The heat of formation for LiMPO\(_4\) structures as a function of the average number of valence electrons per atom \((e/a)\) is shown in figure 2. It is clear from this figure that LiMnPO\(_4\) has the lowest heat of formation as compared to LiFePO\(_4\) and LiCoPO\(_4\). This indicates highest stability for LiMnPO\(_4\) structure over LiFePO\(_4\) and LiCoPO\(_4\), respectively. The observed linear trend predicts that the average
number of valence electrons per atom increases with the heats of formation across the transition metal element (Mn, Fe and Co).

3.2. Electronic properties

![Graphs showing density of states for LiMnPO4, LiFePO4, and LiCoPO4.](image)

Figure 3. Total and partial densities of states of LiMPO4 structures: (a) LiMnPO4, (b) LiFePO4 and (c) LiCoPO4

The total densities of states of LiMPO4 structures were calculated using the spin polarised DFT approach and are presented in fig. 2.

\[ N(E) = \int_{E}^{\Delta E} g(E) dE \]  

(2)

Thus \( g(E) dE \) represents the number of states between \( E \) and \( dE \).

We observe that all structures show relatively wide band gaps around the Fermi level. However the Fermi level falls with the 3d M band suggesting the metallic behaviour of the LiMPO4 systems, particularly for LiMnPO4 and LiFePO4. It is evident that LiMnPO4 shows more states around the Fermi level than LiFePO4 and LiCoPO4, respectively. On the other hand the partial densities of states show that states around the Fermi level are mainly due to contributions from transition metal, M 3d electrons.

3.3. Elastic properties

Elastic constants are calculated by means of a Taylor expansion of the total energy as follows:
\[ U(V, \varepsilon) = U(V_0, 0) + V_0 \left[ \sum_i \tau_i \varepsilon_i \delta_i + \frac{1}{2} \sum_{ij} C_{ij} \varepsilon_i \varepsilon_j \delta_{ij} \right] \] (3)

where \( U(V_0, 0) \) is the unstrained system energy, \( V_0 \) is the equilibrium volume while \( \tau_i \) and \( \varepsilon_i \) are element in the stress tensor and factor to take of Voigt index, respectively. The orthorhombic olive LiMPO\textsubscript{4} crystals have nine \( (C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55}, C_{66}) \) independent elastic constants [12] as listed in table 1. The necessary mechanical stability conditions for orthorhombic systems are given as follows:

\[
\begin{align*}
(C_{11} + C_{22} - 2C_{12}) &> 0, \\
(C_{11} + C_{33} - 2C_{13}) &> 0, \\
(C_{22} + C_{33} - 2C_{23}) &> 0, \\
(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) &> 0,
\end{align*}
\]

where \( V \), \( R \) and \( H \) are Voigt, Reus and Hill, respectively.

It is clear from table 1 that all the independent elastic moduli \( (C_{ij}) \) are positive satisfying all the stability conditions; this suggests that all LiMPO\textsubscript{4} crystals are elastically stable. Their resultant bulk modulus \( B \), shear modulus \( G \) and Young’s modulus \( E \) were also obtained from the calculated elastic constants using the Hill method [13].

\[
B_H = \frac{1}{2}(B_R + B_V) \tag{4}
\]

\[
G_H = \frac{1}{2}(G_R + G_V) \tag{5}
\]

\[
E_H = \frac{9B_HG_H}{G_H + 3B_H} \tag{6}
\]

where \( V \), \( R \) and \( H \) are Voigt, Reus and Hill, respectively.

The highest values of \( B \), \( G \) and \( E \) are obtained for LiFePO\textsubscript{4}, while LiMnPO\textsubscript{4} and LiCoPO\textsubscript{4} are comparable. The \( B \) and \( E \) values suggest hardness and stiffness, respectively of materials. Furthermore, we note that \( G \) is less than \( B \) for all structures, implying that the Shear modulus is the limiting parameter for stability [14].

4. Conclusions
First principle calculations on thermodynamic, structural, electronic and mechanical properties of LiMPO\textsubscript{4} crystals have been performed using the DFT approach. From the calculated properties, the stability trend within LiMnPO\textsubscript{4}, LiFePO\textsubscript{4} and LiCoPO\textsubscript{4} has also been determined. The calculated structural lattice parameters and equilibrium cell volume are in good agreement with the experimental data to within 3%. The predicted formation energies suggest that LiMnPO\textsubscript{4} is the most stable structure over LiFePO\textsubscript{4} and LiCoPO\textsubscript{4}, respectively. Moreover, the independent elastic properties have shown that LiMPO\textsubscript{4} crystals are mechanically stable. There is a good correlation between the heats of formation and, the electronic densities of states, which are consistent with elastic stability.
Acknowledgements
This work has been done at the materials modelling centre, university of Limpopo, supported by the national research foundation.

5. References