

Structural, electronic and mechanical stability study of olivine LiMPO₄ (M: Mn, Fe, Co)

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Abstract. First-principle calculations to investigate the structural, thermodynamic, electronic and mechanical stabilities of LiMPO₄ 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 LiMPO₄ crystal structures. Lastly, the electronic density of states suggests that LiMPO₄ crystal structures are metallic.

1. Introduction

Previous studies have shown that olivine lithium iron phosphate, LiFePO₄ 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 LiMnPO₄ and LiCoPO₄. It is known that LiFePO₄ 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 LiMnPO₄ and LiCoPO₄ 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].

LiMPO₄ (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 LiMPO₄ 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 LiMPO₄ structures.

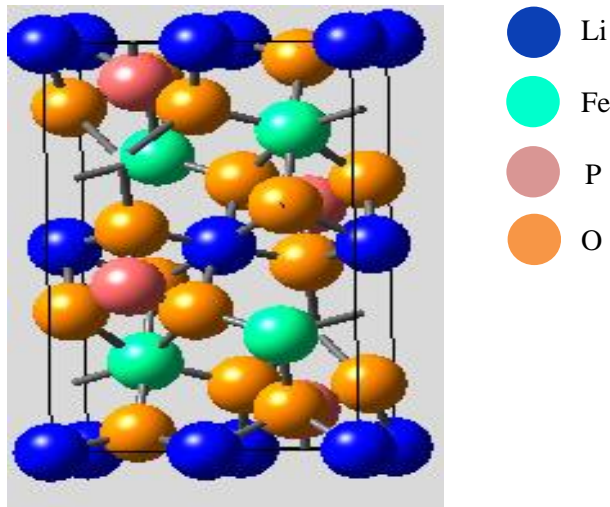


Figure 1: Schematic representation of olivine LiMPO_4 structure.

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 LiMPO_4 polymorphs; the experimental data are in parenthesis.

Structure	LiMnPO_4	LiFePO_4	LiCoPO_4
a (Å)	10.52 (10.4) ^a	10.38 (10.30) ^b	10.42 (10.2) ^c
b (Å)	6.118 (6.09) ^a	6.055 (5.99) ^b	5.886 (5.92) ^c
c (Å)	4.777 (4.74) ^a	4.707 (4.69) ^b	4.734 (4.69) ^c
V (Å ³)	307.3 (301.1) ^a	295.0 (289.8) ^b	290.29 (283.2) ^c
H_f (kJ/mol)	-1340.45	-1184.49	-1097.25
C_{11}	167.61	209.56	152.17
C_{12}	82.33	117.29	68.83
C_{13}	79.07	99.83	61.75
C_{22}	199.84	270.49	192.50
C_{23}	63.41	80.53	51.42
C_{33}	200.78	249.58	199.33

C_{44}	49.99	56.89	47.67
C_{55}	62.56	72.27	59.67
C_{66}	54.79	62.40	58.33
B_H	113.00	146.80	100.53
G_H	55.77	65.97	56.53
E_H	143.67	172.13	142.83

[8]^a [9]^b [10]^c

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:

$$\Delta H_f(\text{LiMPO}_4) = 1/N [E - (E_{\text{Li}} + E_{\text{M}} + E_{\text{P}} + 4E_{\text{O}})] \quad (1)$$

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.

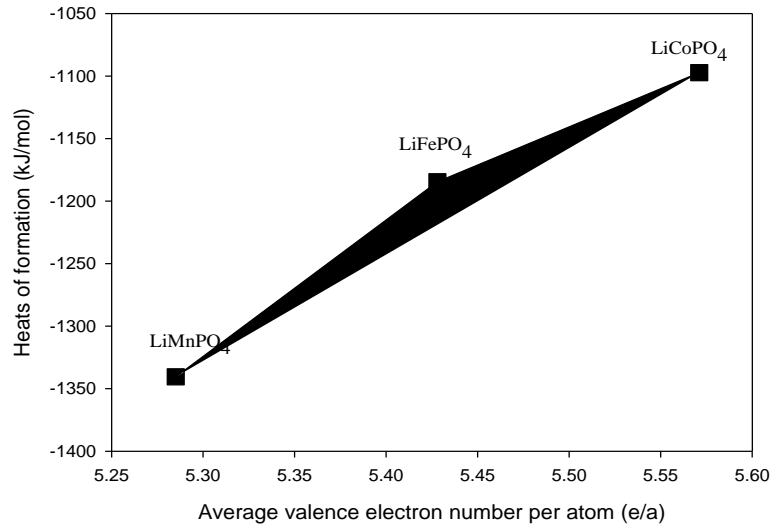


Figure 2: Heats of formation for LiMPO_4 structures as a function of the average number of valence electrons per atom (e/a).

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

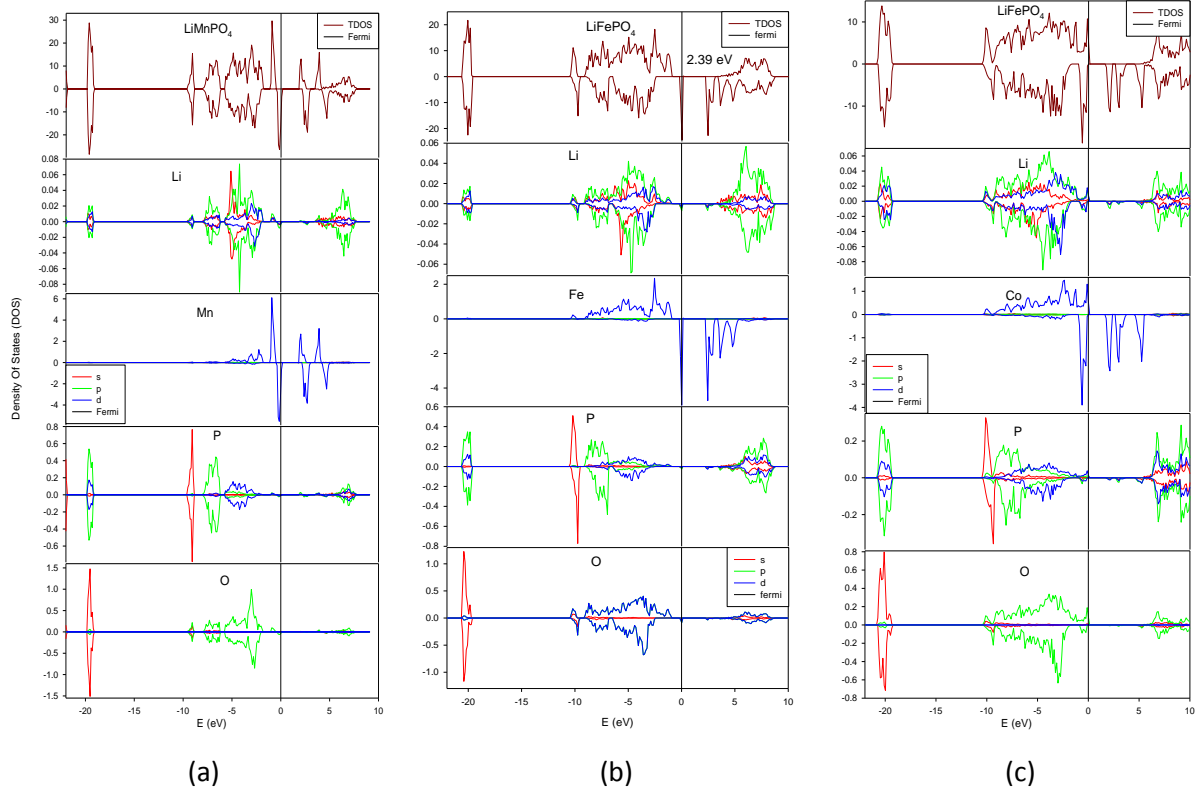


Figure 3. Total and partial densities of states of LiMPO₄ structures: (a) LiMnPO₄, (b) LiFePO₄ and (c) LiCoPO₄

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

$$N(E) = \int_E^{\Delta E} g(E)dE \quad (2)$$

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:

$$U(V, \varepsilon) = U(V_0, 0) + V_0 \left[\sum_i \tau_i \varepsilon_i \delta_i + \frac{1}{2} \sum_{ij} C_{ij} \varepsilon_i \delta_i \varepsilon_j \delta_j \right] \quad (3)$$

where $U(V_0, 0)$ is the unstrained system energy, V_0 is the equilibrium volume while τ_i and ξ_i are element in the stress tensor and factor to take of Voigt index, respectively. The orthorhombic olive LiMPO₄ 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:

$$\begin{aligned} (C_{11} + C_{22} - 2C_{12}) > 0, & \quad (C_{11} + C_{33} - 2C_{13}) > 0, & \quad (C_{22} + C_{33} - 2C_{23}) > 0, \\ (C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0, & \quad C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, & \quad C_{44} > 0, \quad C_{55} > 0, \\ C_{66} > 0 \end{aligned}$$

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 LiMPO₄ 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].

$$B_H = \frac{1}{2}(B_R + B_V) \quad (4)$$

$$G_H = \frac{1}{2}(G_R + G_V) \quad (5)$$

$$E_H = \frac{9B_H G_H}{G_H + 3B_H} \quad (6)$$

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

The highest values of B, G and E, are obtained for LiFePO₄, while LiMnPO₄ and LiCoPO₄ 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 LiMPO₄ crystals have been performed using the DFT approach. From the calculated properties, the stability trend within LiMnPO₄, LiFePO₄ and LiCoPO₄ 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 LiMnPO₄ is the most stable structure over LiFePO₄ and LiCoPO₄, respectively. Moreover, the independent elastic properties have shown that LiMPO₄ 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.

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5. References

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