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First-Principles Study of Doping in $LiMnPO_4$

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A density function theory (DFT) based first-principles study of doping on $LiMnPO_4$ is attempted. The doped $LiMnPO_4$, such as $LiMn_{0.75}Fe_{0.25}PO_4$, $LiMn_{0.75}Al_{0.25}PO_4$ and $LiMnPO_3S$ at the level of electron structure is studied. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), density of states (DOS) and Fermi level of doped and pristine $LiMnPO_4$ are investigated, showing positive effectiveness for Fe and Al substitution of Mn, as well as S substitution of O, on the electronic structure of $LiMnPO_4$ to improve its properties.

Keywords: Highest occupied molecular orbital; lowest unoccupied molecular orbital; density of states; Fermi level; $LiMnPO_4$; doping

1. INTRODUCTION

Olivine $LiMPO_4$ (M=Mn, Fe, Co, Ni) is highlighted as a potential cathode material owing to its relatively high structural stability, high theoretical capacity, low cost, and environmental friendliness [1-9]. In particular, $LiMnPO_4$ behaves similar discharge voltage to that of $LiCoO_2$, presently the most widely used cathode, it is anticipated that replacement of the cathode with this material can be accomplished without major difficulties at the battery system level. And also, its thermal stability is proved to be relatively higher than α-$NaFeO_2$ structure cathode material.[10] However, its sluggish mass and charge transport significantly hindered its application.[1] Efforts have recently been made to improve the performance of the material.[2-9] One of the most popular approaches is doping LiMnPO4 with aliovalent or isovalent cations on Li or Mn sites.[11-14] Interestingly, according to modeling,[15–17] doping on the Li site is however debated, since it is expected to depress the electrochemical performance by blocking conduction pathways and so causes damage in electrochemical performance. Doping on the Mn site has been experimentally supported recently. [11, 13,14] A theoretical cognition and further prognosis is essential to smart structure and synthesis design.

Here report a density function theory (DFT) based first-principles study of several doped $LiMnPO_4$, including $LiMn_{0.75}Fe_{0.25}PO_4$, $LiMn_{0.75}Al_{0.25}PO_4$, $LiMnPO_4$ and $LiMnPO_3S$ at the level of electron structure. Though the electronic structure of materials calculated by LDA+GGA is far from the actual, due to the very approximate treatment of the electron correlation in transition metal orbital, the relative variation among different doped materials and the pristine still make sense. The correlation among composition, electronic structure, chemical bond, and property has been studied.

2. COMPUTATIONAL METHODS

The first-principles study is performed using Materials Studio 4.1 software package. Generalized gradient approximation (GGA) was employed to investigate the electronic structure of pristine $LiMnPO_4$ and the doped. In particular, exchange-correlation effects were taken into account by using the generalized gradient approximation (GGA). The total energy code CASTEP was used, which utilizes pseudo-potentials to describe electron ion interactions and represents electronic wavefunctions using a plane-wave basis set. In calculations shown, an energy cut-off of 500 eV and appropriate k-point of 5×5×5 were chosen so that the total ground state energy is converged to within 1 meV per formula unit. The correlation among composition, electronic structure, chemical bond, and property has been studied.

3. RESULTS AND DISCUSSION

3.1 Cation doping

Here Fe and Al are chosen as typical doping to investigate the effect of cation on electron structure of $LiMnPO_4$. On one hand, $LiMn_{1-x}Fe_xPO_4$ is reported to exhibit better electrochemical performance than pure LiFePO4. On the other hand, It is reported that Al-doping can enhance the ion conductivity of $LiFePO_4$ due to donor effect, [18] while decrease electronic conductivity in accordance with a p-type mechanism [19]. Since Al-doping is generally effective to improve the thermal stability of the virgin material, it is worthy of verifying the role of Al on the electron structure of $LiMnPO_4$. Fe tends to preferably take the substitution of Mn, due to its similarities with Mn. For Al ion, though it is far smaller than Mn ion, theoretical investigation shows that it dose not show a preference for the Li site [20]. The models for calculations are as shown in Fig.1. As CASTEP model only suitable for systems of tens of atoms, the doping content is fixed as M:Mn=1:3 in this study. For just to get a roughly comprehension on doping effect, charge compensation is not considered for the aliovalent substitution.

Fig. 2 shows the calculated density of states (DOS) for $LiMnPO_4$, $LiMn_{0.75}Fe_{0.25}PO_4$ and $LiMn_{0.75}Al_{0.25}PO_4$ materials. The calculated band gap of 1.61 eV, 1.31eV and 2.07 eV for $LiMnPO_4$,

$LiMn_{0.75}Fe_{0.25}PO_4$ and $LiMn_{0.75}Al_{0.25}PO_4$, respectively, is indicative of semiconductor structures for these three materials.

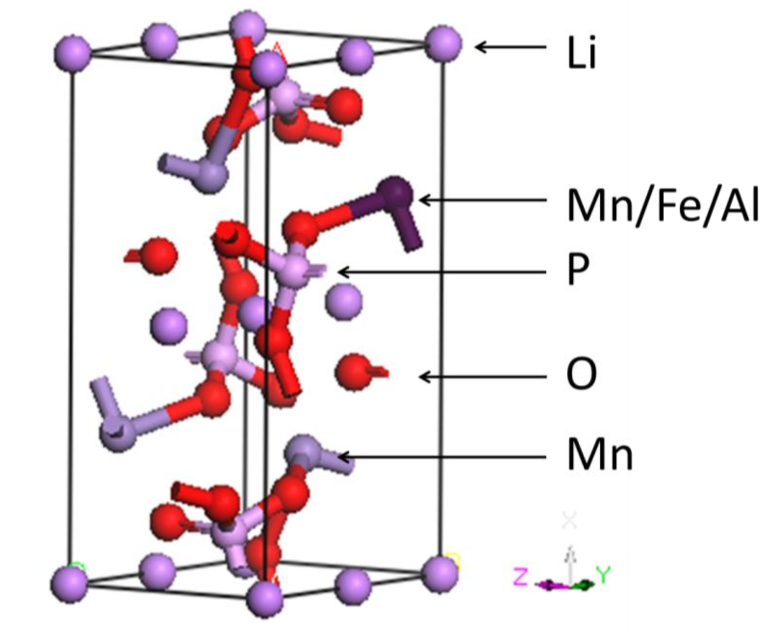


Figure 1. Cell model for cation doped $LiMnPO_4$. 28 atoms are evolved in this model.

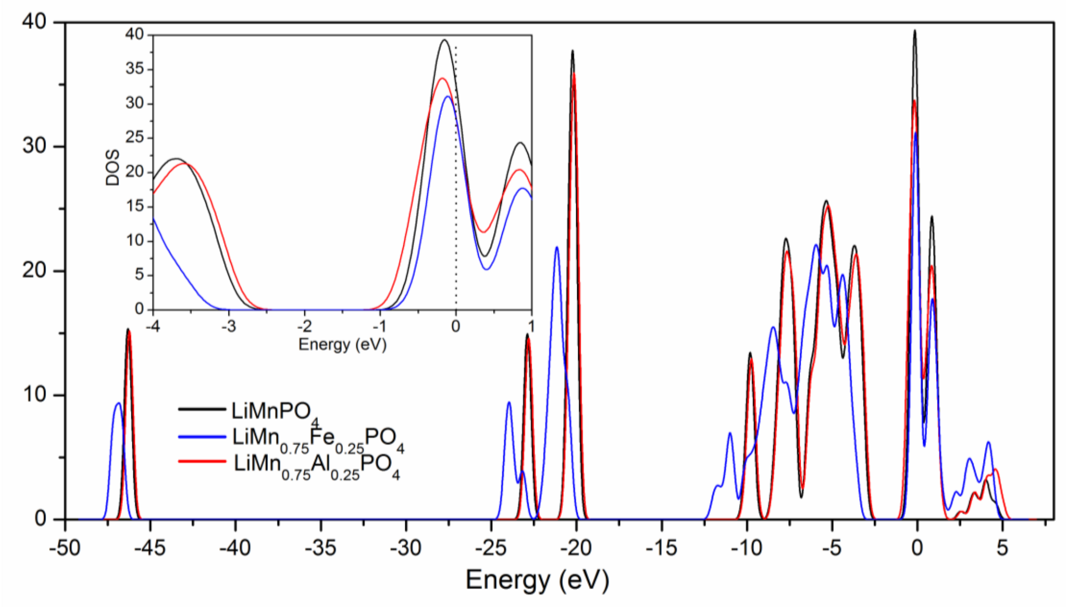


Figure 2. Comparison of total density of states of $LiMnPO_4$, $LiMn_{0.75}Fe_{0.25}PO_4$, and $LiMn_{0.75}Al_{0.25}PO_4$. The insert is a local amplification.

These data are consistent with the ranges found in the previous literatures. In particular, though Mn and Fe atoms have similar electronic structures, substituting Mn atom with Fe atom can improve the conductivity of LiFePO4. However, Al doping results a dramatically increase in band gap, revealing its negative effect on electronic conductivity. It is interesting to note than the valence band for every material can be divided into three segments. Comparing with those of $LiMnPO_4$, the segments of $LiMn_{0.75}Fe_{0.25}PO_4$ present roughly the same width but a small difference in location and intensity, while the segments of $LiMn_{0.75}Al_{0.25}PO_4$ are much wider and shift to lower energy. In particular, the difference in intensity between valence band and conduction band is smaller for $LiMn_{0.75}Fe_{0.25}PO_4$ than for $LiMnPO_4$, revealing the improved electric conductivity by Fe doping. This result confirms that Fe doping not lead great change on bonding structure, however Al doping causes dramatic changes not only on the bonds between metal atoms and oxygen atoms, but also strong covalently bonded PO_4 tetrahedron.

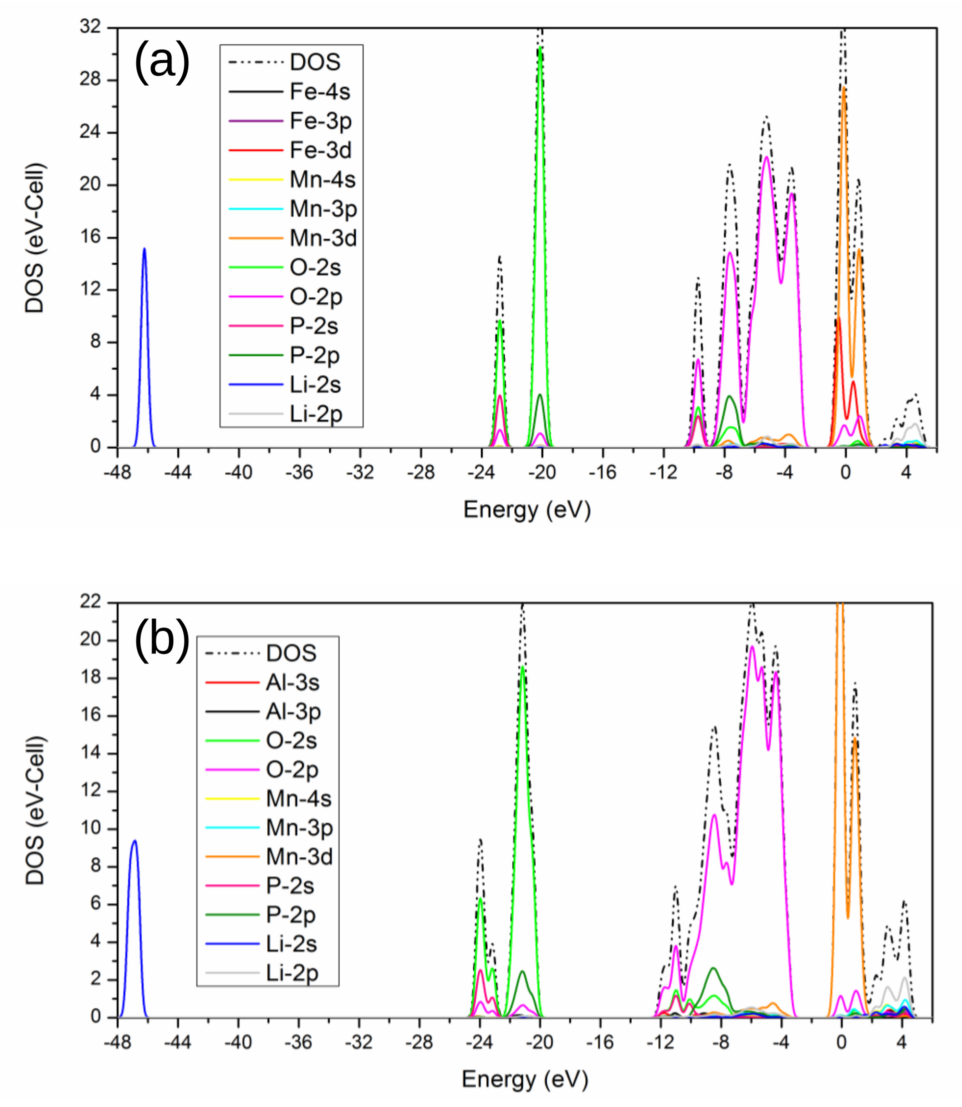


Figure 3. Total DOS and partial DOS of (a) $LiMn_{0.75}Fe_{0.25}PO_4$, and (b) $LiMn_{0.75}Al_{0.25}PO_4$.The Fermi level is set at zero energy.

Partial DOS of every element shows different contributions to the total DOS. The comparison of total DOS and partial DOS for $LiMn_{0.75}Fe_{0.25}PO_4$ and $LiMn_{0.75}Al_{0.25}PO_4$ is showed in Fig. 3(a) and 3(b), respectively. It can be concluded that for both material, O_{2p} mainly contributes to valance band,

and Mn_{3d} mainly contributes to conduction band, while others are far from Fermi level. Fe_{3d} present obvious contribution of conduction band, while Al contributes little to neither valance and conduction band. In fact, calculations for $LiFePO_4$ based on other models leads to similar conclusions [18, 20], suggesting that aliovalent dopant substitution in $LiMPO_4$ is unlikely [15-17] and that any enhancement in electronic conductivity may not be a true lattice doping effect. Besides, correlation among atoms can be judged from resonance phenomena.

3.2 Anion doping

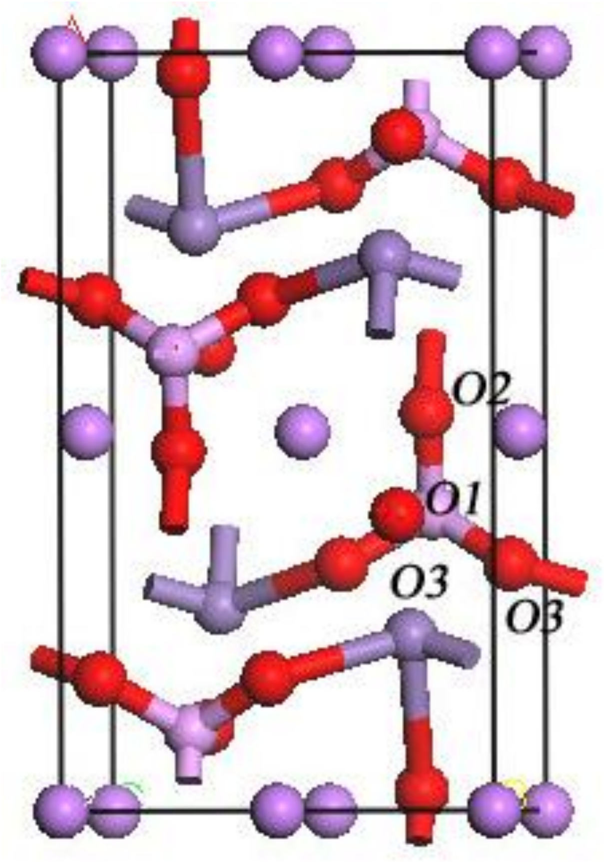


Figure 4. Analysis of O site in $LiMnPO_4$

As a polyanion compound, Mn-O bonds are strong interfered by P atoms via strong interactions like Mn-O-P. So any variations happening on $(PO_4)^{3-}$ will in turn affect the Mn-O bonds [21, 22]. In this sense, anion substitution can also affect the electron distribution of the base material very much. As showed in Fig. 4, O_{2p} contributes to the top of valance band, so substitution of O atoms with less electronegative atom, such as S, may be benefit for the electronic conductivity. However, anion substitution is less often attempted both theoretically and experimentally. Sulfur substitution at oxygen site in oxides semi-conductors has been proved to be effective, similar attempt in $LiMnPO_4$ however has never been reported. As reported, the four O atoms in $LiMnPO_4$ in fact can be divided into three types according to crystal symmetry and chemical surroundings. The calculated bond lengths of different O atoms are listed in table 1, which may help us predict the stability of O atoms. Since O-P bond is much stronger than O-Mn bond, so O3 is relatively more chemically active and easy to be substituted. Base on above discussion, the cell model for $LiMnPO_{3.75}S_{0.25}$ is determined and presented in Fig. 5.

Table 1. Calculated bond length of different O atoms

Site	O1	O2	O3
O-P bond length / Å	1.51702	1.52194	1.56377
O-Mn bond length / Å	None	2.43839	2.23219

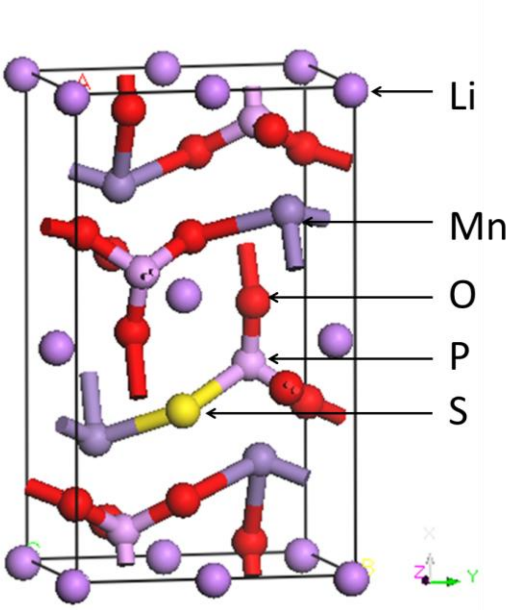


Figure 5. Cell model for $LiMnPO_{3.75}S_{0.25}$. 28 atoms are evolved in this model.

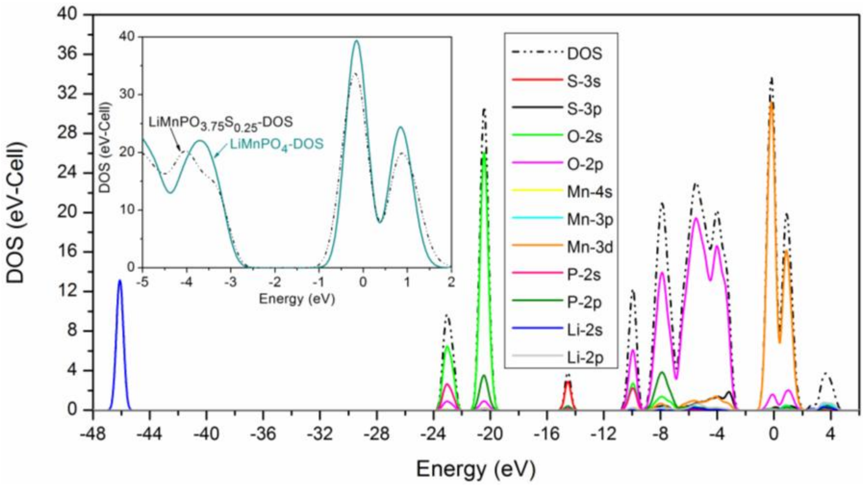
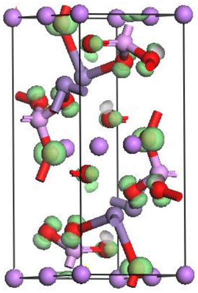
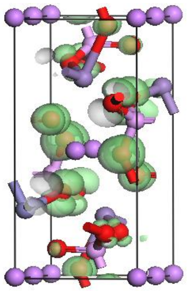
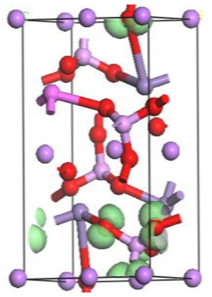
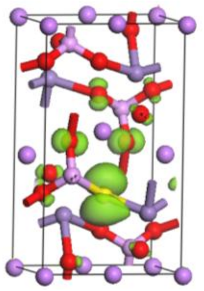
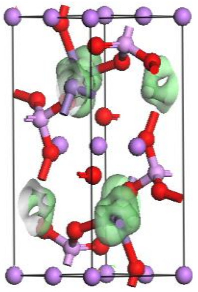
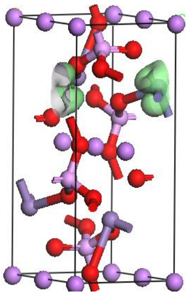
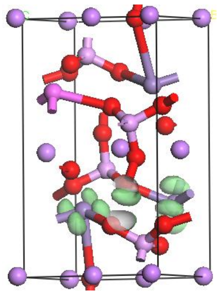
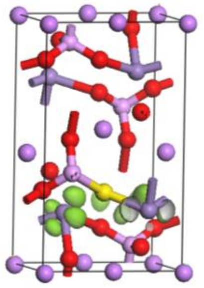


Figure 6. Total DOS and PDOS of $LiMnPO_{3.75}S_{0.25}$.The Fermi level is set at zero energy. The insert DOS comparison of $LiMnPO_{3.75}S_{0.25}$ and $LiMnPO_4$.

Fig. 6 shows the total DOS and partial DOS of $LiMnPO_{3.75}S_{0.25}$. The contribution of Li, O, P and Mn to the total DOS for $LiMnPO_{3.75}S_{0.25}$ is similar to that of $LiMnPO_4$. For example, the partial DOS of Mn around Fermi level shows the splitting of Mn 3d clearly, and Mn_{3d} partial DOS mainly contributes to the lowest conduction band, O_{2p} mainly contributes to the highest valence band near to the Fermi level, while the other partial DOSs are further away from the Fermi Level. It is noticeable that S_{3p} presents a visible contribution to highest valence band, revealing that S doping may improve the electric conductivity of the host material. Besides, the band gap of $LiMnPO_{3.75}S_{0.25}$ is smaller than that of $LiMnPO_4$, indicating also that S substitution of O is helpful for improving of electric conductivity.

Table 2. Compare of HOMO and LUMO of doped and pristine $LiMnPO_4$

Material	$LiMnPO_4$	$LiMn_{0.75}Fe_{0.25}PO_4$	$LiMn_{0.75}Al_{0.25}PO_4$	$LiMnPO_{3.75}S_{0.25}$
HOMO				
LUMO				

* HOMO and LUMO are acronyms for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively.

A visual comparison of HOMO and LUMO for the doped and pristine $LiMnPO_4$ is shown Table 2. It is interesting that both HOMO and LUMO changed greatly after doping. Fe doping makes LUMO focus only around Fe atoms, and the shape of LUMO is similar to that of $LiMnPO_4$. Also, the distribution of HOMO changes by Fe doping. As can be observed, O atoms near Li atoms show bigger HOMO distribution than those in $LiMnPO_4$. However, Al doping not only makes LUMO focus only around Mn atoms, but also causes disappearance of HOMO from O atoms those are near Li atoms. This may imply that Fe doping is helpful for electronic conductivity, while Al doping may be helpful for transference of Li ion. In addition, LUMO distribution in $LiMn_{0.75}Al_{0.25}PO_4$ looks more localized when comparing with those of $LiMn_{0.75}Fe_{0.25}PO_4$ and $LiMnPO_4$, revealing a possible reason for lower electric conductivity. For $LiMnPO_{3.75}S_{0.25}$, the contribution of S doping on valence band can be identified very clear. HOMO in $LiMnPO_{3.75}S_{0.25}$ is more delocalized than that in $LiMnPO_4$. Though the case is on the contrary for LOMO, S doping may be still positive to electric conductivity, due to the well match between HOMO and LOMO.

4. CONCLUSION

Fe and Al substitution of Mn, as well as S substitution of O, on the electronic structure of $LiMnPO_4$ are studied. The results account for positive effect of Fe doping and S doping to the enhancement of electric conductivity. Though Al doping is not favorable for increase of electric conductivity, it may benefit lithium ion diffusion.

ACKNOWLEDGEMENT
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