First-principles GGA+U Study on Structural and Electronic Properties in LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$ and LiCo$_{0.5}$Ni$_{0.5}$O$_2$

B. Liu, B. Xu*, M. S. Wu and C. Y. Ouyang

Department of Physics, Jiangxi Normal University, Nanchang, 330022, China

E-mail: bxu4@mail.ustc.edu.cn

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The structural and electronic properties of lithium mixed transition metal oxides LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$ and LiCo$_{0.5}$Ni$_{0.5}$O$_2$ are studied by using first-principles calculations based on the density functional theory. Results show that the rhombohedral structure with $Rar{3}m$ space group is the most stable configuration for LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$ and LiCo$_{0.5}$Ni$_{0.5}$O$_2$ compounds, indicating that the mixture of cations in the transition metal layers is help to suppress the Jahn-Teller distortion for the Ni- and Mn-containing oxides. Electronic structure calculations suggest that all the three compounds are semiconducting with small band gaps. In the Mn-containing oxides, LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$, charge transfers from Mn ion to Co or Ni ions, resulting in Mn$^{4+}$ and Ni$^{2+}$ or Co$^{2+}$. Charge transfer could be used to explain the suppression of the Jahn-Teller effect. As charge transfer cannot be observed between Co and Ni ions, the Jahn-Teller distortion still exists in LiCo$_{0.5}$Ni$_{0.5}$O$_2$, but mitigated to some extent. The further electronic configurations, density of states and magnetic moments are also discussed. In addition, formation energy calculations show that LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$ and LiCo$_{0.5}$Ni$_{0.5}$O$_2$ compounds are thermodynamic stable when compared to the basic layered LiMO$_2$ ($M$ = Co, Mn, Ni), which means that the mixture of cations in the lithium transition metal oxides could be formed.

Keywords: First-principles, Jahn-Teller effect, Electronic structure, Cathode material.

1. INTRODUCTION

Development and discovery of cathode materials with superior performance are always the concerned issues for Li-ion battery scientists. Layered LiCoO$_2$ is the conventional and most commonly used cathode material. However, many problems associated with the low practical capacity (130-150 mAh/g) [1], the toxicity of cobalt and the limitation of Co resource restrict the large scale application
of LiCoO₂ cathode material. LiNiO₂, on the contrary, is considerably less expensive and has a higher initial capacity (200 mAh/g) than LiCoO₂ [2]. However, LiNiO₂ as cathode material is known to be more difficult to synthesize, which suffers from low reversible capacity and poor cyclability. This is mainly due to the poor structural stability of LiNiO₂ compound caused by the Jahn-Teller (JT) effect of active Ni³⁺ ions in the lattice [3]. Manganese oxides are lower cost and less toxic than cobalt or nickel oxides, and have been proved to be safer on overcharge [4]. Thus, lithium manganese oxide cathodes have received much attention. Unfortunately, due to the more complex structure than those of LiCoO₂ or LiNiO₂, capacity fading, phase instability and structural transformation that occurs with cycling [5-9], there is a distance away from the practical application for the lithium manganese oxide.

Considering the advantages and disadvantages of the basic LiCoO₂ or LiNiO₂ or LiMnO₂, considerable attention has therefore been paid to modify the commercial cathode material LiCoO₂, i.e. partial substitution of Co by other transition metal ions such as Ni or Mn. Because Ni and Mn are more abundant and less expensive and less toxic than Co, while they can improve the materials capacity and stability. LiNiO₂ is usually mixed with LiCoO₂ in unit cell level by applying solid-state chemistry and electrochemistry methods, forming solid solution phase of LiCo₁₋ₓNiₓO₂ [10,11]. It was shown experimentally that Co replacement of Ni ions in a reasonable concentration in LiCo₁₋ₓNiₓO₂ can suppress the JT distortion of Ni³⁺, and thus enhance the thermal stability and cycling performance [12]. Stoyanova et al. reported that Co can be replaced by Mn to prepare a layered LiCo₁₋ₓMnₓO₂ solid solution (0 ≤ y ≤0.2) with a hexagonal lattice [13,14], although Ohzuku et al. believed that LiCoO₂ was immiscible with LiMnO₂ in the whole range of y [15]. Theoretically, Shukla et al. reported that the structural transformation from rhombohedral to monoclinic would occur for the Ni- and Co-doped LiMnO₂ based on first-principles calculations [16]. On the other hand, in order to improve the stability and capacity of LiNiO₂, Mn and Co could also be used to replace the Ni ions. Wang et al. have theoretically studied that the JT distortion in LiNiO₂ is substantially suppressed by Co atoms that replace Ni atoms in the lattice [17]. More recently, Hao et al. have found that Ti doping could further enhance the structural stability of LiCo₀.₅Ni₀.₅O₂, thus improving the electrochemical properties [18]. Furthermore, Mn ions are easily incorporated into the Ni cation layers to prepare LiNi₁₋ₓMnₓO₂. Early work of Rossen et al. [19] investigated the solid-state synthesis and electrochemistry of the solid solution LiMnO₂-LiNiO₂. Ohzuku and Makimura [20] presented recent work on the LiNi₀.₅Mn₀.₅O₂ system, showing a rhombohedral structure, a sloping discharge profile, and a reversible capacity (150 mAh/g) in the voltage range 2.5-4.3 V. Recently, FTIR and Raman experimental analysis has also confirmed the layered rhombohedral structure for the LiNi₀.₅Mn₀.₅O₂ [21].

As introduced above, layered LiMO₂ (M = Co, Mn, Ni) with mixed metal cations in the transition metal layers shows superior electrochemical and safety behavior to the corresponding basic layered oxide. It is apparent in the research area of lithium battery materials that the underlying structural and electronic properties of lithium transition metal oxides are very complex, but are crucial to the complete understanding of the physical nature of cathode materials. Therefore, the present study utilizes computational techniques based on density functional theory (DFT) to systematically investigate the key issues of structures, electronic structures, charge transfer, electronic configuration, valence states and magnetic moment of LiMn₀.₅Ni₀.₅O₂, LiMn₀.₅Co₀.₅O₂ and LiCo₀.₅Ni₀.₅O₂ system at atomic and electronic level.
2. COMPUTATIONAL METHODOLOGIES

All calculations are performed using the Vienna *ab initio* simulation package (VASP) [22]. The core ion and valence electron interaction are described by the projector augmented wave (PAW) [23] method and the exchange-correlation part is described with the spin-polarized generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [24]. In order to correctly reproduce the electronic structure of the transition metal atoms with 3d electrons, GGA+U method is employed [25]. According to the previous studies of Li-ion battery materials [26,27], the effective onsite Coulomb term $U_{\text{eff}}$ are set to be 3.5, 3.9 and 5.3 eV for Mn, Co and Ni, respectively.

The convergence tests of the total energy with respect to the $k$-point sampling and energy cutoff have been carefully examined, which ensure that the total energy is converged. The Brillouin zone (BZ) is sampled by using a $3\times3\times1$ Monkhorst–Pack [28] grids for relaxation calculations and a $5\times5\times2$ one for static calculations. Energy cutoff for the plane waves is chosen to be 550 eV. Both the lattice parameters and the ionic positions are fully relaxed. The final forces on all relaxed atoms are less than 0.01 eV/Å. The calculation of the density of states (DOS) is smeared by the Gaussian smearing method with a smearing width of 0.05 eV.

Li$M$O$_2$ ($M$ = Co, Mn, Ni) adopt the α-NaFeO$_2$ structure. The stable form of LiCoO$_2$ is layered rhombohedral structure with symmetry $R\overline{3}m$. However, the monoclinic structures with $C2/m$ space group symmetry are the stable phases for LiMnO$_2$ and LiNiO$_2$ due to the JT distortion of Mn$^{3+}$ and Ni$^{3+}$. Since $R\overline{3}m$ and $C2/m$ space group could be both observed for the LiMO$_2$ compound, we also consider the two phases in the various lithium mixed transition metal oxides. In order to construct the mixed system with 1:1 ratio of atom number for the two transition metal atoms, a $2\times2\times1$ supercell for $R\overline{3}m$ phase, which contains 48 atoms, and a $2\times2\times2$ supercell for $C2/m$ phase, which contains 32 atoms, are employed in our study. Then, half of the transition metal atoms in each M-O layer are replaced by the other transition metal atoms, because Kim found that the structures of LiNiO$_2$ doping with Co or Mn in the same layer are more stable [29]. For $2\times2\times1$ supercell of $R\overline{3}m$ phase LiCoO$_2$, for example, two Co atoms in each Co-O layer (Co$_4$O$_8$) are substituted by Mn atoms, forming the Co$_2$Mn$_2$O$_8$ layer. In the end, the Li$_{12}$Co$_6$Mn$_6$O$_{24}$ supercell are obtained for the LiCo$_{0.5}$Mn$_{0.5}$O$_2$ $R\overline{3}m$ phase. Similar methods are used to get the LiCo$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Ni$_{0.5}$O$_2$ structures.

In our calculations, we consider both ferromagnetic (FM) and anti-ferromagnetic (AFM) spin configurations as the magnetic atoms play an important role in the electronic properties. It is found that the total energy of the system with AFM ordering is slightly lower than that with FM ordering. Therefore, unless otherwise specified, the results presented in the following sections of this work are according to the AFM configuration. However, our results show that FM or AFM ordering has little influence on the magnetic and valence state of transition metal atoms.
3. RESULTS AND DISCUSSION

3.1 Structures

First, we examine the structures of the lithium mixed transition metal oxides. The structures with different arrangement of the transition metal atoms in both $R\bar{3}m$ and $C2/m$ phases are optimized in our calculations. The most stable structures for LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiCo$_{0.5}$Ni$_{0.5}$O$_2$ and LiMn$_{0.5}$Co$_{0.5}$O$_2$ are obtained and shown in Fig. 1(a), (b) and (c), respectively. The calculated and experimental lattice parameters are listed in Table 1, where the results available from other works are also given for comparison. It is found that our calculated results are reasonably in agreement with other reports and experimental values.

![Figure 1. Schematic views of the atomic structures of (a) LiMn$_{0.5}$Ni$_{0.5}$O$_2$, (b) LiCo$_{0.5}$Ni$_{0.5}$O$_2$ and (c) LiMn$_{0.5}$Co$_{0.5}$O$_2$.](image)

Table 1. Lattice parameters (a, b and c in Å), unit cell volume (V/Å$^3$) of LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiCo$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>c/a</th>
<th>V/Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$<em>{0.5}$Ni$</em>{0.5}$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>2.926</td>
<td>2.926</td>
<td>14.387</td>
<td>4.917</td>
<td>106.69</td>
</tr>
<tr>
<td>Calculated [31]</td>
<td>2.914</td>
<td>2.914</td>
<td>14.398</td>
<td>4.941</td>
<td>105.88</td>
</tr>
<tr>
<td>LiCo$<em>{0.5}$Ni$</em>{0.5}$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>2.857</td>
<td>2.857</td>
<td>14.207</td>
<td>4.973</td>
<td>100.42</td>
</tr>
<tr>
<td>Calculated [18]</td>
<td>2.898</td>
<td>2.898</td>
<td>14.282</td>
<td>4.928</td>
<td>103.87</td>
</tr>
<tr>
<td>Experimental [33]</td>
<td>2.845</td>
<td>2.845</td>
<td>14.123</td>
<td>4.964</td>
<td>98.99</td>
</tr>
<tr>
<td>LiMn$<em>{0.5}$Co$</em>{0.5}$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>2.986</td>
<td>2.986</td>
<td>14.352</td>
<td>4.806</td>
<td>110.82</td>
</tr>
</tbody>
</table>

As mentioned above, LiCoO$_2$ has the layered $R\bar{3}m$ rhombohedral structure, whereas LiMnO$_2$ and LiNiO$_2$ are monoclinic with $C2/m$ space group due to the JT distortion of Mn and Ni ions. This
means that the JT effect lowers the structural symmetry in the LiMO\textsubscript{2} compound. According to our total energy calculations, it is clearly found that LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, LiCo\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, and LiMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2} all keep the α-NaFeO\textsubscript{2} structures, which are rhombohedral with R\textsubscript{3}m symmetry. Obviously, the structural symmetry do not be lowered even if the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, LiCo\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, and LiMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2} compounds possess the Mn and Ni ions which are extremely easy to bring the JT effect. Our results are consistent with that of Prasad et al.[34], where they indicated that the dopants, such as Co and Fe, could destabilize the monoclinic structure relative to the rhombohedral structure for the LiMnO\textsubscript{2} compound. For the lithium mixed transition metal oxides, therefore, the structural distortion resulting from the JT distortion of transition metal atoms are suppressed to some extent. From the application point of view, therefore, the cycling stability of the lithium mixed transition metal oxides should be better than that of LiNiO\textsubscript{2} or LiMnO\textsubscript{2} due to the higher structural symmetry.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Interatomic bond (Å)</th>
<th>M-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}</td>
<td>Co-O 2.063</td>
<td>Ni-O 2×2.052/2×1.965/2×1.892</td>
</tr>
<tr>
<td>LiCo\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}</td>
<td>1.940</td>
<td>Ni-O 2×2.144/4×1.899</td>
</tr>
<tr>
<td>LiMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2}</td>
<td>2.096</td>
<td>Mn-O 2×2.356/4×1.952</td>
</tr>
<tr>
<td>m-LiNiO\textsubscript{2}</td>
<td>1.938</td>
<td>Ni-O 2×2.144/4×1.899</td>
</tr>
<tr>
<td>m-LiMnO\textsubscript{2}</td>
<td>2×2.052/2×1.965/2×1.892</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Interatomic bonds between transition metal atoms and oxygen atoms in LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, LiCo\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, LiMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2}, and LiMO\textsubscript{2} (M = Mn, Ni, Co).

To further confirm the suppressed effect of mixture of transition metal atoms on the structures, we analyze the interatomic bonds between transition metal atoms and oxygen atoms, as listed in Table 2. In order to facilitate comparison, the results of LiMO\textsubscript{2} (M = Mn, Ni, Co) are also provided. For LiCoO\textsubscript{2} structure, six Co-O bonds in CoO\textsubscript{6} octahedron are all equal to 1.938 Å, which indicates that no JT distortion occurs. Nevertheless, the bond lengths of LiNiO\textsubscript{2} and LiMnO\textsubscript{2} are divided into two groups, with two long (2.144 Å for LiNiO\textsubscript{2} and 2.356 Å for LiMnO\textsubscript{2}) and four short (1.899 Å for LiNiO\textsubscript{2} and 1.952 Å for LiMnO\textsubscript{2}) bonds, an indication of typical JT type elongation of the octahedron. The calculated values agree well with those from previous report [35], where two long (2.15 Å) and four short (1.90 Å) bonds could be obtained in monoclinic LiNiO\textsubscript{2}. If two kinds of transition metal atoms are mixed, the situations are significantly different. For the LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2}, which includes both Mn and Ni atoms with 1:1 ratio of atom number, the six Ni-O bond lengths in NiO\textsubscript{6} octahedron become very close to each other. The average Ni-O bond length is 2.063 Å, which is between two types of bond lengths in monoclinic LiNiO\textsubscript{2}. Meanwhile, the Mn-O bond lengths in MnO\textsubscript{6} octahedron of LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} also tend to the same with the average value of 1.948 Å, very close to the short Mn-O bond lengths in monoclinic LiMnO\textsubscript{2}. As a result, from the structure point of view, the distortion of MnO\textsubscript{6} and NiO\textsubscript{6} octahedron in LiMn\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{2} is substantially reduced compared with LiNiO\textsubscript{2} and LiMnO\textsubscript{2} compounds, and thus the JT effect is evidently suppressed. According to Table 2, similar results could be found for the case of LiMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2}. In LiMn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2}, the six Co-O bond lengths of
CoO$_6$ octahedron are still equal to each other, whereas the values of 2.096 Å is evidently larger than that in LiCoO$_2$ (1.938 Å), which imply Co ion reduction. The calculated Co-O bond lengths for LiMn$_{0.5}$Co$_{0.5}$O$_2$ are very close to that of the case for LiMn$_{0.75}$Co$_{0.25}$O$_2$ [36], where the obtained Co-O bond lengths are 2.05 Å. In addition, the equivalent Mn-O bond lengths can also be obtained with 1.956 Å, which is basically equal to the short Mn-O bond lengths in monoclinic LiMnO$_2$.

Different from the case of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ and LiMn$_{0.5}$Co$_{0.5}$O$_2$, the JT distortion can be found in LiCo$_{0.5}$Ni$_{0.5}$O$_2$. Although the six Co-O bond lengths are equal to 1.940 Å, which is almost the same as that in rhombohedral LiCoO$_2$ (1.938 Å), three types of bond lengths are formed for the six Ni-O bonds in the NiO$_6$ octahedron with 2.052, 1.965 and 1.892 Å for every two, respectively. Large differences among Ni-O bond lengths indicate the local structural distortion of the NiO$_6$ octahedron, and thus relating with JT effect. On the other hand, it is found that the differences of Ni-O bond lengths are somewhat smaller than that in monoclinic LiNiO$_2$, as listed in Table 2. As a result, the JT effect is mitigated when the Co atoms are incorporated into the LiNiO$_2$ structure.

### 3.2 Electronic structures

![Figure 2](image.png)

**Figure 2.** Total density of states of (a) LiMn$_{0.5}$Ni$_{0.5}$O$_2$, (b) LiCo$_{0.5}$Ni$_{0.5}$O$_2$, and (c) LiMn$_{0.5}$Co$_{0.5}$O$_2$ obtained from GGA+U method.

As the electrode materials, the electronic conductivity is important to their performance. The band gap is the key criterion. Figure 2(a)-(c) show the total density of states (TDOS) of LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiCo$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$, respectively. From Fig. 2, it is found that the three lithium mixed transition metal oxides all exhibit the semiconducting nature. The energy band gaps are
0.53, 0.23 and 0.33 eV for LiMn_{0.5}Ni_{0.5}O_2, LiCo_{0.5}Ni_{0.5}O_2 and LiMn_{0.5}Co_{0.5}O_2, respectively. The corresponding values are listed in Table 3. The calculated energy band gaps of basic LiMO_2 are also provided, which are 1.97, 0.31 and 0.79 eV for LiCoO_2, LiNiO_2 and LiMnO_2, respectively. Therefore, the band gaps of the mixed transition metal compounds are comparable to that of LiNiO_2, but smaller than that of LiMnO_2 and LiCoO_2. Although the DFT methods generally underestimate the band gap of the semiconducting materials to some extent, the small band gaps indicate that electronic conductivity of the three mixed transition metal compounds are not bad, especially better than LiCoO_2.

Table 3. Physical properties for the layered structures calculated with the GGA+U method. MM represents the magnetic momentum (in unit µ_B) of transition metal atom, and Eg is energy band gap (in unit eV).

<table>
<thead>
<tr>
<th>Compound</th>
<th>TM</th>
<th>Valence state</th>
<th>d-Electrons</th>
<th>MM (µ_B)</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn_{0.5}Ni_{0.5}O_2</td>
<td>Mn</td>
<td>+4</td>
<td>t_{2g}^3</td>
<td>3.1</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>+2</td>
<td>t_{2g}^6 e_g^1</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>LiCo_{0.5}Ni_{0.5}O_2</td>
<td>Co</td>
<td>+3</td>
<td>t_{2g}^6 e_g^1</td>
<td>0</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>+3</td>
<td>t_{2g}^6 e_g^1</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>LiMn_{0.5}Co_{0.5}O_2</td>
<td>Mn</td>
<td>+4</td>
<td>t_{2g}^3</td>
<td>3.2</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>+2</td>
<td>t_{2g}^5 e_g^1</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>LiCoO_2</td>
<td>Co</td>
<td>+3</td>
<td>t_{2g}^5 e_g^1</td>
<td>0</td>
<td>1.97</td>
</tr>
<tr>
<td>m-LiNiO_2</td>
<td>Ni</td>
<td>+3</td>
<td>t_{2g}^5 e_g^1</td>
<td>1.0</td>
<td>0.31</td>
</tr>
<tr>
<td>m-LiMnO_2</td>
<td>Mn</td>
<td>+3</td>
<td>t_{2g}^5 e_g^1</td>
<td>3.83</td>
<td>0.79</td>
</tr>
</tbody>
</table>

The detailed electron configurations of the transition metal atoms play an important role in the structural and magnetic properties. The projected density of states (PDOS) of the transition metal atoms could be conveniently used to study the electron configurations. The calculated PDOS of the transition metal atoms for different compounds are described as following. And the physical properties for the lithium transition metal oxides are listed in Table 3. In order to better compare, the results for LiMO_2 (M = Mn, Ni, Co) are also given.

A. LiMn_{0.5}Ni_{0.5}O_2

Figure 3 compares the Mn-3d PDOS in LiMnO_2 and LiMn_{0.5}Ni_{0.5}O_2 compounds. In LiMnO_2, the e_g orbital of Mn ion in the spin-up channel splits into two orbitals, namely dx^2-y^2 and dz^2 orbitals. The t_{2g} and dx^2-y^2 orbitals in the spin-up channel are occupied, whereas the dx^2-y^2 orbitals in this channel is empty. In addition, the t_{2g} and e_g orbitals in the spin-down channel are entirely empty.

Therefore, the electron configuration of Mn ion is (t_{2g})^3(e_g)^1, which clearly indicates that the valence state of Mn ion is +3, namely Mn^{3+}. Furthermore, the Mn^{3+} ions in LiMnO_2 are in high spin states, and thus the calculated magnetic moment (MM) is 3.83 µ_B, which is close to 4.0 µ_B. On the other hand, however, Mn ions in LiMn_{0.5}Ni_{0.5}O_2 have a (t_{2g})^3(e_g)^0 electron configuration, where the Mn-3d t_{2g} orbital in the spin-up channel are fully occupied and the other orbitals with both spin states are completely empty, indicating that the Mn ion transfers one electron to its neighboring atoms/ions.
and thus forms Mn$^{4+}$. Correspondingly, the magnetic moment of Mn ion in LiMn$_{0.5}$Ni$_{0.5}$O$_2$ is 3.1 $\mu_B$ (as seen in Table 3). As the Mn$^{4+}$ has no JT distortion, the Mn-O bond lengths are equal to each other in MnO$_6$ octahedron of LiMn$_{0.5}$Ni$_{0.5}$O$_2$, which could be used to explain the structural difference of MnO$_6$ octahedron in LiMnO$_2$ and LiMn$_{0.5}$Ni$_{0.5}$O$_2$.

Figure 3. Mn-3$d$ PDOS in LiMnO$_2$ and LiMn$_{0.5}$Ni$_{0.5}$O$_2$. The triplet and the duplet of the d-orbital are denoted as t$_{2g}$ and e$_g$, respectively. The Fermi levels are all set to be 0 eV.

Figure 4. Ni-3$d$ PDOS in LiNiO$_2$ and LiMn$_{0.5}$Ni$_{0.5}$O$_2$. The triplet and the duplet of the d-orbital are denoted as t$_{2g}$ and e$_g$, respectively. The Fermi levels are all set to be 0 eV.

Figure 4 compares the Ni-3$d$ PDOS in LiNiO$_2$ and LiMn$_{0.5}$Ni$_{0.5}$O$_2$ compounds. In LiNiO$_2$, the orbitals in the spin-up channel are similar to that of LiMnO$_2$, while the filled t$_{2g}$ orbitals and empty e$_g$ orbitals in the spin-down channel are formed, which is different from that of LiMnO$_2$. Obviously, the electron configuration of Ni ion in LiNiO$_2$ is (t$_{2g}$)$^6$(e$_g$)$^1$, and thus forming Ni$^{3+}$. The magnetic moment
of Ni$^{3+}$ is 1.0 $\mu$B. When Ni ions are incorporated into LiMnO$_2$ to form LiMn$_{0.5}$Ni$_{0.5}$O$_2$, a $(t_{2g})^6(e_g)^2$ electronic configuration could be found. Comparison with the electron configuration of Ni ion in LiNiO$_2$, Ni ion in LiMn$_{0.5}$Ni$_{0.5}$O$_2$ gains one electron, which is localized at the $dx^2-y^2$ orbital of the spin-up channel, thus forming Ni$^{2+}$. The magnetic moment of Ni$^{2+}$ is calculated to be 1.7 $\mu$B. With such an electronic configuration, the NiO$_6$ octahedron are no longer JT active, and the six Ni-O bonds have almost the same bond lengths. These results coincide with the previous LSDA calculations that are performed by Koyama et al. [15]

B. LiMn$_{0.5}$Co$_{0.5}$O$_2$

Figure 5. Mn-3d PDOS in LiMnO$_2$ and LiMn$_{0.5}$Co$_{0.5}$O$_2$. The triplet and the duplet of the $d$-orbital are denoted as $t_{2g}$ and $e_g$, respectively. The Fermi levels are all set to be 0 eV.

Figure 6. Co-3d PDOS in LiCoO$_2$ and LiMn$_{0.5}$Co$_{0.5}$O$_2$. The triplet and the duplet of the $d$-orbital are denoted as $t_{2g}$ and $e_g$, respectively. The Fermi levels are all set to be 0 eV.
Figure 5 shows the Mn-3d PDOS in LiMnO$_2$ and LiMn$_{0.5}$Co$_{0.5}$O$_2$ compounds. It is found that the results of Mn-3d PDOS in LiMn$_{0.5}$Co$_{0.5}$O$_2$ is extremely similar to that in LiMn$_{0.5}$Ni$_{0.5}$O$_2$. Therefore, the electron configuration of Mn ion in LiMn$_{0.5}$Co$_{0.5}$O$_2$ is (t$_{2g}$)$^3$(e$_g$)$^0$, and thus coming into being +4 valence state (Mn$^{4+}$) and 3.2 $\mu$B magnetic moment (as seen in Table 3). This result is also related with the equal Mn-O bond lengths in LiMn$_{0.5}$Co$_{0.5}$O$_2$ due to the JT inactivity of Mn$^{4+}$.

Due to the full occupation of t$_{2g}$ orbitals and non-occupation of e$_g$ orbitals for Co-3d orbitals in LiCoO$_2$ compound, regardless of spin channels (as seen in Fig. 6), which results in the (t$_{2g}$)$^6$(e$_g$)$^0$ electron configuration, the valence state and the magnetic moment are +3 and 0 $\mu$B, respectively, which are in agreement with the results obtained by Xiong et al. [37] After the mixing of the Mn and Co atoms in the lithium transition metal oxides with 1:1 atomic ratio, the Co-3d PDOS change a lot. All t$_{2g}$ and e$_g$ orbitals with spin down are filled, and two t$_{2g}$ orbitals (d$_{xy}$ and d$_{xz}$) with spin up are also occupied. However, the remanent orbitals in the spin-up channel are unoccupied. As a result, the (t$_{2g}$)$^5$(e$_g$)$^2$ electron configuration is obtained, which results in the +2 valence state and 2.7 $\mu$B. Combining with the Mn-3d characteristic in LiMn$_{0.5}$Co$_{0.5}$O$_2$, it can be found that charge transfers from Mn to Co. Our results are basically in agreement with that reported by Prasad et al. where the LiMn$_{0.75}$Co$_{0.25}$O$_2$ is mainly discussed [36].

C. LiCo$_{0.5}$Ni$_{0.5}$O$_2$

Figure 7 and Fig. 8 show the Co-3d and Ni-3d PDOS. For Co-3d PDOS, the occupation of orbitals in LiCo$_{0.5}$Ni$_{0.5}$O$_2$ is the same as that in LiCoO$_2$. The same thing happens for Ni-3d PDOS. This means that the electron configurations and magnetic moments of Co ion and Ni ion in the LiCo$_{0.5}$Ni$_{0.5}$O$_2$ compound do not change when compared with LiCoO$_2$ and LiNiO$_2$. Therefore, the (t$_{2g}$)$^6$(e$_g$)$^0$ and (t$_{2g}$)$^6$(e$_g$)$^1$ electron configurations for Co$^{3+}$ and Ni$^{3+}$ respectively in LiCo$_{0.5}$Ni$_{0.5}$O$_2$ can be obtained (as seen in Table 3), which is in accordance with the experimental observations [33]. In this case, no charge transfer between Co and Ni occurs.

![Figure 7](image-url)  
**Figure 7.** Co-3d PDOS in LiCoO$_2$ and LiCo$_{0.5}$Ni$_{0.5}$O$_2$. The triplet and the duplet of the d-orbital are denoted as t$_{2g}$ and e$_g$, respectively. The Fermi levels are all set to be 0 eV.
Figure 8. Ni-3d PDOS in LiNiO$_2$ and LiCo$_{0.5}$Ni$_{0.5}$O$_2$. The triplet and the duplet of the $d$-orbital are denoted as $t_{2g}$ and $e_g$, respectively. The Fermi levels are all set to be 0 eV.

3.3 Formation energy

In order to evaluate the thermodynamical stability of the lithium mixed transition metal oxides compared to the simple LiMO$_2$ ($M =$ Co, Mn, Ni) compound, we define the formation energy $\Delta E_{\text{form}}$ as following

$$\Delta E_{\text{form}}(\text{LiM}^{(1)}_{0.5}\text{M}^{(2)}_{0.5}\text{O}_2) = E(\text{LiM}^{(1)}_{0.5}\text{M}^{(2)}_{0.5}\text{O}_2) - \frac{1}{2}(E(\text{LiM}^{(1)}_{0.5}\text{O}_2) + E(\text{LiM}^{(2)}_{0.5}\text{O}_2)) \tag{1}$$

where $M^{(1)}$ and $M^{(2)}$ represent the different transition metal atoms, and $E(\text{LiM}^{(1)}_{0.5}\text{M}^{(2)}_{0.5}\text{O}_2)$, $E(\text{LiM}^{(1)}_{0.5}\text{O}_2)$ and $E(\text{LiM}^{(2)}_{0.5}\text{O}_2)$ are the total energies of LiM$_{0.5}$M$_{0.5}$O$_2$, LiM$_{0.5}$O$_2$ and LiM$_{0.5}$O$_2$, respectively.

Actually, according to the general alloy theory [38], the definition of formation energy represents a measure of the effective $M^{(1)}$ and $M^{(2)}$ interactions when they are mixed. If $\Delta E_{\text{form}}$ is negative, $M^{(1)}$ and $M^{(2)}$ have an effective attractive interaction and the system could be either mixed or ordered, which depends on the strength of the interaction and the preparation temperature. If $\Delta E_{\text{form}}$ is positive, however, local phase separation into $M^{(1)}$ and $M^{(2)}$ rich regions is energetically preferred.

The calculated formation energy of LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiCo$_{0.5}$Ni$_{0.5}$O$_2$ and LiMn$_{0.5}$Co$_{0.5}$O$_2$ are listed in Table 4. And the corresponding total energies for per formula unit are also given.
ase separation is relatively investigated to some extent. According to the Teller effect, which means that a strong ordering (attractive) tendency between Ni and Mn. Our calculated formation energy of LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) is the lowest (377 meV per formula unit) is the lowest, which means that a strong ordering (attractive) tendency between Ni and Mn. Our calculated formation energy of LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) is somewhat lower than that of previous study (-216 meV per formula unit) [31], which is probably because the selected structures for LiMnO\(_2\) and LiNiO\(_2\) in their study are different from our structures. In contrast to the case of LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), the formation energy of LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) is much higher, which is about -6 meV per formula unit. The high formation energy suggests that phase separation is relatively easy to occur though Co and Ni could be mixed in the LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\). Compared with LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) and LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), LiMn\(_{0.5}\)Co\(_{0.5}\)O\(_2\) has a modest formation energy of -62 meV per formula unit. According to the calculated formation energies, therefore, LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) is most likely to be prepared among the three lithium mixed transition metal oxides.

### 4. CONCLUSIONS

In summary, we study the structures, electronic structures, charge transfer, electronic configuration, valence states and magnetic moment of LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), LiMn\(_{0.5}\)Co\(_{0.5}\)O\(_2\) and LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) systems using the GGA+U methods within the DFT frame. Total energy calculations indicate that the rhombohedral structure is more stable than monoclinic one for all the three compounds LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), LiMn\(_{0.5}\)Co\(_{0.5}\)O\(_2\) and LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\). Bond length analysis shows that the Jahn-Teller effect disappears in Mn-containing compounds LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) and LiMn\(_{0.5}\)Co\(_{0.5}\)O\(_2\), while the Jahn-Teller distortion still exist in LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), but mitigated to some extent. According to the electronic results, charge transfers from Mn ion to Ni (Co) ion, which results in forming Mn\(^{4+}\) and Ni\(^{2+}\) (Co\(^{2+}\)), is the main reason of the suppression in LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) and LiMn\(_{0.5}\)Co\(_{0.5}\)O\(_2\). In LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), however, no charge transfer between Co and Ni could be observed. The TDOS results indicates that LiMn\(_{0.5}\)Ni\(_{0.5}\)O\(_2\), LiMn\(_{0.5}\)Co\(_{0.5}\)O\(_2\) and LiCo\(_{0.5}\)Ni\(_{0.5}\)O\(_2\) are all semiconducting with smaller energy band

### Table 4. The calculated total energies and formation energies of the formula units.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Total Energy (eV/f.u.)</th>
<th>Formation Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn(<em>{0.5})Ni(</em>{0.5})O(_2)</td>
<td>-23.661</td>
<td>-377</td>
</tr>
<tr>
<td>LiCo(<em>{0.5})Ni(</em>{0.5})O(_2)</td>
<td>-21.294</td>
<td>-6</td>
</tr>
<tr>
<td>LiMn(<em>{0.5})Co(</em>{0.5})O(_2)</td>
<td>-24.477</td>
<td>-62</td>
</tr>
</tbody>
</table>

As the lithium mixed transition metal oxides LiM\(_{0.5}\)M\(_{0.5}\)\(_{0.5}\)O\(_2\) with the lowest energy adopt the rhombohedral structures, the rhombohedral structures of LiM\(_{0.5}\)O\(_2\) and LiM\(_{0.5}\)O\(_2\) are also taken into account as the references.
gaps compared with the single phase LiMO$_2$ ($M = \text{Co, Ni, Mn}$). In addition, formation energy calculations show that LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Co$_{0.5}$O$_2$ and LiCo$_{0.5}$Ni$_{0.5}$O$_2$ compounds are thermodynamics stable when compared to the basic layered LiMO$_2$ ($M = \text{Co, Mn, Ni}$). Therefore, the mixture of cations in the lithium transition metal oxides could be formed, and the order for the mixture from easy to difficult is LiMn$_{0.5}$Ni$_{0.5}$O$_2$ > LiMn$_{0.5}$Co$_{0.5}$O$_2$ > LiCo$_{0.5}$Ni$_{0.5}$O$_2$.

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