A theoretical study of the structure distortion of Li$_2$FeSiO$_4$

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ABSTRACT

Li$_2$FeSiO$_4$ has potential to be used as the next generation large-scale Li-battery. While its structure is still under controversy: it has been reported an orthorhombic structure by one group, and another group reported a monoclinic structure. In this paper, the first-principle calculation results show that the total energies of the orthorhombic structure and monoclinic structure are so close to each other, which implies the two structures should exist at the same time. The most interesting point is that Li$_2$FeSiO$_4$ maybe exists as a more complicated structure in which the orientation of FeO$_4$-SiO$_4$ tetrahedron is randomly arranged upwards or downwards.

Key words: Li$_2$FeSiO$_4$, First-principle Calculation, Structure, Disorder.

INTRODUCTION

In order to be used in large scale batteries for transportation applications (such as EVs and HEVs), the cathode materials of Li-battery should be low cost, safety and environmentally friendly. LiFePO$_4$, firstly reported by Goodenough et. al. in 1996, is an alternative of the next generation cathode material which have the above listed characteristic [1,2]. Recently, a new silicate-based material, Li$_2$FeSiO$_4$, reported by Nytén et. al. in 2005, has a potential to be applied in large Li-battery as LiFePO$_4$ [3]. Li$_2$FeSiO$_4$ have large theoretical capacity of about 330mAh g$^{-1}$ with M$^{2+}$/M$^{4+}$ two-electron reaction, and many researches are focused it [4-16].

For the crystallographic structure of Li$_2$FeSiO$_4$, Nytén et al. firstly performed Rietveld refinements for Li$_2$FeSiO$_4$ with a powder X-ray profile, and they reported that Li$_2$FeSiO$_4$ has an orthorhombic structure with $Pmn2_1$ symmetry[3]. The orthorhombic structure is accepted by some research group in the follow years [4-7]. Nishimura et. al. re-performed Rietveld refinements for Li$_2$FeSiO$_4$ with a high resolution powder X-ray profile based on a monoclinic structure with $P2_1$ symmetry [11]. The monoclinic structure also accepted by some group [14–16].

In fact, the orthorhombic ($Pmn2_1$) and monoclinic ($P2_1$) structures are very close to each other, and it is very difficult to distinguish the two structure with the X-ray diffraction technique, as the detailed discussion in part III of this paper.

In the paper, the results of the first-principle calculation show that the calculated total energies of the orthorhombic structure and the monoclinic structure are very close to each other, which implies the two structures could exist at the same time.

Calculation Method

The calculations reported in this work were performed using the VASP (Vienna Ab-initio Simulation Package) code [17], which is based on density functional theory (DFT) [18-19]. The projected-augmented wave (PAW) approach is used for ion–electron interactions [20-21]. The exchange-correlation energy of electrons is described in the generalized gradient approximation (GGA) with the functional parameterization of PBE [22]. The electron spin polarization is considered. The tetrahedron method with Bloch is used, which could give a good precision of total
energy [23]. The criterion of at least $1.0 \times 10^{-5}$ eV per unit cell is placed on the self-consistent convergence of the total energy. The lattice parameters (cell shape) and atom positions are fully relaxed. In order to increase the precision, the precision controlling parameter “PREC” is set to the highest level, which could guarantee that “the absolute energies are converged to a few meV” [23]. Because that LDA+U or GGA+U could take into account the strong correlation between Fe-3d electrons, in this work, the GGA+U scheme described by Liechtenstein et al. [24] is implemented and the value of $U_{\text{eff}}$ (U=J) for Fe-3d orbital is 4.3 eV.

RESULTS AND DISCUSSIONS

Relation between Orthorhombic and Monoclinic Structures. The orthorhombic structure and the monoclinic structure are presented in Figure 1a-b, respectively. The relationship between the orthorhombic lattice and the monoclinic lattice is described in Figure 2. The (001) plane of orthorhombic lattice (the original structure) is shown in Figure 2a, and $a$ and $b$ are the lattice vectors. When the angle between $a$ and $b$ is not equal to 90°, the lattice loses some symmetry operations and changes into monoclinic structure (the transformed structure), whose lattice vector is set up as $a'$ and $c'$ as presented in Figure 2b.

Relative Stability of Orthorhombic and Monoclinic Structure. The calculated lattice constant of the orthorhombic structure under GGA+U scheme are $a=6.2859\,\text{Å}, b=5.3674\,\text{Å}$, and $c=4.9998\,\text{Å}$, which is well consistent with the experimental values measured by Nyvén et al. [3] ($a=6.266(1)\,\text{Å}, b=5.329(1)\,\text{Å}$, and $c=5.015(1)\,\text{Å}$), and the theoretical values reported by Larsson et al. [5] ($a=6.313\,\text{Å}, b=5.393\,\text{Å}$, and $c=4.979\,\text{Å}$). For the monoclinic structure, the calculated lattice constant, $a'=8.2511\,\text{Å}, b'=5.1075\,\text{Å}, c'=8.2523\,\text{Å}$ and $\beta'=99.1824^\circ$, which well consist with Nishimura et al. [11] experimental results [15]. It means the present calculation is reliable. Poltiaev et al. [15] mentioned that the Li-Si distance in the orthorhombic structure was too short. Their analysis was based on the X-ray diffraction results of Nyvén et al. [3], in which the lithium position may be is not so exact.

If GGA is applied to calculate the total energy difference between two structures with different symmetry, some error in the order of 10 meV is induced at the same time [25]. Then when the total energy difference between orthorhombic and monoclinic Structure of Li-FeSiO$_4$ is very small, it could not be directly calculated under GGA scheme. Fortunately, the orthorhombic structure could be transformed into a corresponding monoclinic structure with the relationship $a'=a+b, b'=c$ and $c'=a+b$, which is presented in Figure 2 in this paper, and all FeO$_2$ and SiO$_4$ tetrahedrons should be keep upwards in the transform. After full relaxation (including the cell shape and atom position), the transformed structure’s parameters are $a'=8.2657\,\text{Å}, b'=4.9998\,\text{Å}, c'=8.2657\,\text{Å}$ and $\beta'=99.0136^\circ$, respectively. The corresponding orthorhombic structure constant calculated with the operation $a=(c'-a')/2, b=(c'+a')/2$ and $c=b'$, and the values are $a=6.2859\,\text{Å}, b=5.3674\,\text{Å}, c=4.9998\,\text{Å}$, and $\alpha=\beta=\gamma=90^\circ$, respectively, which rigidly consists with the directly calculated orthorhombic structure parameters as mentioned above ($a=6.2859\,\text{Å}, b=5.3674\,\text{Å}, c=4.9998\,\text{Å}$).
Then to compare the total energies of the orthorhombic (Pmn2₁) and monoclinic (P2₁) structure cited in the paper could be replaced to compare the two monoclinic structures: one is transformed from the orthorhombic structure; the other is the real monoclinic structure with P2₁ symmetry. As shown in Table 1, the total energy difference per formula between the two structures is 6meV (GGA) or 4meV (GGA+U). The values are too small for DFT calculation, and it implies that the orthorhombic phase and the monoclinic phase could be exist at the same time.

Table 1 the relative total energy per formula of the structures, (for all the calculation, the electron spin polarization is considered)

<table>
<thead>
<tr>
<th></th>
<th>Orthorhombic</th>
<th>Monoclinic</th>
<th>S₁</th>
<th>S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>0</td>
<td>-6</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>GGA+U</td>
<td>0</td>
<td>-4</td>
<td>11</td>
<td>22</td>
</tr>
</tbody>
</table>

Orientation disorder of FeO₄-SiO₄ tetrahedrons. As the above discussion, the orthorhombic and monoclinic structures could exist at the same time, and in each of the two structures, FeO₄ and SiO₄ tetrahedrons form one-dimensional corner shared chains along [100] axis. In the orthorhombic structure, all tetrahedrons in the chain are orientated in one direction as shown in Figure 3b, which is specified as μ chain, and the lattice configuration in (001) plane is presented in Figure 3a, in which the FeO₄-SiO₄ tetrahedrons in each unit cell are upward. In the monoclinic structure, the tetrahedrons in the one-dimension chain periodically take opposite orientations as shown in Figure 3d, which is specified as ν chain. Its lattice configuration is presented in Figure 3c, and the FeO₄-SiO₄ tetrahedrons in the unit cell of the original lattice periodically take opposite orientation which looks like black-and-white mosaic picture. The heavy lines are the boundary of the monoclinic structure.

In order to evaluate other configurations, two structures are constructed based on the original lattice. One has a 2×2×1 supercell and denoted as S₁, as the zone surrounded by the heavy lines in Figure 4e; the other has a 3×2×1 supercell and denoted as S₂, as shown in Figure 4f. The relative total energies per formula of the two structures are listed in Table 1, which are very close to that of the orthorhombic or monoclinic structure. Then beyond the pure the orthorhombic or monoclinic structure, Li₂FeSiO₄ may exist as some more complex structure, such as S₁ (the above 2×2×1 superlattice) and S₂ (the above 3×2×1 superlattice).
S1 contains two-type chains, μ and ν, which are periodically arranged along [010] direction. Then the structure could be looked as a combination of the orthorhombic and monoclinic structure. In S2, there are also two-type chains: one is μ, the other is ξ, which is shown in Figure 4g. The ξ chain is different from μ and ν chains, and its periodic unit contains two upward FeO4-SiO4 tetrahedrons and one downward FeO4-SiO4 tetrahedron. The structures of S1 and S2 mention that the orientation arrangement of the FeO4-SiO4 tetrahedron does not change the total energy largely, i.e., the order the upward FeO4-SiO4 tetrahedron and downward FeO4-SiO4 tetrahedrons in Li2FeSiO4 could be randomly arranged.

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