Communication

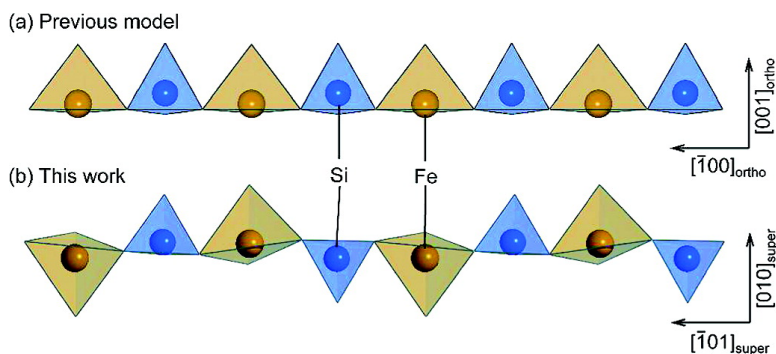# Structure of LiFeSiO

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Structure of Li$_2$FeSiO$_4$

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Chemical energy storage using batteries will become increasingly important for future environmentally friendly ("green") societies. Rechargeable lithium-ion batteries are the most advanced energy storage devices, but their application has been limited to portable electronics devices due to cost and safety issues.[1] The significant bottleneck is in the conventional active cathode material such as Li$_x$CoO$_2$, which includes the expensive Co element and involves a safety risk for explosive electrolyte oxidation.

State of the art lithium iron orthophosphate (LiFePO$_4$) technology has now opened the door for lithium ion batteries to take their place in large-scale applications such as plug-in hybrid vehicles. A high level of safety, significant cost reduction, and greater power generation are on the verge of being guaranteed for the most advanced energy storage system. Many noticeable features of this olivine-type material, such as high stability and reasonably high redox potential, are provided by the orthophosphate (PO$_4$)$^{3-}$ anion, which has a relatively strong P−O covalent bond.[2]

Similar design strategies used for LiFePO$_4$ have been applied to explore materials of the orthosilicate family Li$_2M$SiO$_4$, (M = Mn, Fe, Co) which have been distinguished by the possible M^{4+}/M^{2+} two-electron reaction by removal of all lithium atoms with a large theoretical capacity of *ca.* 330 mAh g^{-1}.[3] Recently, lithium iron orthosilicate, Li$_2$FeSiO$_4$, with a LISICON (LIthium Super Ionic CONductor) based structure was reported to exhibit reversible electrochemical activity of *ca.* 166 mAh g^{-1}.[4] Additionally, as this type of material generally allows a wide range of solid solution with various composition and species, Li$_2$FeSiO$_4$ is an exciting platform for the development of next generation cathode materials.

Although crystal structure is the predominant information for material design and study of the reaction mechanism, the structure of Li$_2$FeSiO$_4$ is still unclear. Nytén et al. performed Rietveld refinements with a conventional powder X-ray diffraction profile of pristine Li$_2$FeSiO$_4$ and proposed a β-Li$_3$PO$_4$-based structure with $Pmn2_1$ symmetry. In this proposed structure, all the cations occupy half of the tetrahedral sites in a slightly distorted hcp oxygen array, forming a corner-sharing network of tetrahedra (trigonal pyramid) with an identical upward direction. This structural model has been used by most of the other groups working on this material.[5] However, the analysis and the structural model itself include three major important problems: (i) a significant amount of Li$_2$SiO$_3$ impurity was included in the pristine sample; (ii) there are a large number of unidentified diffraction peaks, which were unable to be indexed to $Pmn2_1$; and (iii) the Li−Si distance is too short as pointed out by Politaev et al.[6]
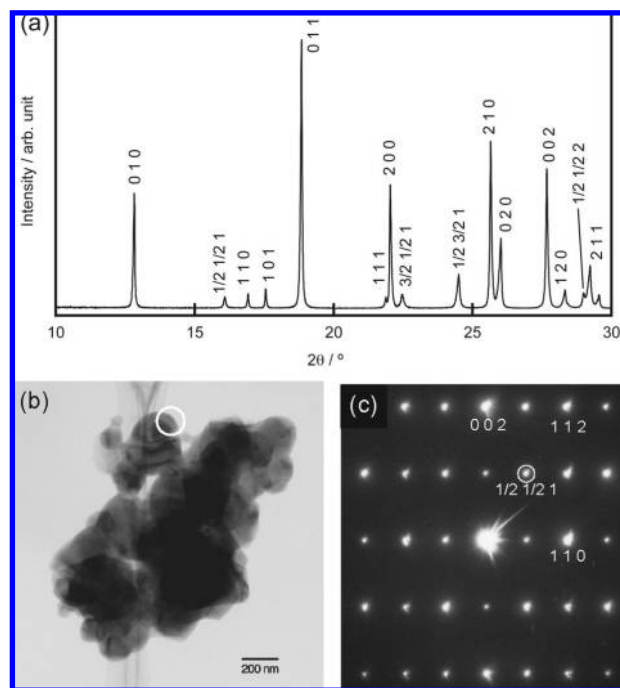

Figure 1. (a) Synchrotron XRD pattern indexed with the β-Li$_3$PO$_4$-based fundamental lattice, (b) typical TEM image, and (c) single crystalline SAED pattern of the $^{1}_{10}$$_{\text{ortho}}$ zone axis, taken for a crystallite marked in (b).

To address these issues, higher quality Li$_2$FeSiO$_4$ samples were prepared by sintering at 1073 K and high-resolution synchrotron XRD (HR-XRD) experiments were performed at the High Energy Accelerator Research Institute (KEK) Photon Factory (PF) BL-4B$_2$, Japan.[7] Analysis of the HR-XRD pattern from a highly monochromatic beam with a resulting diffraction peak having a small full width at half-maximum led us to identify the correct cell configuration and refine the structure with much better reliability. The low angle region of the HR-XRD pattern indexed with the unit cell based on the $Pmn2_1$ model is shown in Figure 1a. Several extra reflections, having previously been assigned as unidentified impurity phases, can be clearly indexed as $h/2$ $k/2$ l and should not be excluded to determine the accurate structure. There is no ambiguity that a larger asymmetric unit should be set along the $a−b$ plane in the $Pmn2_1$ model. Figure 1b shows a typical bright field transmission electron microscope (TEM) image and a selected area electron diffraction (SAED) pattern of the [1$\bar{1}$0]$_{\text{ortho}}$ zone axis. The extra spots in the single crystalline SAED pattern also confirm the existence of a supercell and are consistent with the powder HR-XRD results.

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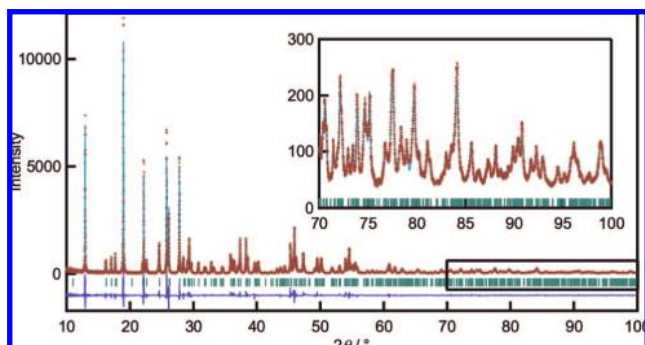[§] Yamaguchi University.

Figure 2. Rietveld refinement pattern of the X-ray diffraction data for Li_2FeSiO_4.

With respect to the systematic extinction and observed reflections, which is carefully confirmed by the powder HR-XRD and SAED patterns of various zone axes (summarized in the Supporting Information (SI)), two types of unit cell configuration and three space groups were considered as candidates: a primitive monoclinic lattice with $P2_1$ or $P2_1/m$ symmetry ($\boldsymbol{a}_{super} = (-\boldsymbol{a} + \boldsymbol{b})$, $\boldsymbol{b}_{super} = \boldsymbol{c}$, $\boldsymbol{c}_{super} = (\boldsymbol{a} + \boldsymbol{b})$) and a C-centered orthorhombic lattice with $C222_1$ symmetry ($\boldsymbol{a}_{super} = 2\boldsymbol{a}$, $\boldsymbol{b}_{super} = 2\boldsymbol{b}$, $\boldsymbol{c}_{super} = \boldsymbol{c}$). $P2_1$ symmetry with a monoclinic supercell with $a = 8.22898(18)$ Å, $b = 5.02002(4)$ Å, $c = 8.23335(18)$ Å, $\beta = 99.2027(5)°$ was adopted, as the $P2_1/m$ symmetry did not allow the construction of a reasonable structural model and the $C222_1$ based model gave a rather large value for the reliability factor of integrated intensities R_I (>8%).

Rietveld refinement was performed with Topas-Academic Ver. 4.1, and the final calculated, observed, and residual patterns are shown in Figure 2. The details of refinement are summarized in the SI. The fit reliability was converged to give $R_{wp} = 9.67\%$, $R_p = 9.79\%$, $\chi^2 = 0.871$, $R_I = 3.14\%$ $R_F = 0.83\%$. Very low R_I and R_F (reliability factor of structure factors) strongly support the new structural model. The origin of the relatively high weighted reliability factor R_{wp} is not an incomplete structure model but rather a peak asymmetry. This indicates that a small amount of systematic structural disorder, such as stacking faults with some cation displacement, is involved, as confirmed by lattice image observations by TEM (SI). However, this should not cause a significant problem for the overall structure refinement, because the probability of such displacement is less than a few percent, which is also confirmed by the TEM observations (see SI).

The refined crystal structure and structure parameters are shown in Figure 3 and in the SI, respectively, where the Li–Si distances are reasonably long. The crystal structure is illustrated using the computer program VESTA.[8] The intensities of the supercell reflection were successfully explained by considering the modified cation arrangement in the new set of monoclinic unit cell. The structural modulation to form the supercell originates from the availability of vacant tetrahedral sites in the pseudohexagonal packing of oxygen atoms. This leads to a variation in the orientation of trigonal pyramids, particularly those in the corner shared one-dimensional FeO_4–SiO_4 chains along the $[\bar{1}01]_{super}$ direction. In the present model, FeO_4/SiO_4 trigonal pyramids periodically take opposite orientations as shown in Figure 3b. This shows a striking contrast to the previous orthorhombic model, where the orientations of all trigonal pyramids are identical. This structure is also obtained
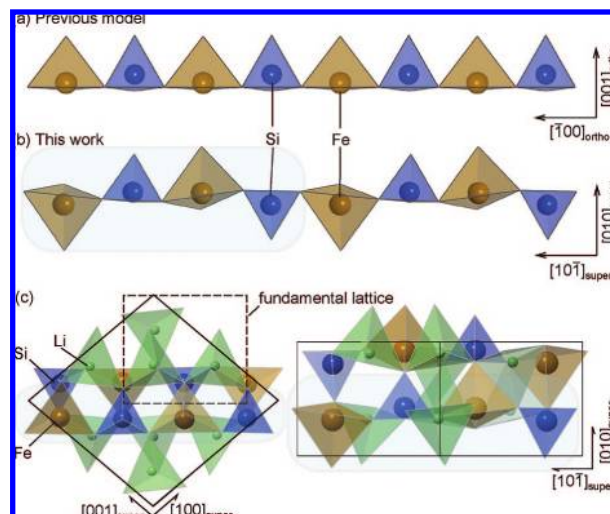

Figure 3. Corner-shared FeO_4–SiO_4 one-dimensional chain in (a) the previous model and (b) the proposed model in this work. (c) Refined crystal structure of Li_2FeSiO_4.

with a lower synthesis temperature of 873 K, as confirmed by Rietveld refinement given in the SI.

In summary, a valid crystal structure of Li_2FeSiO_4 was determined by combined HR-XRD and TEM approaches. A definitive starting point is now given for advanced material design and battery reaction mechanism studies of this important class of cathode materials for lithium batteries.

Supporting Information Available: Experimental methods, crystallographic information, electron density distribution, electrochemical properties, SAED and HR-TEM results. This material is available free of charge via the Internet at http://pubs.acs.org.

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