Room temperature synthesis and phase transformation of lithium phosphate Li$_3$PO$_4$ as solid electrolyte

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1. Introduction

Lithium phosphate Li$_3$PO$_4$ is one of the attractive solid electrolyte materials due to its wide electrochemical potential, strong glass-forming capability, and simple composition for the next generation all-solid-state lithium battery (LIB) applications [1–4]. Especially, an amorphous form of Li$_3$PO$_4$ exhibits low electrode/solid electrolyte interfacial resistance in use as solid electrolyte for all-solid-state thin-film LIB [5–7].

There are three crystalline forms of Li$_3$PO$_4$: α-, β-, and γ-type structures depending on the stable temperature region. The low-temperature β-form of Li$_3$PO$_4$ is stable below 400°C and undergoes a phase transition to γ-type structure irreversibly [8]. Furthermore, γ-Li$_3$PO$_4$ reversibly undergoes a phase transition to α-Li$_3$PO$_4$ above 1167°C [8]. A phase relationship between β- and γ-Li$_3$PO$_4$ phases has been reported in the literatures. Zemann first determined the crystal structure of γ-Li$_3$PO$_4$, as shown in Figure 1b) [9]. Tatré reported that the sample prepared by hydrothermal treatment at 245°C for 4 days crystallized in the low-temperature β-form of Li$_3$PO$_4$ for the first time [10]. Keff er et al. described the crystal structure of β-Li$_3$PO$_4$ (Figure 1a) using the single-crystal sample prepared by neutralizing a slurry of lithium carbonate by slowly adding phosphoric acid [11]. They also reported the phase transformation from β- to γ-Li$_3$PO$_4$ at 502°C irreversibly by differential thermal analysis [11]. On the other hand, a continuous and martensitic transformation phenomenon between 340°C and 410°C was investigated by ex-situ X-ray diffraction technique using the commercial grade of β-Li$_3$PO$_4$ sample having the particle grain size approximately between 0.1 μm and 5 μm [12]. The relative intensities of the 002 reflection peaks for these phases were used as a measurement of the degree of the β/γ transformation. Moreover, Popović et al. reported the β/γ transition temperature above 580°C [13]. From these situations, the reported transition temperatures vary in a wide range of temperatures from 340°C to 580°C. This may be affected by the different synthetic procedures of β-Li$_3$PO$_4$ at low temperatures, however, unfortunately, chemical information for these samples could not be reported in the literatures [12,13]. Recently, Ayu et al. re-investigated the crystal structure of β-Li$_3$PO$_4$ using the sample prepared by reaction of LiOH and H$_3$PO$_4$ at 40°C [14]. However, they have never revealed the structure transformation from β- to γ-Li$_3$PO$_4$ using the as-prepared β-Li$_3$PO$_4$ sample.

The β-Li$_3$PO$_4$ has an ordered wurtzite structure in which lithium and phosphorus are ordered over one set of tetrahedral sites, as shown in Figure 1a) [11]. The γ-Li$_3$PO$_4$ has a closely related structure with LiO$_2$ and PO$_4$ tetrahedra (Figure 1b) [9]. The structural difference between β- and γ-Li$_3$PO$_4$ can be explained by the arrangement of both the PO$_4$ and LiO$_2$ tetrahedra to
2. Experimental procedure

In the present study, the sample preparation was performed at room temperature without heating. The starting materials were LiOH·H$_2$O (Kojundo Chemical Lab. Co., Ltd.) and NH$_4$H$_2$PO$_4$ (FUJIFILM Wako Pure Chemical Corp.). First, LiOH·H$_2$O was dissolved in deionized water. Then, NH$_4$H$_2$PO$_4$ powder was put into the LiOH solution with magnetic stirring for 10 min. The resulting precipitate was collected by filtration and dried in a vacuum at room temperature overnight. To reveal the structure transformation upon heating, the obtained Li$_3$PO$_4$ sample was heated in alumina crucibles at 50°C, 100°C, 150°C, 200°C, 250°C, 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, and 650°C for 1 h using an oven or electric furnace in air.

The phase identification of the obtained samples was examined using the powder X-ray diffraction (XRD, Rigaku SmartLab) at room temperature with Cu Kα$_1$ radiation (λ = 1.54056 Å; operating conditions: 40 kV, 30 mA) equipped with Johansson-type X-ray mirror over a 2θ range from 5° to 100°. The lattice parameters were determined by Rietveld analysis using the reported structural data for β-Li$_3$PO$_4$ [11] and γ-Li$_3$PO$_4$ [15]. The refinement software Jana2006 [16] was used for the calculations. The particle size and morphology of the samples were observed by field emission-scanning electron microscope (FE-SEM, Hitachi S-4300) at an accelerating voltage of 5 kV. Chemical composition was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 720-ES).

3. Results and discussion

3.1. Preparation of the β-Li$_3$PO$_4$ phase at room temperature

Figure 2 shows powder XRD pattern of the Li$_3$PO$_4$ sample after vacuum-drying at room temperature. All the diffraction peaks were attributed to orthorhombic β-Li$_3$PO$_4$ structure having the space group of Pmn2$_1$, and impurities were not detected in the XRD pattern. The lattice parameters were determined to be $a = 6.1281(6)$ Å, $b = 5.2674(5)$ Å, $c = 4.8923(2)$ Å, and $V = 157.92(2)$ Å$^3$. These values were in good agreement with the previous results, e.g. $a = 6.1295(2)$ Å, $b = 5.2546(2)$ Å, and $c = 4.8705(1)$ Å [14]. Chemical composition of the Li$_3$PO$_4$ sample was analyzed by ICP-OES. The analytical ratio of Li:P was determined to be 3.11:1 suggesting the stoichiometric chemical composition of Li$_3$PO$_4$ for the present sample. These results indicated that the single-phase sample of β-Li$_3$PO$_4$ can be easily prepared at room temperature without heating in this study.
Figure 3 shows the particle morphology of Li₃PO₄ prepared at room temperature, which is observed using a field emission scanning electron microscope (FE-SEM). The secondary particles were spheres of submicron size (0.2–0.3 μm). In addition, very small primary particles (spherical particle size: 20–30 nm) gather on the surface of the secondary particles were observed. Considering the effects of particle size and electrostatic force on the aggregation process, it is presumed that these small primary particles aggregate to form larger secondary particles in the vacuum drying process. Accordingly, the present synthetic procedure enables to produce nano-sized particles of the β-Li₃PO₄ phase at room temperature.

3.2. Preparation of the γ-Li₃PO₄ phase at 650°C

Figure 4 presents powder XRD pattern of the sample after heating the as-prepared β-Li₃PO₄ sample at 650°C for 1 h in air. Compared to the XRD pattern of β-Li₃PO₄ (Figure 2), new diffraction peaks corresponding to the γ-Li₃PO₄ structure at 2θ = 19.9°, 28.7°, 29.2°, 34.5°, and 35.5° can be observed (Figure 4). This fact clearly indicated that the β-Li₃PO₄ phase was transformed to the γ-Li₃PO₄ phase by heating the present β-Li₃PO₄ phase at 650°C. Accordingly, all the diffraction peaks can be explained as a single phase of the γ-Li₃PO₄ structure. The orthorhombic lattice parameters in the space

Figure 2. Powder XRD pattern of the β-Li₃PO₄ sample prepared at room temperature.

Figure 3. FE-SEM image of the β-Li₃PO₄ sample prepared at room temperature.

Figure 4. Powder XRD pattern of the sample after heating the as-prepared β-Li₃PO₄ sample at 650°C for 1 h in air.
group of \( Pmn b \) were refined to be \( a = 6.12569(5) \) \( \text{Å} \), \( b = 10.48730(9) \) \( \text{Å} \), \( c = 4.92957(4) \) \( \text{Å} \), and \( V = 316.685(4) \) \( \text{Å}^3 \). These values were in good agreement with the previous results, e.g. \( a = 6.1113(1) \) \( \text{Å} \), \( b = 10.4612(2) \) \( \text{Å} \), and \( c = 4.9208(1) \) \( \text{Å} \) \[15\].

Figure 5 shows the FE-SEM image for the \( \text{Li}_3\text{PO}_4 \) sample after heating at 650°C. The spherical secondary particle morphology having the submicron order of 0.2–0.3 \( \mu \text{m} \) was maintained unchanged from the as-prepared sample, as shown in Figure 3. Moreover, very small spherical primary particles with the size of ca. 30 nm on the surface of the secondary particles were also observed even after 650°C heating. Consequently, the nano-sized particles of the \( \gamma \)-type \( \text{Li}_3\text{PO}_4 \) can be prepared utilizing the present synthetic route.

3.3. Phase change upon heating in the temperature range from 25°C to 650°C

The structural transformation upon heating of the present \( \beta \)-\( \text{Li}_3\text{PO}_4 \) sample was demonstrated by ex-situ XRD measurements using the heated samples in the temperature range from 25°C to 650°C. Figure 6 shows the powder XRD patterns of the present \( \text{Li}_3\text{PO}_4 \) samples at elevated temperatures. As elevating the temperature, the peak width and intensity changed sharply. No impurity phases were observed in these patterns. Figure 7 shows the magnified XRD patterns for these samples. Additional peaks, e.g. 2\( \theta \) = 19.9° (indicated by an arrow) suggesting the \( \gamma \)-type structure can be observed above 450°C. This

Figure 4. Powder XRD pattern of the \( \gamma \)-\( \text{Li}_3\text{PO}_4 \) phase after heating at 650°C for 1 h.

Figure 5. FE-SEM image of the \( \gamma \)-\( \text{Li}_3\text{PO}_4 \) phase after heating at 650°C for 1 h.
fact indicated that the phase transformation temperature from β- to γ-Li$_3$PO$_4$ was around 450°C for the present Li$_3$PO$_4$ sample.

Figure 8 and Table 1 summarize the lattice parameters for the present Li$_3$PO$_4$ samples. It should be noted the refined lattice parameters confirmed the continuous phase change in the temperature range between 25°C and 650°C. Especially, a continuous change in the c-axis length upon heating is characteristics. The contraction for the c-axis length for the β-Li$_3$PO$_4$ phase was observed between 150°C and 350°C. In fact, the peak position of 002 reflections drastically changed at these temperatures, as shown in Figure 7. These facts may be explained the continuous local structural change in both β- and γ-type Li$_3$PO$_4$. We are now examining the precise structure determination upon heating using synchrotron XRD data and will publish in another paper.

4. Conclusion

In summary, we successfully prepared the β-Li$_3$PO$_4$ sample utilizing the room temperature reaction without heating. The obtained sample showed nano-sized particle morphology of 20–30 nm that is suitable for the fabrication of dense solid electrolyte in all-solid-state lithium battery application. The phase

![Figure 6](image1)

Figure 6. Powder XRD patterns of the as-prepared and heated Li$_3$PO$_4$ samples in the temperature range from 25°C to 650°C.

![Figure 7](image2)

Figure 7. Powder XRD patterns in the 2θ range between 25° and 40° of the as-prepared and heated Li$_3$PO$_4$ samples.
transformation temperature from $\beta$- to $\gamma$-Li$_3$PO$_4$ was confirmed around 450°C for the present Li$_3$PO$_4$ sample. In addition, the present $\beta$-Li$_3$PO$_4$ sample exhibited a continuous structural change upon heating in the temperature range from 25°C to 650°C. Even for the $\beta$-Li$_3$PO$_4$ phase, the lattice volume contraction was observed between 150°C and 350°C. We are now attempting to determine the precise crystal structure so as to reveal the mechanism of the continuous lattice parameter change upon heating.

**Acknowledgments**

We express our gratitude to Dr. Yoshitaka Matsushita of National Institute for Materials Science (NIMS) for his experimental help and discussions regarding the structure change upon heating.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

| Temperature (°C) | Structure | $a$ (Å)    | $b$ (Å)    | $c$ (Å)    | $V$ (Å$^3$) |
|-----------------|-----------|------------|------------|------------|-------------|
| 25              | $\beta$-type | 6.1281(6)  | 5.2674(5)  | 4.8923(2)  | 157.92(2)   |
| 50              | $\beta$-type | 6.1287(8)  | 5.2727(5)  | 4.8913(3)  | 158.06(3)   |
| 100             | $\beta$-type | 6.1259(6)  | 5.2688(5)  | 4.8896(2)  | 157.82(2)   |
| 150             | $\beta$-type | 6.1244(5)  | 5.2590(4)  | 4.8864(2)  | 157.19(2)   |
| 200             | $\beta$-type | 6.1329(4)  | 5.2588(3)  | 4.8781(2)  | 157.33(2)   |
| 250             | $\beta$-type | 6.1375(4)  | 5.2558(3)  | 4.8752(1)  | 157.26(1)   |
| 300             | $\beta$-type | 6.1344(6)  | 5.2586(5)  | 4.8738(2)  | 157.22(2)   |
| 350             | $\beta$-type | 6.1326(4)  | 5.2573(3)  | 4.8763(2)  | 157.22(2)   |
| 400             | $\beta$-type | 6.1336(6)  | 5.2615(5)  | 4.8836(3)  | 157.60(2)   |
| 450             | $\gamma$-type | 6.1361(3)  | 10.5151(5) | 4.8969(1)  | 315.95(3)   |
| 500             | $\gamma$-type | 6.1342(3)  | 10.5086(4) | 4.9101(1)  | 315.52(3)   |
| 550             | $\gamma$-type | 6.1315(2)  | 10.5008(3) | 4.9187(1)  | 316.69(2)   |
| 600             | $\gamma$-type | 6.1271(1)  | 10.4902(2) | 4.9244(7)  | 316.518(9)  |
| 650             | $\gamma$-type | 6.1256(5)  | 10.4873(9) | 4.92957(4) | 316.685(4)  |

Figure 8. Lattice parameters for the as-prepared and heated Li$_3$PO$_4$ samples in the temperature range from 25°C to 650°C.
Funding
A part of this work was supported by Japan Science and Technology Agency (JST) ALCA-SPRING Grant Number [JPMJAL1301, Japan].

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