Surface crystallization tendency of Na$_2$FeP$_2$O$_7$ glass

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Crystallization behavior of bulk Na$_2$FeP$_2$O$_7$ glass produced by a melt-quenching method was examined. The valence state of iron is 76% Fe$^{2+}$ in glass matrix by using Fe(II)O and carbon crucible during glass melting. After mirror polishing crystallization was performed. Surface crystallization of triclinic Na$_2$FeP$_2$O$_7$ was confirmed by heat-treatment of the bulk sample in a nitrogen atmosphere. The outermost surface of crystallized sample have no crystal orientation but, strong (122) and (133) orientation was confirmed by X-ray diffraction of surface crystalized glass obtained after polish 10 $\mu$m thick. This technique may be effective to control ionic conductive channel in phosphate derived active material for secondary batteries.

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1. Introduction

Recently, sodium ion batteries are expected as one of the alternative battery of a lithium ion battery. The reason for the interests of sodium ion battery is that sodium is similar in nature with lithium, because it is a low-cost elements present inexhaustible in the earth’s crust. 1)-3) Although the typical of phosphates are proposed as cathode active materials, 4) anode active materials 5) as well as solid electrolytes 6) for lithium ion battery, recently, some of phosphates are also proposed as promising active materials for cathode, 7)-10) anodes, 11) and solid electrolytes 12)-14) in sodium ion batteries.

Phosphoric acid is well known as good glass-former. Present author group propose glass-ceramics route to fabricate active materials for lithium ion batteries 15)-18) and sodium ion batteries 19)-22). We found that Na$_2$FeP$_2$O$_7$ crystal successfully synthesized from the precursor glass by conventional heat-treatment and clarified its electro-chemical activity as cathode active materials in sodium ion batteries. 23) We also reported the other Na$_2$MnP$_2$O$_7$ (M = Fe, Mn) glass and glass-ceramics prepared by melt-quenching method 23)-27). Triclinic Na$_2$FeP$_2$O$_7$ single phase was successfully obtained by conventional heat-treatment of precursor glass above crystallization temperature. 19), 23), 24) Triclinic Na$_2$FeP$_2$O$_7$ also obtained by substitution of Na site by Fe and the discharge voltage and capacity is obtained as 2.9 V, 90 mAh/g at 0.1 C in room temperature. Furthermore, Na$_2$MP$_2$O$_7$ precursor glasses are also active as the cathode material; hence, compositional range to form active material in the system NaO$_{0.5}$–FeO–PO$_{2.5}$ is broad. 24)

Meanwhile Na$_2$MnP$_2$O$_7$ is expected a high discharge potential compared to Na$_2$FeP$_2$O$_7$. 25), 26), 28) The present authors have succeeded in the selective crystallization of two different polymorphism from Na$_2$MnP$_2$O$_7$ precursor glass. 25) In the electrochemical characterization of pseudo binary Na$_2$MnP$_2$O$_7$–Na$_3$FeP$_2$O$_7$ glass-ceramics, Mn$^{3+}$/ Mn$^{2+}$ redox was activated in layered Na$_2$Mn$_{0.75}$Fe$_{0.25}$P$_2$O$_7$ glass-ceramic cathodes at room temperature.

In the previous study, the crystallization mechanism of Na$_2$FeP$_2$O$_7$ glass have been evaluated for the glass powder to characterize electrochemical performance. Powder glass may be sensitive for oxidation, moisture, and carbon dioxide from atmosphere due to higher Na$_2$O and FeO concentration in glass. In order to know the basic crystallization mechanism of Na$_2$FeP$_2$O$_7$ glass, we carefully checked thermal property and crystallization behavior of examined bulk glass was examined. This article reports the surface crystallization tendency of Na$_2$FeP$_2$O$_7$ bulk glass.

2. Experimental procedure

Precursor glass with the composition of 33.3Na$_2$O–33.3FeO–33.3PO$_3$ (mol %) corresponding stoichiometric composition of Na$_3$FeP$_2$O$_7$, was prepared by conventional melt quenching method. Reagent grade Na$_2$PO$_4$ (Nakarai Tesque, Japan), FeO (Kojundo chemicals, Japan) was weighted and mixed well by mortar. A 20 g mixture batch of oxide raw material powder was put into a graphite crucible and melted in an electrical furnace at 900°C for 30 min. During the melting of a glass batch, 5 L·min$^{-1}$ of nitrogen gas with 10 ppm or less air introduced to keep valence state of Fe$^{2+}$. Thereafter, the melt was poured on an iron plane to obtain a quench solidified product by press quenching.
In order to characterize thermal properties of precursor glass, differential thermal analysis was performed. For the differential thermal analysis (DTA) measurements Rigaku Ltd. Thermo plus TG8120, at a heating rate of 10 K min$^{-1}$ under 150 mL min$^{-1}$ N2 flow from room temperature to 800°C. X-ray photoelectron spectroscopy (XPS) (PHI5000 Versa Probe II, ULVAC-PHI Ltd.) was performed to characterize valence state of Fe in precursor glass. AlKé X-rays provided the excitation radiation. In order to avoid oxidation of glass surface, sample specimen was mounted on sample holder in argon-filled glove box. Before mounting a specimen to the holder, the sample specimen was polished roughly with sandpaper in glove box. Then the sample was introduced into XPS chamber without being exposed to the air by using a transfer vessel. XPS spectra of the Fe2p core level of the glass surface were recorded. The drift of the electron binding energy (EB) due to the surface charging effect was calibrated by utilizing the C1s peak of the contamination of the pumping oil (EB = 284.6 eV). For scanning electron microscopy (SEM) observations, crystallized samples were examined using a scanning electron microscope (VE-8800; KEYENCE, Osaka, Japan).

3. Results and discussion

Figure 1 shows the Fe 2p$_{3/2}$ XPS spectra of Na$_2$FeP$_2$O$_7$ precursor glass. The results of peak fitting is also shown. Peak fitting was done by using an asymmetric function (Gaussian/Lorentzian = 60/40) and half-width was fixed at 2.20. For the peak fitting of Fe 2p XPS spectra, Fe$^{2+}$ peak position of 709 eV and Fe$^{3+}$ peak position is reported to be 711 eV. When we look at the sample after DTA measurements, powder sample color changed from white gray to white brown. Color change may concern oxidation of ferrous ion in precursor glass even in high purity N2 flow. We think that oxidation of ferrous ion occur during pulverization process before DTA measure. In this study, we focus on crystallization process of bulk glass. The discussion of resistance of atmosphere in iron valence will be discuss in another setting.

![Fig. 1. Fe2p$_{3/2}$ X-ray photoelectron spectra and fitted curves of Na$_2$FeP$_2$O$_7$ glass.](image1)

Figure 2 shows the DTA profile of Na$_2$FeP$_2$O$_7$ glass. Glass transition $T_g$ at 385°C, crystallization onset $T_s$ at 460°C and crystallization peak at 487°C was confirmed in 20 mg of bulk glass. On the other hand, glass powder exhibits high $T_p$ at 573°C. In generally, either $T_g$ observe at almost identical temperature for homogeneous nucleation or surface crystallized glass exhibits lower $T_p$ in glass powder. Such irregular thermal stability between glass powder and bulk sample may corresponds valence state of iron oxide in precursor glass. To obtain fine glass powder most of milling process was performed under air atmosphere. Partially oxidation of iron involve a missing of sodium ion from precursor glass. In previous study, thermal stability of LiFePO$_4$ precursor glass de fined by $\Delta T = T_p - T_g$ increased in Fe$^{3+}$ concentrated glass. When we avoid devitrification in LiFePO$_4$ glass a trace amount of Nb$_2$O$_5$ is effective. On the other hand, both ferric and ferrous rich Na$_2$FeP$_2$O$_7$ glass matrix tend good glass forming ability without any glass forming additive agents such as Nb$_2$O$_5$ in this study. It is found the thermal stability of valence kept well as Fe$^{2+}$ when melting performed under nitrogen flow and use of carbon crucible.

![Fig. 2. Differential thermal analysis curves of bulk and powder Na$_2$FeP$_2$O$_7$ glass.](image2)
glass melts for crystallization is stable rather than that of LiFePO₄ glass system.

**Figure 3** shows the aspects of (a) as quenched precursor glass, (b)–(d) heat-treated at various temperature for 3 h in nitrogen flowing tubular furnace. The glass was prepared by the melt-quenching method. Na₂FeP₂O₇ glass is showing black color. Despite mirror polishing before heat-treatment, heat-treated sample at 430°C or higher is deformed in the process of crystallization. We also confirm breaking, swelling of bulk sample after heat-treatment.

To investigate in detail the changes in morphology due to crystallization, X-ray diffraction (XRD) measurements were performed for bulk sample subjected to heat treatment at each temperature as shown in **Fig. 4** and the results of powder sample after grinding it as shown in **Fig. 5**.

As shown in **Fig. 4**, it was confirmed the formation of Na₃.₁₂Fe₂.₄₄(P₂O₇)₂, identified from XRD pattern at 430°C or higher. Meanwhile in the powder sample as shown in **Fig. 5**, it cannot be confirmed diffractions at 430°C. As discussed at DTA profiles between bulk and glass powder, glass powder have higher T_g, T_x and T_p due to oxidation of ferrous ions in glass. Ferric ion concentrated glass have higher thermal stability for crystallization. The halo XRD patterns at 430°C in glass powder show consistent with DTA profiles as shown in **Fig. 5**. It is found that the crystallization mechanism sensitively depends on specific surface, atmosphere and valence state of iron in precursor glass.
The results on XRD in bulk glass imply that Na$_2$FeP$_2$O$_7$ glass preferentially crystallize on bulk surface due to heterogeneous nucleation and crystal growth. Figure 6 shows scanning electron micrographs of the fractured surface of heat-treated sample. Figures 6(a)–6(c) shows the results at various heat treatment time by fixing at 430°C. Although the sample is deformed macroscopically as shown in Fig. 3(b), the crystalline layer about 10 µm on the surface can be confirmed. As increasing of treatment time, the thickness of surface layer was increased. It was confirmed 70 µm for 5 h and 200 µm for 10 h treatment. Finally as shown in Fig. 6(d), it was confirmed that crystallization is complete up to 460°C for 3 h.

The combination of heterogeneous nucleation and growth in anisotropic crystal forming glass system may possible to prepare surface oriented crystallized glass. There are several typical literature to form surface crystal layer during conventional heat treatment. Fresnoite Ba$_2$TiGe$_2$O$_8$, Sr$_2$TiSi$_2$O$_8$, Ba$_2$TiSi$_2$O$_8$, LaBGeO$_5$, BiBO$_3$ and so on, can easily form precursor glass and they exhibits surface crystallization with highly crystal orientation. In the case of Sr$_2$TiSi$_2$O$_8$, precursor glass shows fully transparent crystallization tendency. XRD pattern as seen in Fig. 4 did not show any crystal orientation. However, as shown in Fig. 7, strong diffractions from (122) and (133) are clearly detected from glass ceramics polished 10 µm surface layer.

The results of XRD are integrated, and Fig. 8 shows a schematic diagram of the surface crystallization mechanism of Na$_2$FeP$_2$O$_7$ glass. The outermost surface shows random orientation due to heterogeneous nucleation, then the ions are supplied from the inside of the bulk during isothermal heat-treatment, and the dominant growth axis survive into bulk in crystal growth process. This crystal growth is similar to the behavior of surface crystallization of fresnoite crystals. Although the reason why the (122) and (133) planes are preferentially oriented is unknown at the present time, it is interesting phenomena that enables orientation control of the active material for sodium ion batteries, and future studies on differences in electrochemical evaluation have an interest in the future.
Fig. 8. Schematic illustration of surface crystallization in Na$_2$FeP$_2$O$_7$ glass.

4. Conclusion

In conclusion, crystallization mechanism of Na$_2$FeP$_2$O$_7$ glass was examined. Comparing with crystallization of the powder glass examined previously, bulk Na$_2$FeP$_2$O$_7$ glass clearly showed surface crystallization tendency. Furthermore, surface orientation was also confirmed at first and preferable orientation directions are (122) and (133) those perpendicular to bulk surface. Control of the crystal orientation in cathode material is important to improve ionic conduction. The technique of crystallization of glass can easily provide a self-organized surface oriented glass-ceramics.

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