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Direct observation of a non-isothermal crystallization process in precursor $Li_{10}GeP_2S_{12}$ glass electrolyte

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HIGHLIGHTS

- TEM observation is conducted for a precursor $Li_{10}GeP_2S_{12}$ glass electrolyte.
- Crystallization process is directly examined via in-situ TEM observation.
- Dark-field TEM images visualize precipitated nanocrystallites.
- Crystallization degree is evaluated from electron diffraction patterns.

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ABSTRACT

Crystallization of a precursor $Li_{10}GeP_2S_{12}$ (LGPS) glass electrolyte by heat treatment significantly improves its ionic conductivity. The LGPS crystalline phase obtained by heat treatment above 450 °C shows an ionic conductivity on the order of 10^{-2} S/cm. To clarify the correlation between the crystallization behavior of precursor LGPS glasses and ionic conductivity, we developed an observation technique to visualize precipitated nanocrystallites and a new method to evaluate the crystallization degree via transmission electron microscopy (TEM). In-situ TEM observation revealed that LGPS nanocrystallites precipitated above 450 °C and their size remained fundamentally intact during heating. That is, the crystallization behavior could be characterized by only the formation of LGPS nanocrystallites in an amorphous matrix. In addition, the crystallization degree was quantitatively evaluated from electron diffraction patterns. The crystallization degree remarkably increased at around 450 °C and reached more than 60% above 450 °C. Based on these results, a high ionic conductivity of approximately 1.0×10^{-2} S/cm was confirmed to be directly associated with the appearance of the LGPS crystalline phase.

1. Introduction

Lithium-ion secondary batteries are expected to be a next-generation power source for portable electronic equipment because they exhibit excellent charge–discharge cycle performance and high energy densities. However, there are safety concerns about using flammable organic liquid electrolytes in the batteries. To resolve this safety issue, all-solid-state lithium secondary batteries using non-flammable inorganic solid electrolytes have received much attention in recent years. To realize all-solid-state batteries, solid electrolytes with high ionic conductivities and chemical stabilities are the key to enhancing battery properties for practical applications. Sulfide-based inorganic solid electrolytes are highly promising materials for developing all-solid-state batteries because they exhibit high lithium ion conductivities on the order of 10^{-2} S/cm at room temperature, which is equivalent to that of liquid electrolytes.

Sulfide-based glass solid electrolytes exhibit higher conductivities than oxide-based ones such as $Li_7La_3Zr_2O_{12}$ (3.0×10^{-4} S/cm) and $Li_{2.9}B_{0.9}S_{0.1}O_{3.1}$ (1.0×10^{-5} S/cm) [1–4]. In addition, it is also

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easy to improve the conductivity of sulfide-based glass solid electrolytes by densification [5]. As typical examples, two types of crystalline systems were reported to exhibit high ionic conductivities. One is the $Li_2S-P_2S_5$ system and the other is the $Li_4GeS_4-Li_3PS_4$ system, the latter of which is the so-called thio-LISICON. In the former $Li_2S-P_2S_5$ system, the conductivity of the glasses varies depending on the Li_2S content [6,7]. A notable feature is that the conductivity can be greatly enhanced by crystallization, and the glass-ceramics obtained by heat treatment exhibit a high ionic conductivity of more than 1.0×10^{-3} S/cm at room temperature [8–10]. This large conductivity enhancement by crystallization is attributed to the precipitation of metastable $Li_7P_3S_{11}$ and thio-LISICON* II analog ($Li_{3.25}P_{0.95}S_4$) crystal phases [11–13]. To evaluate the crystallization degree of Li–P–S type crystals, ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy experiments have been conducted [14,15]. For instance, Y. Seino et al. reported that high conductivities over 10^{-3} S/cm could be realized by an approximate 80% degree of crystallization of the $Li_7P_3S_{11}$ phase in $70Li_2S \cdot 30P_2S_5$ glass ceramics [14]. That is, the ionic conductivity of glass-ceramics strongly depends on precipitated crystalline phases and their degree of crystallinity.

In the latter $Li_4GeS_4-Li_3PS_4$ system, on the other hand, a tetragonal $Li_{10}GeP_2S_{12}$ (LGPS) crystal phase with the space group $P4_2/nmc$ was reported to show an extremely high conductivity of 1.2×10^{-2} S/cm, together with an electrochemical window of up to 3 V vs. Li/Li^+ [16,17]. Its crystal structure is characterized by a three-dimensional framework structure comprising one-dimensional chains formed by both $(Ge_{0.5}P_{0.5})S_4$ tetrahedra and LiS_6 octahedra. In addition, the $Li_4GeS_4-Li_3PS_4$ system has several other crystal phases, e.g., α-, β-, and γ-type Li_3PS_4 as well as Li_4GeS_4 [18–22]. All of these thio-LISCON type crystals are characterized by a three-dimensional framework structure comprising PS_4 tetrahedra. Among these crystal phases, in particular, Li_4GeS_4 (LGS) and β-type Li_3PS_4 (LPS), which have an orthorhombic crystal structure with the space group *Pnma*, show high ionic conductivities over 10^{-3} S/cm [22]. Thus, to realize high ionic conductivities in this system, the precipitation and crystallization degree of β-type thio-LISICON (LGS and LPS) and LGPS crystalline phases are critical.

In this work, we focus on the super-ionic conducting LGPS crystal phase in the $Li_4GeS_4-Li_3PS_4$ system. To understand the correlation between the crystallization process of precursor LGPS glasses and the ionic conductivity associated therewith, the

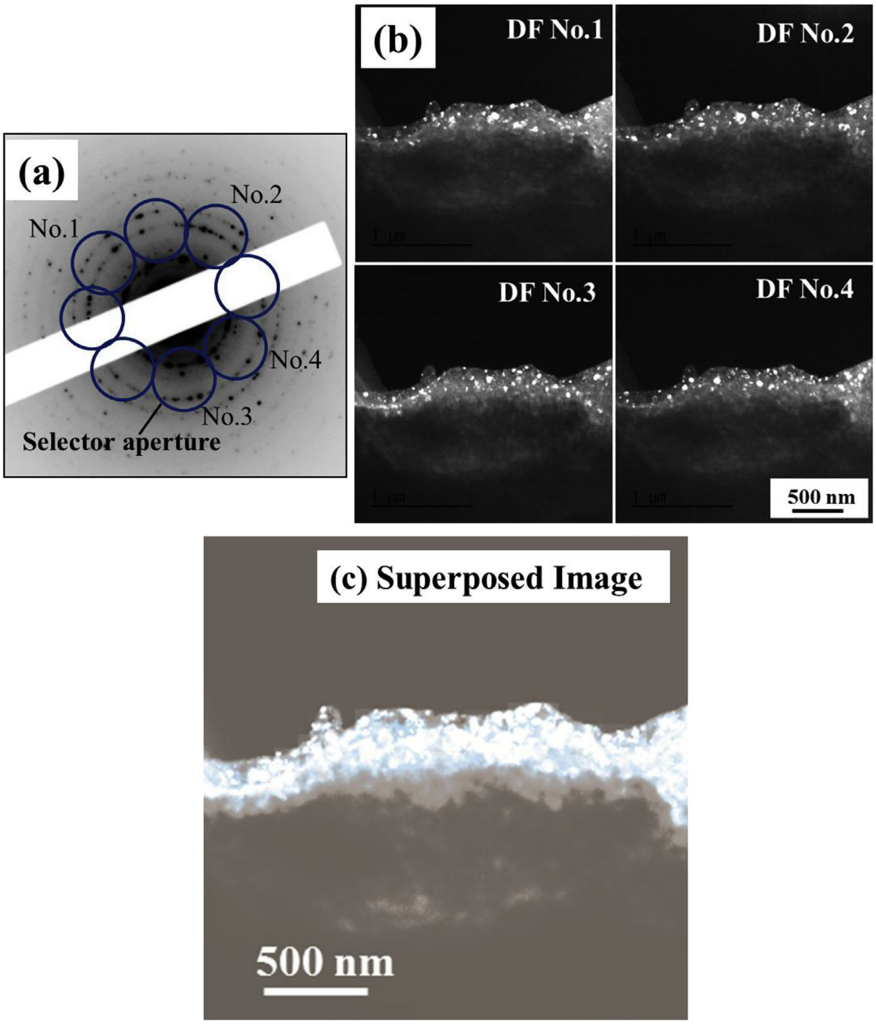

Fig. 1. The observation method for the crystallization process in glass solid electrolytes. (a) The ED pattern from the polycrystalline region. Blue circles indicate the positions where a selector aperture is inserted. (b) DF images taken using the spots in No.1–4 blue circles of the ED pattern (a). (c) A superposed image obtained from all the DF images. All the spots in (a) can be reflected as bright-contrast regions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)