doi:10.1017/S1431927622007619
Microsc. Microanal. 28 (Suppl 1), 2022

Local Structure and Crystallization Process in Mechanochemically Prepared Na_3PS_4

Hiroshi Nakajima[1], Hirofumi Tsukasaki[1], Takuya Kimura[2], Atsushi Sakuda[2], Akitoshi Hayashi[2], and Shigeo Mori[1*]

[1.] Department of Materials Science, Osaka Prefecture University, Sakai, Osaka, Japan
[2.] Department of Applied Chemistry, Osaka Prefecture University, Sakai, Osaka, Japan
* Corresponding author: mori@mtr.osakafu-u.ac.jp

All-solid-state batteries have attracted much attention due to their safety and high density. To reduce the cost of batteries, utilizing abundant resources is advantageous. The ranking of Clarke numbers, which is a measure of the crustal abundance ratio of each element, suggests that sodium (Na) is about 1,000 times larger than lithium (Li). Thus, Sodium batteries are expected to be next-generation storage batteries that have safety, economy, and high energy density. To realize this battery, it is essential to develop a solid electrolyte that exhibits high sodium ionic conductivity at room temperature.

It is reported that Na_3PS_4 shows ionic conductivity of more than 10^{-4} S cm^{-1} at room temperature when it is annealed to crystallize a cubic structure [1]. The glass-ceramics can be densified easily by pressing and operated as a second battery at room temperature. Although several crystallographic characteristics of the glass-ceramics were reported, microstructures of Na_3PS_4 glass-ceramics have not been revealed. In this study, we observed microstructures of Na_3PS_4. Furthermore, we performed in situ heating observation to reveal how the glass crystallizes into the glass-ceramics in real space [2].

The observation was done using a transmission electron microscope (TEM) (JEM-2100F, JEOL Co. Ltd.). Na_3PS_4 glass was heated with a heating holder in the TEM. The observation results were compared with specimens annealed at 240℃ and 480℃, which are crystallized into a cubic and a tetragonal phase, respectively. Nanocrystallites were segmented to evaluate average crystal sizes in dark-field images via machine learning [3].

Figure 1 shows in situ observation results in Na_3PS_4 glass. The specimen shows a glass structure at 20℃, as revealed in the diffraction pattern. When the specimen was heated, bright spots of approximately 20 nm appeared, indicating that nanocrystallites are formed. Accordingly, Bragg reflection spots were also observed in the diffraction patterns. Noticeably, the diffraction pattern showed a single crystal pattern at 400℃. The dark-field image reveals that micro-sized grains were formed as marked with the dotted line. This observation reveals that the nanocrystallites merged into the large grain by heating. Note that the crystal of 400℃ corresponds to the tetragonal phase. Thus, the observed results reveal that the cubic structure has nanosize crystallites while the tetragonal phase has microsize.

As shown in Figure 2, the lattice image could be obtained at 240℃ and the electron diffraction pattern was indexed by the cubic structure (space group I-43m). These results show that the specimen had a high crystalline structure without lattice defects. Furthermore, this demonstrates that Na_3PS_4 is stable against electron irradiation at 240℃. The observation area disappeared at room temperature when we tried to obtain a high-resolution image in Na_3PS_4. Another sulfide-electrolyte $Li_{10}GeP_2S_{12}$ study showed that a high-resolution image can be obtained only at high temperatures without damaging the specimen [4]. Electron irradiation damage is considered to be mitigated by cooling a specimen. However, as for sulfide-based electrolytes prepared by ball-milling, higher temperature makes the specimens more stable against electron irradiation probably because they have higher electron conductivity to prevent charging.

In summary, we observed microstructures and crystallization processes in the superionic conductor of Na_3PS_4. The nanocrystallites were revealed in the cubic phase while they are grown to large grains in the tetragonal phase, which could be attributable to the difference in the conductivity of these phases.

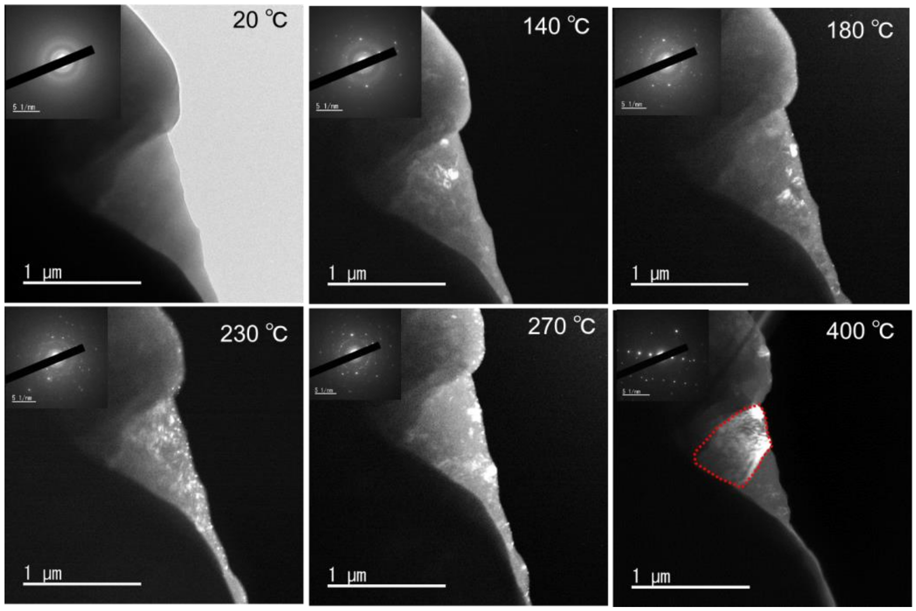

Figure 1. Crystallization behaviors in Na_3PS_4. The images at 20°C and 140°C–400°C are bright- and dark-field imaging, respectively. The insets are diffraction patterns.

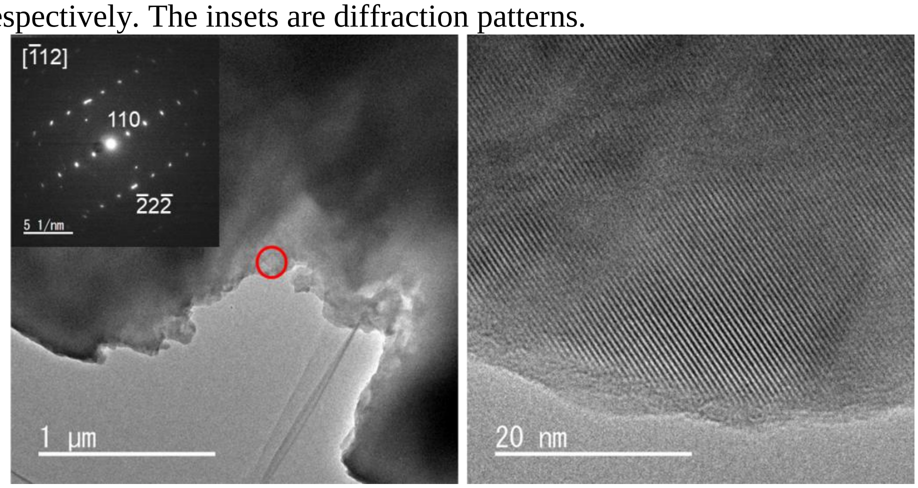

Figure 2. (Left) Bright-field image of Na_3PS_4 at 240°C. The inset is an electron diffraction pattern. (Right) High-resolution image in the area marked by the circle.

References:
[1] A. Hayashi *et al*., Nature communications **3** (2012), p. 856. doi: 10.1038/ncomms1843
[2] H. Nakajima *et al*., Journal of Power Sources **511** (2021), p. 230444. doi: 10.1016/j.jpowsour.2021.230444
[3] T. Ayama *et al*., ACS Applied Energy Materials **4** (2021), p. 6290. doi: 10.1021/acsaem.1c01074
[4] H. Tsukasaki *et al*., Journal of Power Sources **369** (2017), p. 57. doi: 10.1016/j.jpowsour.2017.09.070