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Structural origin of ionic conductivity for $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal by neutron and X-ray diffraction

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Abstract. Reverse Monte Carlo modeling was carried out for $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass based on time-of-flight neutron and synchrotron X-ray diffraction data. Polyhedral analysis of three-dimensional structures for $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass were gave us not only structural characteristics but also structural origins related to their high ionic conductivity.

1. Introduction

$\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal, which can be synthesized by aging of $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass at 513K, showed a high ionic conductivity in the order of 10^{-3} S/cm at room temperature (RT) [1]. In order to elucidate the relationship between the structure and the excellent electrical conduction properties, we have carried out a polyhedral analysis of three-dimensional atomic structures constructed by reverse Monte Carlo (RMC) modeling based on the time-of-flight neutron diffraction and the synchrotron X-ray diffraction data [2]. In the polyhedral analysis, it was found that a large number of vacant S_4 tetrahedra (“ ac - $[\text{S}_4]$ units”), which fully accept Li^+ cation, are located around a LiS_4 tetrahedron ($[\text{LiS}_4]$ unit) in $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal.

In this study, we progressed the polyhedral analysis focused on “bottle-necks” and “connectivity” of $[\text{LiS}_4]$ and ac - $[\text{S}_4]$ units. These structural characteristics are strongly related to the Li^+ conductivity for $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal.

2. Experimental

The details of the synthesis of samples and experimental procedures are described in ref. [2]. The time-of-flight neutron diffraction (TOF-ND) measurements were carried out with the General Material Diffractometer (GEM) installed at the ISIS in the Rutherford Appleton Laboratory, UK [3]. The synchrotron X-ray diffraction (SXRD) experiments were performed with a horizontal two-axis diffractometer at the BL04B2 beam line of the SPring-8 synchrotron radiation facility [4]. In addition, the TOF-ND and SXRD data were corrected for the polarization, multiple scattering, absorption, and incoherent scattering in order to obtain the structure factors, $S(Q)$, of $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and



$(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass [5-9]. To construct the three-dimensional structures of $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass, the RMC modeling was carried out for $g(r)$ of $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $S(Q)$ of $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass, using RMCA [10], where $g(r)$ is the atomic pair distribution function. The refined crystal structure of $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal [11] was used as the starting configuration for the RMC modeling (the detailed procedure of the RMC modelling is also described in ref. [2]).

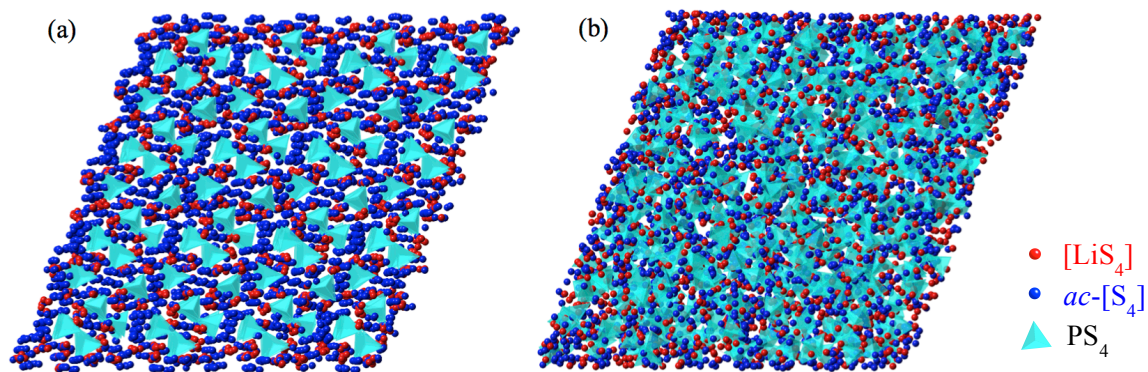


Figure 1. Spatial distribution of $[\text{LiS}_4]$ units (red spheres) and $ac\text{-}[\text{S}_4]$ units (blue spheres), and PS_4 tetrahedra (light blue tetrahedra) for (a) $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and (b) $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass.

3. Results and discussion

In our previous study [2], we found that $[\text{LiS}_4]$ units, PS_4 tetrahedra, and $ac\text{-}[\text{S}_4]$ units are distributed in the three dimensional structures of $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass derived by the RMC modeling. Figure 1 shows three dimensional structures of $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass, visualized with $[\text{LiS}_4]$ units, PS_4 tetrahedra and $ac\text{-}[\text{S}_4]$ units. In these three dimensional structures, it can be considered that Li^+ cations occupy $[\text{LiS}_4]$ units (red spheres) and can move into $ac\text{-}[\text{S}_4]$ units (blue spheres), in other words, Li^+ conduction pathways are adjacent to connection of $[\text{LiS}_4]$ and $ac\text{-}[\text{S}_4]$ units. Therefore, to discuss the relationship between structure and ionic conductivity more deeply, we focused on a local and a long-range connectivity of $[\text{LiS}_4]$ units and $ac\text{-}[\text{S}_4]$ units.

Figure 2 shows the local connection of $[\text{LiS}_4]$ units and $ac\text{-}[\text{S}_4]$ units. Concerning the migration of Li^+ cation from $[\text{LiS}_4]$ unit to another $[\text{LiS}_4]$ unit, it is clear that Li^+ cation needs to escaping from a $[\text{LiS}_4]$ unit and passing through $ac\text{-}[\text{S}_4]$ units. Thus, S_3 triangular planes formed a $[\text{LiS}_4]$ unit can be regarded as bottle-necks for Li^+ conduction. In order to elucidate a size of the bottle-neck, radii of all inscribed circles of S_3 triangular planes for $[\text{LiS}_4]$ units were calculated. Figure 3 shows the size distribution of radii of the inscribed circles of the S_3 triangular planes, which were calculated for the three-dimensional structures of $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass. The radius of the inscribed circle for $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal was estimated to be 1.12 Å on average, but on the other hand, 1.08 Å for $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass, as shown in Fig. 3. The result indicates that the larger bottle-necks in $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal allow Li^+ cations to move easily from $[\text{LiS}_4]$ units to $ac\text{-}[\text{S}_4]$ units in comparison with those in $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass.

Next, we investigated the long-range connectivity of $[\text{LiS}_4]$ units and $ac\text{-}[\text{S}_4]$ units in the chain networks formed by “ $[\text{LiS}_4]\text{-}ac\text{-}[\text{S}_4]\text{-}[\text{LiS}_4]\text{-}ac\text{-}[\text{S}_4]\text{-}[\text{LiS}_4]\text{-}ac\text{-}[\text{S}_4]$ ” chain. Here, $[\text{LiS}_4]\text{-}ac\text{-}[\text{S}_4]$ correlations up to 2.70 Å in length were allowed as chain formers. Total number, N_{chain} , of $[\text{LiS}_4]$ and $ac\text{-}[\text{S}_4]$ units in the “ $[\text{LiS}_4]\text{-}ac\text{-}[\text{S}_4]\text{-}[\text{LiS}_4]\text{-}ac\text{-}[\text{S}_4]\text{-}[\text{LiS}_4]\text{-}ac\text{-}[\text{S}_4]$ ” chain was calculated in the parallelepiped box including 5376 atoms (Li: 1792, P: 768, and S: 2816) for $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass [2]. Table 1 is summarized the number of $[\text{LiS}_4]$ and $ac\text{-}[\text{S}_4]$ units in

the longest “-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-” chain and a ratio of the number of [LiS₄] and ac-[S₄] units in the longest chain to the total number of all [LiS₄] and ac-[S₄] site in the parallelepiped box for Li₇P₃S₁₁ metastable crystal and (Li₂S)₇₀(P₂S₅)₃₀ glass. As indicated in Table 1, most of [LiS₄] units and ac-[S₄] units connect with each other and form an exceedingly-long chain in Li₇P₃S₁₁ metastable crystal. In contrast, various lengths of chains exist in (Li₂S)₇₀(P₂S₅)₃₀ glass and the total number of [LiS₄] and ac-[S₄] units in the longest chain is only 515.

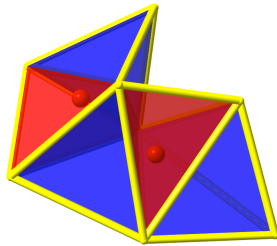


Figure 2. Local connection of [LiS₄] units (red tetrahedra) and ac-[S₄] units (blue tetrahedra).

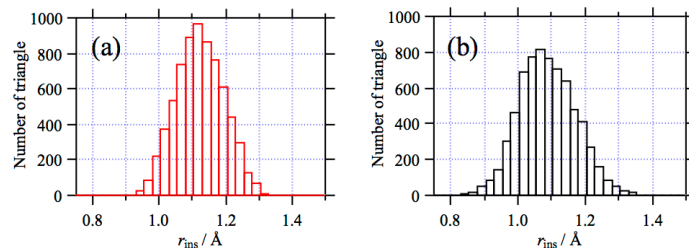


Figure 3. Distributions of the radii of inscribed circles in S₃ triangular planes for each [LiS₄] unit for (a) Li₇P₃S₁₁ metastable crystal and (b) (Li₂S)₇₀(P₂S₅)₃₀ glass.

In Fig. 4, the spatial distribution of the longest “-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-” chain in Li₇P₃S₁₁ metastable crystal and (Li₂S)₇₀(P₂S₅)₃₀ glass are shown together with PS₄ tetrahedra. As can be seen in Fig. 4(a), continuously “-[LiS₄]-[ac-[S₄]]-[LiS₄]-” chain forms net-like structure throughout the ordered framework of PS₄ tetrahedra in Li₇P₃S₁₁ metastable crystal, whereas the chain may be shredded into narrow strips by disordered framework of PS₄ tetrahedra in (Li₂S)₇₀(P₂S₅)₃₀ glass. This result allows us to deeply understand that a well-developed conduction pathway of Li⁺ cations exists in Li₇P₃S₁₁ metastable crystal.

Table 1. The analysis of the longest “-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-” chain in Li₇P₃S₁₁ metastable crystal and (Li₂S)₇₀(P₂S₅)₃₀ glass.

	Li ₇ P ₃ S ₁₁ metastable crystal	(Li ₂ S) ₇₀ (P ₂ S ₅) ₃₀ glass
Total number of [LiS ₄] and ac-[S ₄] units in the longest chain, N_{chain}	5665	515
Number of all site, N_{all} ([LiS ₄] + ac-[S ₄])	6283	4480
$N_{\text{chain}} / N_{\text{all}}$	0.90	0.12

4. Conclusions

Two structural origins of high ionic conductivity for Li₇P₃S₁₁ metastable crystal could be recognized through the polyhedral analysis of three-dimensional structures constructed by the reverse Monte Carlo modeling. Firstly, [LiS₄] units in Li₇P₃S₁₁ metastable crystal have larger bottle-necks of S₃ triangular planes than those in (Li₂S)₇₀(P₂S₅)₃₀ glass. Secondly, the exceedingly-long “-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-[LiS₄]-[ac-[S₄]]-” chain network corresponding to well developed Li⁺ conduction pathway exists in Li₇P₃S₁₁ metastable crystal.

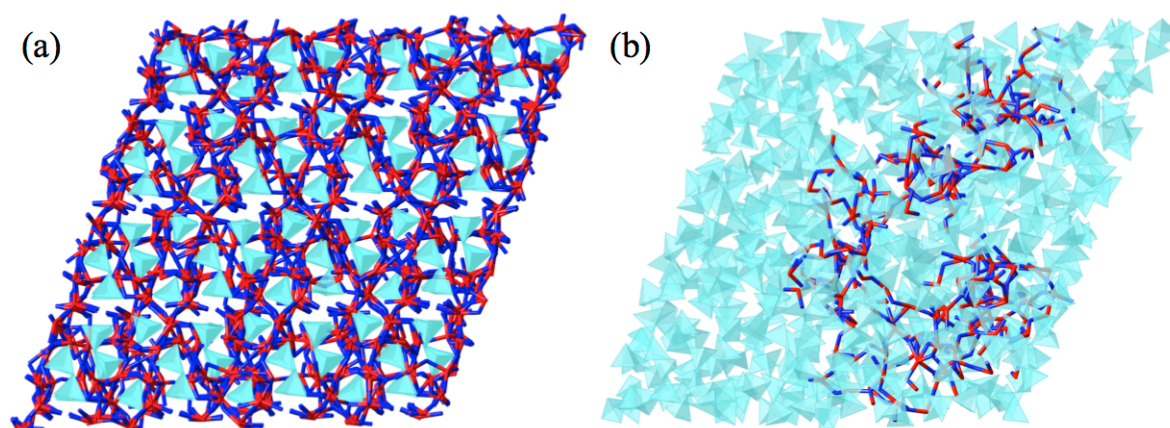


Figure 4. Spatial distribution of the longest $-[\text{LiS}_4]-[\text{ac}-[\text{S}_4]]-[\text{LiS}_4]-$ chain network (red-and-blue-banded cylinders), together with PS_4 tetrahedra (light blue tetrahedra) for (a) $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable crystal and (b) $(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass.

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References

- [1] Mizuno F, Hayashi A, Tadanaga K, Minami T, Tatsumisago M 2005 *Electrochem. Solid-State Lett.* **8** A603.
- [2] Onodera Y, Mori K, Otomo T, Sugiyama M, Fukunaga T 2012 *J. Phys. Soc. Jpn.* **81** 044802.
- [3] Williams W G, Ibberson R M, Day P, Enderby J E 1998 *Physica B* **241-243** 234.
- [4] Kohara S, Suzuya K, Kashihara Y, Matsumoto N, Umesaki N, Sakai I 2001 *Nucl. Instrum. And Methods A* **467** 1030.
- [5] Sasaki S 1991 *KEK report* **90-16**.
- [6] Hubbell J H, Veigele W J, Briggs E A, Brown R T, Cromer D T, Howerton R J 1993 *J. Phys. Chem. Ref. Data* **4** 61.
- [7] Paalman H H, Pings C J 1962 *J. Appl. Phys.* **33** 2635
- [8] Blech I A, Averbach B L 1965 *Phys. Rev.* **137** 1113.
- [9] Faber T E, Ziman J M 1965 *Philos. Mag.* **11** 153.
- [10] McGreevy R L, Putztai L 1988 *Mol. Simul.* **1** 359.
- [11] Onodera Y, Mori K, Otomo T, Hannon A C, Kohara S, Itoh K, Sugiyama M, Fukunaga T 2010 *J. Phys. Soc. Jpn. Suppl. A* **79** 87.