FULL PAPER

Glassy oxide electrolytes in the system $\text{Li}_4\text{SiO}_4\text{--Li}_2\text{SO}_4$ with excellent formability

Yohei YONEDA¹, Chie HOTEHAMA¹, Atsushi SAKUDA¹,
Masahiro TATSUMISAGO¹ and Akitoshi HAYASHI^{1,†}

¹Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
1–1 Naka-ku, Sakai, Osaka 599–8531, Japan

All-solid-state batteries using oxide electrolytes are regarded as safe batteries. However, most crystalline oxide solid electrolytes require high-temperature sintering for densification. Oxide electrolytes with high formability, which enable the construction of high-performance batteries, are thus required. In this study, $\text{Li}_4\text{SiO}_4\text{--Li}_2\text{SO}_4$ glasses and glass-ceramics were prepared by mechanochemical treatment and subsequent heat treatment at 270 °C to achieve electrolytes with high formability. As the Li_2SO_4 content was increased, the formability of the electrolyte increased. The $90\text{Li}_4\text{SiO}_4\cdot 10\text{Li}_2\text{SO}_4$ glass-ceramic electrolyte with a hexagonal structure (a $P6_3/mmc$ space group) showed the highest ionic conductivity of $2.2 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C. In this crystal structure, oxygen anions form a hexagonal close-packed structure, and silicon and sulfur cations randomly occupy the tetrahedral sites formed by oxygen anions. An all-solid-state $\text{Li-In/LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cell using a $90\text{Li}_4\text{SiO}_4\cdot 10\text{Li}_2\text{SO}_4$ glass-ceramic electrolyte operated at 100 °C as a secondary battery without high-temperature sintering. These oxide materials are promising solid electrolytes for oxide-type all-solid-state batteries.

©2021 The Ceramic Society of Japan. All rights reserved.

Key-words : All-solid-state battery, Lithium ion conductor, Oxide electrolyte, Glass-ceramic electrolyte, Formability, Li_2SO_4

[Received February 6, 2021; Accepted April 19, 2021]

1. Introduction

All-solid-state batteries are attracting attention as next-generation batteries because of their safety and low-risk of ignition or leakage.^{1),2)} Various desirable qualities, such as improved power density,³⁾ high-temperature operation,⁴⁾ and high-voltage electrodes,⁵⁾ are expected to be achieved with all-solid-state batteries. Oxide electrolytes are widely used in all-solid-state battery due to their high atmospheric and chemical stability.^{4),6)} Several types of crystalline oxide electrolytes such as garnet type,^{7),8)} perovskite type,^{9),10)} NASICON type,^{11),12)} and LiTa_2PO_8 ¹³⁾ have been reported. These oxide electrolytes have a corner-sharing structure of metal-centered octahedra and tetrahedra and exhibit a high bulk ionic conductivity of approximately 10^{-4} to $10^{-3} \text{ S cm}^{-1}$ at room temperature. However, crystalline oxide electrolytes are generally difficult to be densified only by pressing at room temperature because of their low formability, which leads to a large grain boundary resistance.¹⁴⁾ High-temperature sintering is usually required to reduce the grain boundary resistance in typical oxide electrolytes.^{7)–13)} However, high-temperature sintering often increases the occurrence of unfavorable side-reactions with the electrode

active material, making it difficult to construct high-performance oxide-type all-solid-state batteries.

To address this drawback, we have focused on Li_2SO_4 as a low-melting oxide and reported that the relative density of powder-compressed pellets of $\text{Li}_3\text{BO}_3\text{--Li}_2\text{SO}_4$ ^{15)–17)} and $\text{Li}_4\text{GeO}_4\text{--Li}_2\text{SO}_4$ glasses¹⁸⁾ increases with increasing the Li_2SO_4 content. The relative density of the $60\text{Li}_4\text{GeO}_4\cdot 40\text{Li}_2\text{SO}_4$ (mol %) glass cold-pressed at 720 MPa had a relatively high value of approximately 87 %. Moreover, in the $\text{Li}_4\text{GeO}_4\text{--Li}_2\text{SO}_4$ system, a hexagonal phase with a $P6_3/mmc$ space group was crystallized as a metastable phase by heat-treating the glasses at 250 °C.¹⁸⁾ The prepared glass-ceramics with the metastable phase demonstrated a lower activation energy and higher ionic conductivity of greater than $10^{-6} \text{ S cm}^{-1}$ compared to the glasses.^{18),19)}

In this study, $\text{Li}_4\text{SiO}_4\text{--Li}_2\text{SO}_4$ glasses and glass-ceramics were prepared by replacing Ge with Si. Silicon is abundant in the earth's crust, which contributes to the supply of inexpensive oxide electrolytes. Glass-ceramic electrolytes were prepared by mechanochemical treatment and subsequent heat treatment (HT) at a relatively low temperature of 270 °C. The formability and ionic conductivity of the prepared electrolytes were evaluated, and the performance of glass-ceramics as an electrolyte layer in oxide-type all-solid-state batteries without high-temperature sintering was examined.

[†] Corresponding author: A. Hayashi; E-mail: hayashi@chem.osakafu-u.ac.jp

2. Experimental procedure

Solid electrolytes of $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ were prepared using Li_2O (Furuuchi, 99.9%), SiO_2 (Sigma Aldrich, 99.5%, 5 to 15 nm), and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Wako) as starting materials. $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was heated at 200 °C for 2 h under an Ar gas flow to obtain anhydrous Li_2SO_4 crystals. A mixture of the starting materials was placed in ZrO_2 pots (45 mL) containing ZrO_2 balls (5 mm Φ , 40 g) in an Ar-filled glovebox, and mechanochemical treatment was conducted at 370 rpm for 60 to 90 h using a planetary ball mill (Fritsch Pulverisette 7) to obtain Li_4SiO_4 - Li_2SO_4 glasses. After mechanochemical treatment, the obtained samples were heat-treated at 270 °C for 2 h in the presence of Ar gas to obtain the glass-ceramic samples.

X-ray diffraction (XRD) patterns of the synthesized powders were obtained using an X-ray diffractometer (SmartLab, Rigaku) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The diffraction data were collected at a scan rate of $10^\circ \text{ min}^{-1}$ with a step width of 0.02° over a 2θ range of 10 to 80° . Further, to determine the crystal structure of the Li_4SiO_4 heat-treated at 270 °C, the diffraction data were collected at a scan rate of $1^\circ/\text{min}$ with a step width of 0.02° over a 2θ range of 5 to 100° . The structural parameters were refined by Rietveld refining using SLS2 software (Rigaku). The structure model was described using VESTA software.²⁰⁾ Differential thermal analysis (DTA) curves were measured for the obtained powder samples in a Pt pan in a N_2 atmosphere using a thermal analyzer (Thermo-plus 8110, Rigaku). The heating rate was fixed at $10^\circ \text{ C min}^{-1}$ from room temperature to 1000 °C. A Raman spectrophotometer (LabRAM HR-800, Horiba) equipped with a 325 nm He-Cd laser was used to identify the structural units in the solid electrolytes. Bulk densities of the powder-compressed pellets were estimated from the weight and volume of the pellets. Relative densities were calculated by dividing the bulk density of the pellet by the powder true density of the obtained powder determined by an Ar gas pycnometer (AccuPyc II 1340, Shimadzu). The ionic conductivity was measured using AC impedance measurements. The applied voltage was 50 mV and the frequency range was from 10 Hz to 8 MHz. The milled samples were pelletized to 10 mm in diameter by pressing at 720 MPa at 25 °C and then heat-treated at 270 °C to obtain sintered bodies of glass-ceramics. The thickness of the pellets was about 0.8 mm, and the ionic conductivity of the glass-ceramics was measured for these sintered pellets. Gold current collectors were used to cover the entire surface of both sides of the pellet using a quick coater (SC-701 MkII ADVANCE; Sanyu Electron). The impedance spectra were recorded using an impedance analyzer (1260 Solartron). The activation energy for conduction was calculated from the slope of the Arrhenius equation, $\sigma = \sigma_0 \exp(-E_a/RT)$, where σ is the ionic conductivity, T is the absolute temperature, σ_0 is the pre-exponential factor for ionic conduction, E_a is the activation energy for ionic conduction, and R is the gas constant. An all-solid-state Li-In/ $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) cell using the

$90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$ (mol %) glass-ceramic electrolyte was constructed to investigate its electrochemical performance. LiNbO_3 -coated NMC particles (Toda Kogyo) were used as active materials. The positive electrode was composed of various particles at a ratio of LiNbO_3 -coated NMC: $90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$:acetylene black (AB) = 70:30:4 (wt %). A $90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$ glass-ceramic electrolyte was used as the separator. Stainless steel powder was used as the current collector for the positive electrode side for determining the electronic conduction and mechanical strength of the pellets. Three-layer pellets (10 mm Φ) consisting of a current collector, a positive electrode, and separator layers were prepared by pressing the stainless-steel powder, LiNbO_3 -coated NMC, and $90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$ glass under 720 MPa at room temperature ($\sim 25^\circ \text{C}$). The pellets were heated at 270 °C to crystallize the $90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$ glass. The Li-In alloy negative electrode was prepared using indium foil (99.999%; 0.3 mm thickness; Furuuchi Chemical) and lithium foil (99.99%; 0.25 mm thickness; Furuuchi Chemical), and Cu foil was attached to the pellets as the current collector. Then, the pellets were pressed at 120 MPa to form a Li-In alloy negative electrode.

3. Results and discussion

Figure 1(a) shows the XRD patterns of the $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ samples after mechanochemical treatment at 370 rpm for 60 to 90 h. Glass materials were obtained with a composition of $0 \leq x \leq 50$ mol %. At $x = 75$ mol %, a weak peak attributable to β - Li_2SO_4 remained. Figure 1(b) shows the Raman spectra of the glass samples. The peaks at approximately 850 and 1010 cm^{-1} were attributed to the SiO_4^{4-} ²¹⁾ and SO_4^{2-} ²²⁾ units, respectively. The intensity ratio of these peaks varied with the composition. A broad peak attributed to $\text{Si}_2\text{O}_7^{6-}$ ²¹⁾ was slightly observed.

Fig. 1. (a) XRD patterns of the $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ samples after mechanochemical treatment and (b) Raman spectra of the $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ glasses.

Fig. 2. (a) Relative density of the $(100-x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ pellets pressed into glass powders at 720 MPa and (b, c) SEM images of fracture cross-section of the $(100-x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ pellets ($x = 10$ and 50 mol %).

Table 1. Bulk density, powder true density, and relative density of $(100-x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ pressed at 720 MPa

Composition	Bulk density of pellets / g cm^{-3}	Powder true density / g cm^{-3}	Relative density / %
$x = 0$	1.78	2.23	79.8
$x = 10$	1.81	2.21	82.0
$x = 20$	1.85	2.23	83.1
$x = 30$	1.91	2.25	84.7
$x = 40$	1.96	2.25	86.9
$x = 50$	2.01	2.26	88.9
$x = 75$	2.05	2.29	89.6

Figure 2(a) shows the relative density of the pellets of the $(100-x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ sample prepared by cold pressing at 720 MPa. As the Li_2SO_4 content increased, the relative density of the pellets increased. The bulk density of the pellets, the powder true density, and the relative density of $(100-x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ pressed at 720 MPa are summarized in **Table 1**. Figures 2(b) and 2(c) show SEM images of the fracture cross-sections of the pellets with $x = 10$ and 50 mol %, respectively. As the Li_2SO_4 content increased, the fraction of voids decreased and smooth contact interfaces among the particles were formed.

Figure 3(a) shows the DTA curves of the Li_4SiO_4 ($x = 0$) glass sample from 31 to 1000 °C, as well as a magnified view from 200 to 400 °C. A small exothermic phenomenon was observed at approximately 260 °C, while a large exothermic peak was observed at approximately 350 °C. **Figure 3(b)** shows the XRD patterns of the samples heat-treated at 270, 400, and 900 °C. After HT at 270 °C, a new crystal phase was obtained. Conversely, after HT at 400 °C, monoclinic Li_4SiO_4 with a $P1\ 2_1/m\ 1$ space group was obtained, and HT at 900 °C increased the crystallinity of the sample. Therefore, the two exothermic peaks of DTA were attributed to the crystallization of each crystalline phase.

Figure 4(a) shows the fitting results for the Rietveld analysis of the XRD data for Li_4SiO_4 heat-treated at 270 °C, and **Fig. 4(b)** shows the crystal structure of

Fig. 3. (a) DTA curves of the Li_4SiO_4 glass and (b) XRD patterns of the Li_4SiO_4 heat-treated at 270, 400, and 900 °C.

Fig. 4. (a) X-ray Rietveld refinement pattern of the Li_4SiO_4 heated at 270 °C. (b) Schematic diagram of the crystal structure of hexagonal Li_4SiO_4 as determined from the XRD analysis.

Table 2. Crystal data and atomic coordinates for hexagonal Li_4SiO_4

Chemical formula sum	$\text{Li}_2\text{Si}_{0.5}\text{O}_2$					
Chemical formula weight	59.924					
Space group	Hexagonal					
Crystal system	$P6_3/mmc$ (No. 194)					
Lattice parameters, volume, Z	$a, b = 3.1087(6) \text{ \AA}, c = 5.0531(10) \text{ \AA}, \alpha, \beta = 90^\circ, \gamma = 120^\circ, V = 42.292(14) \text{ \AA}^3, Z = 1$					
Atom	x	y	z	Site	Occupancy	$U/\text{\AA}^2$
O	1/3	2/3	1/4	2c	1	0.0691(12)
Si	2/3	1/3	0.1261(3)	4f	0.125	0.0694(11)
Li1	2/3	1/3	0.1261(3)	4f	0.375	0.0694(11)
Li2	0	0	0	2a	0.25	0.054(5)

$R_{\text{wp}} = 1.38, R_c = 0.65, S = 2.1314, R_p = 0.93$

Fig. 5. XRD patterns of the $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ samples heat-treated at 270°C .

Li_4SiO_4 , as determined from the XRD analysis. The original structure of this analysis was based on hexagonal Li_4GeO_4 ¹⁸⁾ and the occupancy of each Li site in the hexagonal phase was used here. The refined cell parameters, R factors, and atomic coordinates are listed in **Table 2**. The obtained Li_4SiO_4 has a hexagonal structure with a $P6_3/mmc$ space group (194), and the reliability factors based on the powder profile, $R_{\text{wp}} = 1.38$ and $S = 2.13$, were obtained from this refinement. In this crystal structure, oxygen anions form a hexagonal close-packed structure, and silicon cations randomly occupy the tetrahedral sites formed by the oxygen anions. It has been clarified that the hexagonal phase is a metastable phase and it transforms to a thermodynamically stable monoclinic phase at 400°C or higher.

The prepared $\text{Li}_4\text{SiO}_4\text{--Li}_2\text{SO}_4$ glasses were also heat-treated at 270°C to form the hexagonal phase. **Figure 5** shows the XRD patterns of the $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ samples heat-treated at 270°C . Glass-ceramics with the hexagonal phase were obtained for compositions of $0 \leq x \leq 50 \text{ mol } \%$. The full width at half maximum (FWHM) of the strongest line at $2\theta = 33^\circ$ was smallest at the

Fig. 6. (a) Nyquist plots and (b) temperature dependence of the ionic conductivities of the $90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$ glass and glass-ceramic samples. (c) Composition dependence of the ionic conductivities at 25°C of the $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ glass and glass-ceramic samples.

composition $x = 10 \text{ mol } \%$, suggesting that crystallinity of the hexagonal phase was high at the composition. The peaks attributable to the $\text{Li}_6(\text{SiO}_4)_3(\text{SO}_4)_2$ crystal with an orthorhombic structure (space group: $Pmnm$) were also observed at $x = 40$ and $50 \text{ mol } \%$.

Figure 6(a) shows the Nyquist plots of the $90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$ (mol %) glass and glass-ceramic samples. Only one semicircle was observed in the Nyquist plots and it was difficult to be separated into bulk and grain-boundary components. Therefore, the conductivity of the electrolytes was calculated from the total resistance calculated from the intersection at the x-axis of the semicircle in the relatively low frequency region. **Figure 6(b)** shows the temperature dependence of the ionic conductivities of the $90\text{Li}_4\text{SiO}_4 \cdot 10\text{Li}_2\text{SO}_4$ glass and glass-ceramic samples. The temperature dependence of the conductivities obeyed the Arrhenius equation, and the activation energies for conduction were calculated from the slope. The glass-ceramic sample showed a lower activation energy of 47 kJ mol^{-1} than the glass sample (52 kJ mol^{-1}). **Figure 6(c)** shows the composition dependence of the ionic conductivities at 25°C of $(100 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ glass and glass-ceramic samples. The ionic conductivities at 25°C and activation energies of these samples are listed in **Table 3**. The glass samples with $0 \leq x \leq 50 \text{ mol } \%$ showed almost identical ionic conductivities of about $10^{-6} \text{ S cm}^{-1}$. The glass-ceramic samples showed higher ionic conductivities than the glass samples for compositions of $0 \leq x \leq 30$

Table 3. Ionic conductivities and activation energies of the $(100-x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ glasses and glass-ceramics heat-treated at 270 °C

Composition	Phase	$\sigma_{25}/\text{S cm}^{-1}$	$E_a/\text{kJ mol}^{-1}$
$x = 0$	Glass	1.1×10^{-6}	52
	Glass-ceramic	1.9×10^{-6}	49
$x = 10$	Glass	1.3×10^{-6}	52
	Glass-ceramic	2.2×10^{-6}	47
$x = 20$	Glass	1.0×10^{-6}	51
	Glass-ceramic	1.6×10^{-6}	47
$x = 30$	Glass	1.1×10^{-6}	53
	Glass-ceramic	1.3×10^{-6}	48
$x = 40$	Glass	9.7×10^{-7}	52
	Glass-ceramic	2.1×10^{-7}	50
$x = 50$	Glass	8.2×10^{-7}	54
	Glass-ceramic	5.8×10^{-8}	56

Fig. 7. Charge-discharge curves of the all-solid-state Li-In/LiNbO₃-coated NMC cell using a 90Li₄SiO₄·10Li₂SO₄ glass-ceramic as the electrolyte.

mol %. The 90Li₄SiO₄·10Li₂SO₄ glass-ceramic showed the highest conductivity of $2.2 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C. This value is higher than that of the high-temperature sintered bodies of $1.3 \times 10^{-6} \text{ S cm}^{-1}$ in a previously reported Li₄SiO₄–Li₂SO₄ system.²³⁾ The conductivity enhancement here is due to the introduction of Li₂SO₄ and the enhancement of crystallinity in the hexagonal phase. Conversely, the ionic conductivity decreased with HT at $x = 40$ and 50 mol %. This may be related to the presence of the Li₁₆(SiO₄)₃(SO₄)₂ crystal, as observed in the XRD measurements.

All-solid-state cells using the 90Li₄SiO₄·10Li₂SO₄ glass-ceramic with a hexagonal phase as a solid electrolyte were constructed. The cells operated at 100 °C under a constant current density of 0.13 mA cm^{−2} and cutoff voltages of 1.9 and 3.8 V vs. Li–In. The glass-ceramic electrolyte exhibited the conductivity of approximately $10^{-4} \text{ S cm}^{-1}$ at 100 °C. **Figure 7** shows the charge-discharge curves of the all-solid-state Li–In/LiNbO₃-coated NMC cells. The initial charge and discharge capacities were 178 and 156 mAh g^{−1}, respectively, which are almost comparable to the capacity of the cell using sulfide Li₃PS₄ electrolyte.²⁴⁾ The all-solid-state cells were constructed by HT at 270 °C and it is noteworthy that all-solid-state cells using the Li₄SiO₄–Li₂SO₄ glass-ceramics operated as

secondary batteries without high-temperature sintering process.

4. Conclusions

$(100-x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_2\text{SO}_4$ ($x = 0, 10, 20, 30, 40, 50$, and 75 mol %) glasses and glass-ceramics were prepared by mechanochemical treatment and subsequent HT at 270 °C. As the Li₂SO₄ content was increased, the relative density of the powder-compressed pellets increased. The obtained glass-ceramics exhibited a hexagonal phase with a $P6_3/mmc$ space group. At compositions of $0 \leq x \leq 30$ mol %, the glass-ceramics prepared by heating at 270 °C showed higher ionic conductivities than the corresponding glasses. The 90Li₄SiO₄·10Li₂SO₄ glass-ceramic electrolyte showed the highest ionic conductivity of $2.2 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C. All-solid-state Li–In/NMC cells using 90Li₄SiO₄·10Li₂SO₄ glass-ceramic as an electrolyte were operated as a secondary battery without high-temperature sintering. The oxide glass-based materials with good formability and lithium ion conductivity are promising electrolytes for oxide-type all-solid-state batteries.

Acknowledgments This research was financially supported by JST ALCA-SPRING project (grant number JPMJAL1301).

References

- 1) K. Takada, *Acta Mater.*, **61**, 759–770 (2013).
- 2) J. M. Tarascon and M. Armand, *Nature*, **414**, 359–367 (2001).
- 3) Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba and R. Kanno, *Nat. Energy*, **1**, 16030 (2016).
- 4) A. Manthiram, X. Yu and S. Wang, *Nat. Rev. Mater.*, **2**, 16103 (2017).
- 5) G. Oh, M. Hirayama, O. Kwon, K. Suzuki and R. Kanno, *Chem. Mater.*, **28**, 2634–2640 (2016).
- 6) Y. Zhu, X. He and Y. Mo, *ACS Appl. Mater. Inter.*, **7**, 23685–23693 (2015).
- 7) V. Thangadurai, S. Adams and W. Weppner, *Chem. Mater.*, **16**, 2998–3006 (2004).
- 8) R. Murugan, V. Thangadurai and W. Weppner, *Angew. Chem. Int. Edit.*, **46**, 7778–7781 (2007).
- 9) Y. Inaguma, C. Liqun, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta and M. Wakihara, *Solid State Commun.*, **86**, 689–693 (1993).
- 10) A. G. Belous, *J. Eur. Ceram. Soc.*, **21**, 1797–1800 (2001).
- 11) H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka and G. y. Adachi, *Solid State Ionics*, **40–41**, 38–42 (1990).
- 12) K. Arbi, W. Bucheli, R. Jiménez and J. Sanz, *J. Eur. Ceram. Soc.*, **35**, 1477–1484 (2015).
- 13) J. Kim, J. Kim, M. Avdeev, H. Yun and S.-J. Kim, *J. Mater. Chem. A*, **6**, 22478–22482 (2018).
- 14) A. Sakuda, A. Hayashi and M. Tatsumisago, *Sci. Rep.*, **3**, 2261 (2013).
- 15) M. Tatsumisago, H. Narita, T. Minami and M. Tanaka, *J. Am. Ceram. Soc.*, **66**, C210–C211 (1983).
- 16) M. Tatsumisago, R. Takano, K. Tadanaga and A. Hayashi, *J. Power Sources*, **270**, 603–607 (2014).
- 17) M. Tatsumisago, R. Takano, M. Nose, K. Nagao, A.

- Kato, A. Sakuda, K. Tadanaga and A. Hayashi, *J. Ceram. Soc. Jpn.*, **125**, 433–437 (2017).
- 18) Y. Yoneda, M. Shigeno, T. Kimura, K. Nagao, C. Hotehama, A. Sakuda, M. Tatsumisago and A. Hayashi, *Solid State Ionics*, **363**, 115605 (2021).
- 19) K. Kanazawa, S. Yubuchi, C. Hotehama, M. Otoyama, S. Shimono, H. Ishibashi, Y. Kubota, A. Sakuda, A. Hayashi and M. Tatsumisago, *Inorg. Chem.*, **57**, 9925–9930 (2018).
- 20) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, **44**, 1272–1276 (2011).
- 21) N. Iwamoto, N. Umesaki, M. Takahashi, M. Tatsumisago, T. Minami and Y. Matsui, *J. Non-Cryst. Solids*, **95–96**, 233–240 (1987).
- 22) K. Nakamoto, “Infrared and Raman Spectra of Inorganic and Coordination Compounds”, 3rd ed., Wiley, New York (1978).
- 23) M. A. K. L. Dissanayake and A. R. West, *J. Mater. Chem.*, **1**, 1023–1025 (1991).
- 24) K. Nagao, A. Sakuda, A. Hayashi and M. Tatsumisago, *J. Power Sources*, **424**, 215–219 (2019).