Effect of sintering temperature and sintering additives on ionic conductivity of LiSi_2N_3

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The effect of sintering temperature and sintering additives on the ionic conductivity of LiSi_2N_3 was studied by performing complex impedance measurements. LiSi_2N_3 materials were fabricated by the reaction of Li_3N , Si_3N_4 , and sintering additives at temperatures of 1873–2073 K. Dense hot-pressed bodies were obtained at 1973–2073 K in the case of undoped LiSi_2N_3 and at 1873 K in the case of Y_2O_3 , CaF_2 , and B_2O_3 addition. The ionic conductivity increased greatly with increasing sintering temperature and exhibited a strong dependence on the type of sintering additive. When the sintering temperature was constant at 1873 K, although the conductivities of Y_2O_3 -doped LiSi_2N_3 and CaF_2 -doped LiSi_2N_3 were lower than that of undoped LiSi_2N_3 , the conductivity of B_2O_3 -doped LiSi_2N_3 was higher than that of undoped LiSi_2N_3 . The enhanced conductivity of B_2O_3 -doped LiSi_2N_3 can be attributed to the increase in the density of the sintered material without the formation of a phase of significant resistance at the grain boundaries.

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1. Introduction

Lithium solid electrolytes are of considerable interest for the production of solid-state lithium batteries. Among the binary and ternary lithium nitrides, Li_3N has the highest lithium ion conductivity of about $10^{-3} \Omega^{-1}\text{cm}^{-1}$.¹⁾ However, the decomposition voltage of Li_3N has a rather low value of 0.44 V at room temperature, and it decreases rapidly with increasing temperature.¹⁾ Thus, the applicability of binary lithium nitride as a solid-state electrolyte at elevated temperatures is limited. To compensate for this disadvantage, several ternary lithium nitrides have been investigated and their lithium ion conductivity has been measured.^{2)–6)}

Ternary lithium silicon nitrides are examples of such interesting materials. Among the Li_3N – Si_3N_4 systems, there are several ternary compounds, including LiSi_2N_3 ,^{4),7),8)} Li_2SiN_2 ,^{4),9),10)} Li_5SiN_3 ,^{4),11),12)} $\text{Li}_{18}\text{Si}_3\text{N}_{10}$,⁴⁾ $\text{Li}_{21}\text{Si}_3\text{N}_{11}$,⁴⁾ and Li_8SiN_4 .⁴⁾ Despite the crystal structure of some of these compounds remaining unclarified, the Li^+ ion conductivity of lithium silicon nitride compounds tends to increase with the Li/Si ratio.^{4),13)} Li_8SiN_4 has been reported to have the highest ionic conductivity of the above ternary lithium nitrides.⁴⁾ However, it is unstable in the presence of moisture and soluble in water.⁴⁾

Among the lithium silicon nitrides, LiSi_2N_3 is the most stable compound and has a well-defined crystal structure that is isostructural with $\text{Si}_2\text{N}_2\text{O}$ and Li_2SiO_3 , which have a wurtzite-type structure (space group $\text{Cmc}2_1$).^{7),8)} Similar to $\text{Si}_2\text{N}_2\text{O}$, the framework of $[\text{Si}_2\text{N}_3]^-$ in LiSi_2N_3 is built up of two-dimensional infinite, parallel layers of condensed $[\text{Si}_6\text{N}_6]$ twelve-membered rings formed by sharing the nitrogen atoms at the corners of the SiN_4 tetrahedra.⁸⁾ Li^+ occupies the 4a site and is directly connected with four or five nitrogen atoms within the unit cell ($\sim 2.3 \text{ \AA}$) or the crossover unit cell ($\sim 2.7 \text{ \AA}$), respectively.

Regarding the practical use of the lithium silicon nitrides, LiSi_2N_3 is of particular interest.

Therefore, in this study we focused on the most stable compound, LiSi_2N_3 . To the best of our knowledge, there have been no detailed reports on the dependence of the ionic conductivity of LiSi_2N_3 on sintering temperature and the addition of sintering additives. Accordingly, the aim of this study is to investigate the effects of sintering temperature and the addition of sintering additives on the ionic conductivity of LiSi_2N_3 .

2. Experimental procedure

Undoped, Y_2O_3 -doped, CaF_2 -doped, and B_2O_3 -doped LiSi_2N_3 were prepared by the reaction of Li_3N (>99% purity, Kojundo Chemical Lab. Co., Ltd, Saitama, Japan), α - Si_3N_4 (SN-E10, UBE Industries, Tokyo, Japan), and a sintering additive. Three additives, Y_2O_3 (99.9% purity, Shin-Etsu Chemical Co., Ltd, Tokyo, Japan), CaF_2 (>99.9% purity, Kojundo), and B_2O_3 (99.98%, Aldrich, Milwaukee, WI, USA) were selected as sintering additives. Li_3N powder, α - Si_3N_4 powder, and the sintering additive were mixed using a silicon nitride mortar in a dry state. **Table 1** shows the compositions of the starting powders (A–F) used in this study. The Li_3N powder and α - Si_3N_4 powder were mixed in stoichiometric compositions. The mixed powder was placed in a 26-mm-diameter graphite mold and a thin BN plate was added between the mold cap and the mixed powder to separate them. All the processes were carried out in a nitrogen-filled glove box. Hot pressing was performed at 1873, 1973, and 2073 K for 1 h under a pressure of 20 MPa in a N_2 atmosphere (0.10 MPa).

The crystal structure of each sample was determined by X-ray diffractometry (D8 ADVANCE, Bruker, Germany) using $\text{Cu K}\alpha$ radiation. The densities of the samples were measured using Archimedes' method, with distilled water as the immersion medium. The microstructures of the samples were observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, Ltd., Japan).

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Table 1. Compositions, sintering temperatures, and characteristics of hot-pressed materials

Material	Composition of starting powder (wt%)					Sintering temperature (K)	Density (g/cm^3)	Primary phase
	Si_3N_4	Li_3N	Y_2O_3	CaF_2	B_2O_3			
A	89.0	11.0	—	—	—	2073	3.0	LiSi_2N_3
B	89.0	11.0	—	—	—	1973	2.9	LiSi_2N_3
C	89.0	11.0	—	—	—	1873	2.0	LiSi_2N_3
D	85.9	10.7	3.4	—	—	1873	3.0	LiSi_2N_3
E	86.8	10.8	—	2.4	—	1873	2.9	LiSi_2N_3
F	88.0	10.9	—	—	1.1	1873	2.9	LiSi_2N_3

Fig. 1. SEM micrographs of fracture surface of sintered bodies of LiSi_2N_3 .

Both sides of each sintered sample were polished to a $9\mu\text{m}$ finish, and Au paste (Tanaka Kikinokoku, Japan) was applied to both sides of the sample by firing at 773 K for 30 min in N_2 . Subsequently, a circular Pt electrode was attached to each side of the sample before it was mounted on the support tube in a ProboStat (NorECs AS., Norway) measurement cell for electrochemical characterization (two-electrode measurements).^{14),15)} Relatively strong spring loads were applied with alumina parts to hold the assembly together and to maintain contact between the sample and the electrodes. Each sample was heated to measurement temperature in dry nitrogen then maintained at this temperature for 0.5 h prior to the measurement of complex impedance.

The complex impedance measurements were performed using a Solartron 1260 impedance analyzer equipped with a Solartron 1296 dielectric interface. The measurement conditions were as follows: frequency range 2 mHz–10 MHz, temperature range 293–673 K, and flowing N_2 gas atmosphere.

3. Results and discussion

The compositions of the starting powders, the sintering temperature, and the microstructural characteristics of the as-hot-pressed materials (A–F) are summarized in Table 1. All materials contained mostly LiSi_2N_3 and were relatively stable in air at room temperature. XRD analysis indicates that LiSi_2N_3 is a primary phase and small amount of $\beta\text{-Si}_3\text{N}_4$ exists as a secondary phase in all materials. No other phase except the LiSi_2N_3 and the $\beta\text{-Si}_3\text{N}_4$ was detected by the XRD analysis in the case of undoped- LiSi_2N_3 and B_2O_3 -doped LiSi_2N_3 . On the other hand, a small amount of unidentified phases were detected by the XRD

analysis in the case of Y_2O_3 -doped LiSi_2N_3 and CaF_2 -doped LiSi_2N_3 . Lattice parameter of each sample was obtained by fitting the XRD peak data using software Jade 7. The lattice parameter and the unit cell volume of all materials (A–F) were approximately the same. The total lattice volume change is less than 0.02%. These results indicate that the amount of additive incorporated into LiSi_2N_3 grain was very small in materials D–F.

The microstructures of the as-hot-pressed materials are shown in Fig. 1. As shown in the figure, no abnormal grain growth was observed, and the grains had an almost equiaxed form and size at a fine scale in all materials. The absence of residual porosity in the SEM images of materials A, B, D, E, and F indicates that these materials were almost fully densified. Material C had larger pores because its density was lower. Dense hot-pressed bodies were obtained at 1973–2073 K for undoped LiSi_2N_3 and at 1873 K in the case of Y_2O_3 , CaF_2 , and B_2O_3 addition. These results indicate that the addition of Y_2O_3 , CaF_2 , and B_2O_3 promotes the densification of LiSi_2N_3 .

The complex impedance was measured to determine the conductivity. In general, the AC impedance of an ionic conductor measured by a two-probe method contains contributions from the grain interior, the grain boundaries, and the electrode–electrolyte interface, which can be illustrated in the complex plane by three successive arcs as shown in Fig. 2(b).^{16),17)} The frequency increases from right to left in the plot. The arc at the high-frequency end of the spectrum represents the grain-interior resistivity, that at the middle of the spectrum is a consequence of the grain-boundary effect, and the low-frequency arc is assigned to the electrode response. An idealized equivalent circuit for polycrystalline ceramic materials corresponding to the impe-

Fig. 2. Idealized equivalent circuit (a) and its corresponding impedance plot (b): R_{gi} and C_{gi} , R_{gb} and C_{gb} , and R_{el} and C_{el} represent the resistances and capacitances of the grain interior, grain boundaries, and the electrode-electrolyte interface, respectively.

Fig. 4. Impedance spectra (recorded at 573 K in N_2) for material A. The diameter of the semicircular arc was taken as the total resistance of the sample.

Fig. 3. Impedance spectra (recorded at 573 K in N_2) of materials A–F.

dance plot is shown in Fig. 2(a). In practice, however, not all these arcs can be observed, depending on the nature of the sample and the measurement conditions.

Figure 3 illustrates complex impedance diagrams for $LiSi_2N_3$ samples A–F recorded at 573 K in N_2 . Each complex impedance diagram (2 mHz–10 MHz) consists of a semicircular arc and a straight line. The shape of the arc changes with the sintering temperature and the addition of a sintering additive. In this context, the semicircular arc is attributed to $LiSi_2N_3$ grains and grain boundaries, while the low-frequency straight line is considered to correspond to the sample–electrode charge transport process as shown in **Fig. 4**.

Figure 3 shows that for materials A–C as the sintering temperature decreases, the shape of the semicircular arc changes. The arc for material C indicated greater resistance in the intermediate-frequency region (about 5 kHz–100 Hz) than that of materials A and B. Material C was not fully densified because of the low temperature of sintering (see Table 1). Therefore, as shown in Fig. 1, many pores remained in the microstructure of material C, particularly at the grain boundaries, after sintering. These pores may deteriorate the electrical properties at grain boundaries,^{18),19)} and thus enhance the resistance there. In general, the resistance at grain boundaries contributes to the middle part of the spectrum shown in Fig. 2(b). The resistance at

Fig. 5. Temperature dependences of ionic conductivities of materials A–C.

Fig. 6. Temperature dependences of ionic conductivities of materials C–F.

grain boundaries might contribute to resistance in the intermediate-frequency region, corresponding to the semicircular arc for material C.

As can be observed in Fig. 3, the shape of the semicircular arc for materials D–F also changed with the addition of a sintering additive. The arcs for D (Y_2O_3 -doped material), and E (CaF_2 -doped material) indicated greater resistance in the intermediate-frequency region (about 4 kHz–1 Hz for D and about 5 kHz–10 Hz for E) than that of material A, which was undoped and fully densified. These results showed that a phase with significant resistance formed at the grain boundaries of materials D and E, because such a phase generally contributes to the middle of the spectrum.^{16),17)} On the other hand, the resistance in the intermediate-frequency region for F (B_2O_3 -doped material) was considerably less than that of materials D and E, and the shape of the semicircular arc for F was similar to that for A. These results show that the addition of B_2O_3 does not cause the formation of a high-resistance phase at the grain boundaries.

The total conductivity of each sample was estimated from the intersections between the extrapolated semicircular arc and the real axis. Yamane et al. reported that the electronic conductivity of LiSi_2N_3 was less than 1% of the total conductivity at temperatures between 423 and 673 K.⁴⁾ The experimental condition of complex impedance measurements was almost same as our experimental condition. So, we believe that most of the conductivity of LiSi_2N_3 materials obtained in this study is caused by the migration of lithium ions as well as Yamane et al.'s report.

Figures 5 and 6 show the temperature dependences of the ionic conductivity for materials A–F, respectively. As shown in Figs. 5 and 6, the plots of $\ln(\sigma T)$ against $1000/T$ were found to be linear and closely fit the Arrhenius equation, $\sigma T =$

Table 2. Ionic conductivity and activation energy of lithium silicon nitrides

Material	$\sigma/\text{S}\cdot\text{m}^{-1}$ (600 K)	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)
A	1.2×10^{-3}	66
B	6.3×10^{-4}	67
C	1.1×10^{-4}	78
D	1.9×10^{-5}	87
E	9.9×10^{-5}	110
F	7.0×10^{-4}	69
Ref. 4 (LiSi_2N_3)	5.3×10^{-3}	64

$A \exp(-E_a/RT)$, where A is the preexponential factor, E_a is the activation energy for conduction, and R is the gas constant. Table 2 summarizes the conductivities at 600 K and the activation energies of conduction.

The ionic conductivity increased and the activation energy of ionic conduction decreased with increasing sintering temperature and material density, shown by the results for materials A–C. The high ionic conductivity of materials A and B may be caused by the increased density of the sintered sample, which enhances grain boundary conductivity, and the low activation energy. Material C has the lowest conductivity and the largest activation energy among materials A–C, probably because its structure has many large pores, which block the migration of lithium ions.

Although the densities of materials D and E were higher than that of material C, their conductivities were lower than that of material C, and their activation energies were larger than that of material C. These findings might be due to the formation of a phase with significant resistance at the grain boundaries of materials D and E. The unidentified phases detected by XRD analysis might be the phase with significant resistance. This phase blocks the migration of lithium ions, and thus decreases the ionic conductivity. In contrast, the conductivity of material F is higher than that of material C, and its activation energy is smaller than that of material C, probably due to the increase in the density of material F upon sintering without the formation of a phase with significant resistance at the grain boundaries. Accordingly, the conductivity of material F increased to a value comparable to that of the undoped and fully densified material B.

Although the amount of additive incorporated into LiSi_2N_3 grain was very small in materials D–F, we cannot rule out the possibility that the incorporation of the additive into LiSi_2N_3 grain might change the LiSi_2N_3 grain conductivity and the total conductivity. Further investigation and more detailed characterization are under progress to elucidate this point.

The conductivity of material A (undoped LiSi_2N_3 , $1.2 \times 10^{-3} \text{ S}\cdot\text{m}^{-1}$ at 600 K) was the highest and its activation energy (66 kJ/mol) was the lowest among the compounds prepared in this study. The high ionic conductivity can be explained as follows. The density of material A was the highest among materials A to F, and thus the ionic conductivity at grain boundaries was enhanced by the greatest amount. Moreover, no sintering additive was added to material A, therefore its structure did not have a high-resistance phase resulting from a sintered additive at the grain boundaries. Yamane et al. reported the preparation and ionic conductivity of LiSi_2N_3 . They prepared LiSi_2N_3 at a low temperature of 1475 K in a nitrogen gas flow for a short duration to minimize lithium vaporization.⁴⁾ Although the sintering temperature of material A in this study was very high (2073 K), the conductivity of A was comparable to that of Yamane et al.'s material. The high ionic conductivity may have

been caused by the hot pressing at 20 MPa in a N₂ atmosphere (0.10 MPa). In this study, lithium vaporization might have been suppressed by the hot pressing.

4. Conclusions

The effect of sintering temperature and sintering additives on the ionic conductivity of LiSi₂N₃ was studied by performing complex impedance measurements. LiSi₂N₃ materials were prepared by the reaction of Li₃N, Si₃N₄, and sintering additives at temperatures of 1873–2073 K. Dense hot-pressed bodies were obtained at 1973–2073 K in the case of undoped LiSi₂N₃ and at 1873 K in the case of Y₂O₃, CaF₂, and B₂O₃ addition. These results indicated that the addition of Y₂O₃, CaF₂, or B₂O₃ promotes the densification of LiSi₂N₃. All the obtained materials were relatively stable in air. The ionic conductivity of the materials was investigated from near-ambient temperature up to 673 K by complex impedance spectroscopy in a N₂ atmosphere. The complex impedance diagram (2 mHz–10 MHz) of each material consisted of a semicircular arc and a straight line. The shape of the arc in the complex impedance diagram changed with the sintering temperature and with the addition of a sintering additive. The semicircular arc was attributed to LiSi₂N₃ grains and grain boundaries, while the low-frequency straight line was considered to be due to the sample–electrode charge transport process.

The ionic conductivity was enhanced greatly with increasing sintering temperature. The improved ionic conductivity might have been caused by the decrease in the size of pores in the microstructure with the increased density of the sintered sample, which enhanced the grain boundary conductivity. In porous LiSi₂N₃ ceramics, the pores inhibit the movement of carriers; thus, porous LiSi₂N₃ ceramics have lower conductivity than dense LiSi₂N₃ ceramics. The conductivity was also affected by the addition of sintering additives. When the sintering temperature was constant at 1873 K, although the conductivities of Y₂O₃-doped LiSi₂N₃ and CaF₂-doped LiSi₂N₃ were lower than that of undoped LiSi₂N₃, the conductivity of B₂O₃-doped LiSi₂N₃ was higher than that of undoped LiSi₂N₃. The enhanced conductivity of B₂O₃-doped LiSi₂N₃ can be attributed to the increase in the density of the sintered material without the formation of a phase of significant resistance at the grain boundaries, which thus enhanced the grain boundary conductivity.

Undoped LiSi₂N₃, which had the highest density among the materials investigated in this study, had the highest lithium ionic conductivity ($1.2 \times 10^{-3} \text{ S} \cdot \text{m}^{-1}$ at 600 K) and the lowest activation energy (66 kJ/mol).

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