

Mechanochemical Synthesis and Li⁺ Ion Conductivity of Li₃N-based Amorphous Solid Electrolytes

A. HAYASHI, T. OHTOMO, F. MIZUNO and M. TATSUMISAGO

Department of Applied Chemistry, Graduate School of Engineering,
Osaka Prefecture University, Sakai, Osaka 599-8531 (Japan)

E-mail: hayashi@chem.osakafu-u.ac.jp

Abstract

Amorphous solid electrolytes were synthesized in the systems Li₃N–P₂S₅ and Li₃N–P *via* mechanochemical route. Amorphous materials were obtained at the compositions with $x = 50$ and 60 in the system $x\text{Li}_3\text{N} \cdot (100 - x)\text{P}_2\text{S}_5$ (mol. %), while crystalline Li₂S was obviously formed at the compositions with $x = 70$ and 80 . The conductivity increased with increasing Li₃N content, and then decreased in the composition range $x > 60$. The highest conductivity of $2.2 \cdot 10^{-5}$ S/cm at room temperature was achieved at the composition with $x = 60$. The formation of insulative Li₂S in the compositions with higher Li₃N content is responsible for the decrease of conductivity. Li₃N was reacted with P instead of P₂S₅ by milling in order to prevent the formation of Li₂S. The obtained materials were basically amorphous, but partially included crystalline materials such as Li₃P and Li₇PN₄. The 80Li₃N · 20P (mol. %) material exhibited the highest conductivity of $1.0 \cdot 10^{-5}$ S/cm at room temperature in the system Li₃N–P.

INTRODUCTION

The development of highly Li⁺ ion conducting amorphous solid electrolytes is desired for establishing all-solid-state lithium rechargeable batteries with high safety and reliability. Li₂S-based sulphide glassy materials prepared by the melt-quenching method are promising candidates as solid electrolytes for all-solid-state batteries because of their favourable properties of high Li⁺ conductivity over 10^{-4} S/cm at room temperature and wide electrochemical window [1–3].

The sulphide amorphous solid electrolytes were also synthesized *via* mechanochemical route [4]. The preparation procedure using a high-energy ball mill apparatus is very useful for obtaining amorphous fine powders, which achieve close contact between electrolyte and electrode in solid-state batteries. The Li₂S–SiS₂ amorphous materials prepared by milling for several hours exhibited the conductivity of 10^{-4} S/cm at room temperature [5, 6]. Solid-state NMR measurements revealed that the local structure around silicon atoms of the Li₂S–SiS₂ materials milled for 20 h was almost the

same as that of the corresponding melt-quenched glasses.

In the case of using Li₃N as a lithium source instead of Li₂S, Li⁺ conducting amorphous materials were prepared in the system Li₃N–SiS₂ by milling for very short periods such as 20 min (the reaction would be based on “compulsion reaction”) [7]. The 40Li₃N · 60SiS₂ (mol. %) material showed excellent properties such as high conductivity of $2.7 \cdot 10^{-4}$ S/cm at room temperature, unity of Li⁺ ion transference number, and wide electrochemical window of 10 V.

On the other hand, sulphide amorphous electrolytes with different glass-formers such as P₂S₅ [8], Al₂S₃ [9], and GeS₂ [10] instead of SiS₂ were also synthesized by milling. In particular, the Li₂S–P₂S₅ amorphous materials are one of the excellent solid electrolytes; the conductivity can be further improved by crystallization of the amorphous sample [11] and all-solid-state batteries with the Li₂S–P₂S₅ solid electrolytes exhibited excellent cycling performance [12]. The combination of Li₃N as a lithium source and P₂S₅ as a glass former is a most attractive system for solid electrolytes.

In the present study, the Li_3N -based amorphous solid electrolytes were synthesized in the system $\text{Li}_3\text{N}-\text{P}_2\text{S}_5$ by mechanical milling using a planetary ball mill apparatus. The $\text{Li}_3\text{N}-\text{P}$ materials using elemental P instead of P_2S_5 were also prepared. Structure and electrical properties of the obtained materials were investigated.

EXPERIMENTAL

Reagent-grade Li_3N and P_2S_5 or P (red phosphorus) powders were used as starting materials for sample preparation. The Li_3N and P_2S_5 powders were crystalline and P was amorphous. The mechanical milling treatment was carried out for the batch (1 g) of the mixed materials placed into a stainless steel pot (volume of 45 ml) with 10 stainless steel balls (10 mm in diameter) using a high-energy planetary ball mill apparatus (Fritsch Pulverisette 7). The rotation speed was fixed at 370 rpm and all processes were conducted at room temperature in a dry Ar-filled glove box.

X-ray diffraction (XRD) measurements were carried out using a Mac-Science M18XHF²²-SRA diffractometer with $\text{CuK}\alpha$ radiation for the obtained materials. The sample was sealed in an Ar-filled container with the beryllium windows.

The electrical conductivity of the samples was measured by using AC impedance methods. The powder samples were pelletized by cold pressing at 3700 kg/cm^2 and carbon paste was painted on both sides of the pellet to serve as electrodes. The electrical conductivity of the pellet was measured in a dry Ar atmosphere from 10 Hz to 8 MHz with an impedance analyzer (Model 1260, Solartron) in the temperature range of 25–180 °C.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of powder samples of $50\text{Li}_3\text{N} \cdot 50\text{P}_2\text{S}_5$ (mol. %) with different milling periods. Numbers in the Figure mean the milling periods of time. Diffraction peaks due to the crystals of Li_3N and P_2S_5 are observed in the powder mixture without mechanical milling (0 h). As the milling period increases, the intensity of those crystalline peaks decreases and the halo pat-

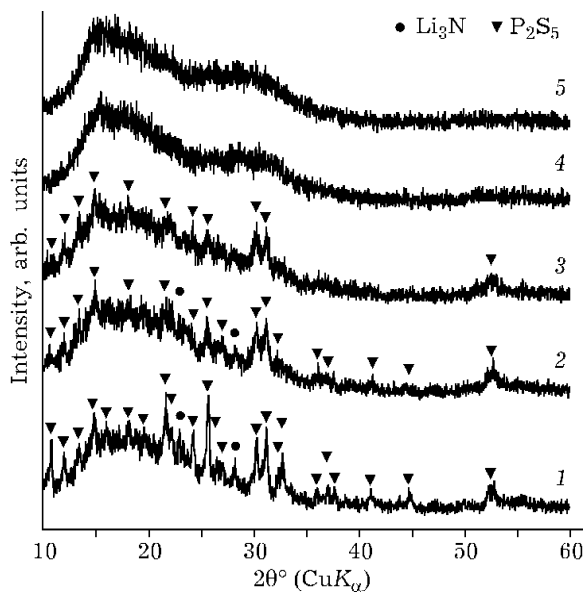


Fig. 1. XRD patterns of the $50\text{Li}_3\text{N} \cdot 50\text{P}_2\text{S}_5$ (mol. %) sample prepared by mechanical milling for different periods, h: 0 (1), 1 (2), 5 (3), 10 (4), 20 (5).

tern becomes dominant. The peaks due to Li_3N disappear after milling for 5 h, and the peaks due to P_2S_5 disappear after milling for 10 h. Amorphization gradually proceeds during milling, and the amorphous material is obtained after milling for at least 10 h.

Figure 2 shows the XRD patterns of the $x\text{Li}_3\text{N} \cdot (100 - x)\text{P}_2\text{S}_5$ (mol. %) ($x = 50, 60, 70,$ and 80) samples mechanically milled for 20 h. The samples of $x = 50$ and 60 basically show

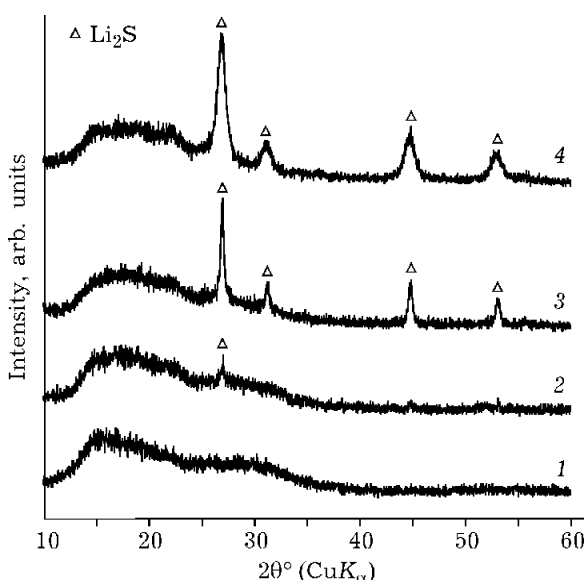


Fig. 2. XRD patterns of the $x\text{Li}_3\text{N} \cdot (100 - x)\text{P}_2\text{S}_5$ samples prepared by mechanical milling for 20 h. x value: 50 (1), 60 (2), 70 (3), 80 (4).

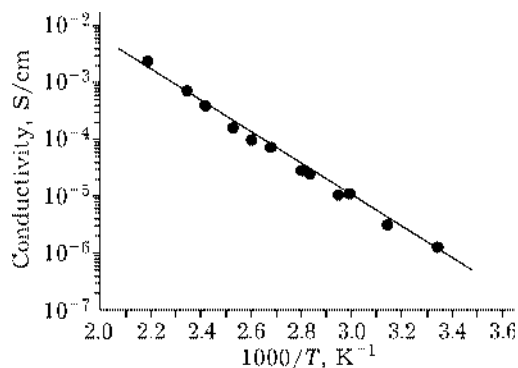


Fig. 3. Temperature dependence of conductivity of the $50\text{Li}_3\text{N} \cdot 50\text{P}_2\text{S}_5$ (mol. %) sample prepared by mechanical milling for 20 h.

halo patterns on XRD measurements, suggesting that the obtained materials are amorphous. The peaks due to Li_2S crystal are obviously observed for the samples of $x = 70$ and 80 . The reaction between Li_3N and P_2S_5 by mechanical milling produces Li_2S at the higher Li_3N compositions.

Figure 3 shows the temperature dependence of electrical conductivity of the pelletized $50\text{Li}_3\text{N} \cdot 50\text{P}_2\text{S}_5$ amorphous sample prepared by milling for 20 h. The conductivities of the sample follow the Arrhenius equation and the activation energy (E_a) for conduction was calculated from the slope. Figure 4 shows the composition dependence of conductivity at 25°C (σ_{25}) and the activation energy (E_a) for conduction of the $x\text{Li}_3\text{N} \cdot (100 - x)\text{P}_2\text{S}_5$ samples prepared by milling for 20 h. The conductivity increases with increasing Li_3N content, and then decreases in the composition range $x > 60$. The high-

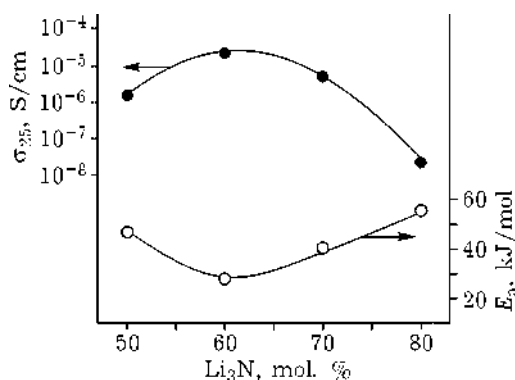


Fig. 4. Composition dependence of conductivities at 25°C (σ_{25}) and activation energies for conduction (E_a) for the $x\text{Li}_3\text{N} \cdot (100 - x)\text{P}_2\text{S}_5$ (mol. %) ($x = 50, 60, 70$ and 80) samples prepared by mechanical milling for 20 h.

est conductivity of $2.2 \cdot 10^{-5} \text{ S/cm}$ at room temperature is achieved at the composition with $x = 60$. The composition dependence of E_a corresponds to that of σ_{25} and the minimum E_a of 28 kJ/mol is obtained at the composition with $x = 60$. The increase in Li_3N content improves conductivity because of increasing Li^+ carrier concentration in amorphous matrix. On the other hand, the formation of insulative Li_2S in the compositions with higher Li_3N content is responsible for the decrease of conductivity.

Li_3N was then reacted with elemental P instead of P_2S_5 by milling in order to prevent the formation of Li_2S . Figure 5 shows the XRD patterns of the $y\text{Li}_3\text{N} \cdot (100 - y)\text{P}$ (mol. %) ($y = 50, 60, 70$ and 80) samples mechanically milled for 20 h. The obtained materials were basically amorphous, but partially included crystalline materials formed during milling. The Li_3P crystal is precipitated at the compositions $y = 50$ and the Li_7PN_4 crystal is mainly precipitated at the compositions $y = 60$ and 70 . The Li_3N phase as a starting material partially remains at the composition $y = 80$. It is revealed that phosphide and phosphorus nitride compounds can be synthesized by mechanochemical route using the starting materials Li_3N and P.

Since the lithium phosphorus nitride, Li_7PN_4 , is formed in the milled materials, the P-N bonds would also be formed in amorphous matrix. The formation of lithium phosphide Li_3P indicates that elemental P is reduced from P^0

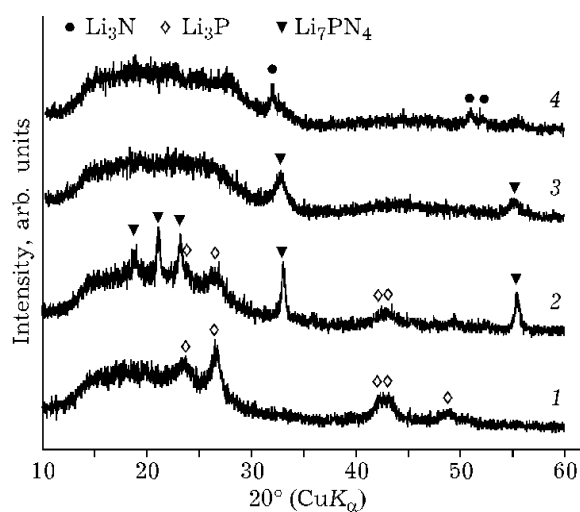


Fig. 5. XRD patterns of the $y\text{Li}_3\text{N} \cdot (100 - y)\text{P}$ (mol. %) samples prepared by mechanical milling for 20 h. y value: 50 (1), 60 (2), 70 (3), 80 (4).

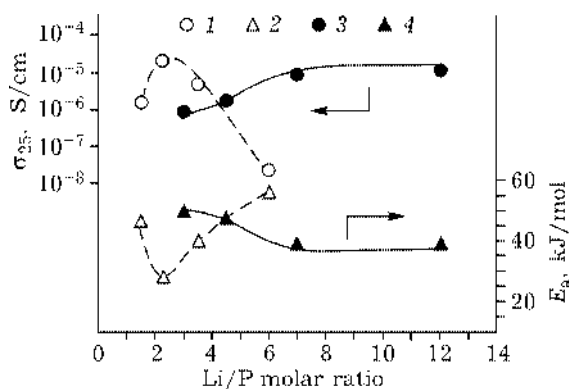


Fig. 6. Composition dependence of conductivities at 25 °C (σ_{25}) and activation energies for conduction (E_a) of the $\text{Li}_3\text{N}-\text{P}_2\text{S}_5$ and $\text{Li}_3\text{N}-\text{P}$ samples prepared by mechanical milling for 20 h: 1, 2 - σ_{25} and E_a of the $\text{Li}_3\text{N}-\text{P}_2\text{S}_5$ samples, respectively; 3, 4 - σ_{25} and E_a of the $\text{Li}_3\text{N}-\text{P}$ samples, respectively.

to P^{3-} and then N_2 gas would be generated during milling.

Figure 6 shows the composition dependence of conductivities at 25 °C (σ_{25}) and activation energies for conduction (E_a) of the $\text{Li}_3\text{N}-\text{P}$ samples prepared by mechanical milling for 20 h. The data of the $\text{Li}_3\text{N}-\text{P}_2\text{S}_5$ milled sample are also shown. The conductivity increases with increasing Li_3N content in the system $\text{Li}_3\text{N}-\text{P}$; the $80\text{Li}_3\text{N} \cdot 20\text{P}$ material exhibits the highest conductivity of $1.0 \cdot 10^{-5}$ S/cm at room temperature.

The conductivity of the milled materials depends on the Li^+ concentration in amorphous matrix and the precipitated crystal phases. The Li_3P crystal was reported to show high conductivity of $7.0 \cdot 10^{-4}$ S/cm at room temperature [13], while the Li_7PN_4 crystal exhibited low conductivity of $1.4 \cdot 10^{-7}$ S/cm [14]. The sample $x = 50$ partially included the Li_3P phase, but its conductivity is in the order of 10^{-6} S/cm. Both insufficient crystallinity of Li_3P and low Li^+ concentration would be the reason for low conductivity of the sample $x = 50$. On the other hand, the conductivity increases with an increase in x ($x > 60$) in spite of the presence of less conductive Li_7PN_4 phase because the Li^+ concentration in amorphous matrix increases.

The conductivities of Li_3N -based amorphous materials were compared with those of the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ amorphous materials. The $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ amorphous material ($\text{Li}/\text{P} = 2.25$) showed the maximum conductivity of $2.2 \cdot 10^{-5}$ S/cm at room temperature. The higher conductivity of

$5 \cdot 10^{-5}$ S/cm was reported for the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ amorphous material with almost the same Li content ($\text{Li}/\text{P} = 2.33$) [8]. The incorporation of nitrogen atoms into sulphide amorphous matrix is one of the reasons for decreasing conductivity in the Li_3N -based materials. The use of P instead of P_2S_5 results in preventing the formation of insulative Li_2S crystal and increasing Li^+ concentration and, however, the conductivity is still low (in the order of 10^{-5} S/cm). It is assumed that the $\text{Li}-\text{P}-\text{N}$ amorphous matrix is less conductive than the $\text{Li}-\text{P}-\text{S}$ amorphous matrix.

The conductivity of the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ amorphous material was increased by heat treatment at the crystallization temperature, and the obtained glass ceramic electrolyte exhibited high conductivity of over 10^{-3} S/cm at room temperature [11]. The precipitation of superionic $\text{Li}_7\text{P}_3\text{S}_{11}$ metastable phase is responsible for the high conductivity. The $60\text{Li}_3\text{N} \cdot 40\text{P}_2\text{S}_5$ amorphous sample was crystallized at 290 °C (just over the crystallization temperature) and the ambient temperature conductivity of the sample was also increased from $2.2 \cdot 10^{-5}$ to $9.1 \cdot 10^{-5}$ S/cm, which is, however, lower than the conductivity of the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass ceramics. This is because less conductive $\text{Li}_4\text{P}_2\text{S}_6$ and unknown phases were precipitated in the $\text{Li}_3\text{N}-\text{P}_2\text{S}_5$ glass ceramic material.

CONCLUSIONS

Amorphous solid electrolytes were synthesized in the systems $\text{Li}_3\text{N}-\text{P}_2\text{S}_5$ and $\text{Li}_3\text{N}-\text{P}$ via mechanochemical route. Amorphous materials were obtained at the compositions with $x = 50$ and 60 in the system $x\text{Li}_3\text{N} \cdot (100 - x)\text{P}_2\text{S}_5$, while crystalline Li_2S was obviously formed at the compositions with $x = 70$ and 80. The conductivity increased with increasing Li_3N content, and then decreased in the composition range $x > 60$. The highest conductivity of $2.2 \cdot 10^{-5}$ S/cm at room temperature was achieved at the composition with $x = 60$. The formation of insulative Li_2S in the compositions with higher Li_3N content is responsible for the decrease of conductivity. The materials obtained by milling for the mixture of Li_3N and P, were basically amorphous, but partially included crystalline

materials such as Li₃P and Li₇PN₄. The 80Li₃N · 20P (mol. %) material exhibited the highest conductivity of $1.0 \cdot 10^{-5}$ S/cm at room temperature in the system Li₃N–P.

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