Synthesis and characterization of lithium-ion-conductive glass-ceramics of lithium chloroboracite Li_{4+x}B_{7}O_{12+x/2}Cl (x = 0–1)

Naoto TEZUKA, Yuta OKAWA, Koichi KAJIHARA1 and Kiyoshi KANAMURA

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1–1 Minami-Osawa, Hachioji, Tokyo 192–0397, Japan

Nearly single-phase and almost fully-crystallized glass-ceramics of lithium chloroboracite Li_{4+x}B_{7}O_{12+x/2}Cl (x = 0–1) were prepared by crystallization of precursor glasses derived from the Li_{2}O-B_{2}O_{3}-LiCl ternary system. The crystal structure of Li_{4}B_{2}O_{5}Cl (x = 0) was refined by the Rietveld method in the space group F43c (no. 219). The precursor glass partially crystallized into Li_{2}B_{4}O_{7} at ~500°C and was subsequently converted to Li_{4}B_{2}O_{5}Cl at ~600°C. The decomposition of Li_{4}B_{2}O_{5}Cl started at ~700°C. The conductivity of Li_{4}B_{2}O_{5}Cl was much higher than that of Li_{4}B_{2}O_{5}Cl (x = 1). The glass-ceramic sample with the highest weight fraction of Li_{4}B_{2}O_{5}Cl (~0.98 of crystalline part with a degree of crystallinity of ~0.96) exhibited a conductivity of ~4.6 × 10^{-4} S cm^{-1} at 200°C and an activation energy of conductivity of ~0.52 eV.

Key-words : Lithium-ion-conductive glass-ceramics, Lithium chloroboracite

1. Introduction

All-solid-state lithium-ion batteries have been developed actively because of the absence of flammable liquid electrolytes and increased safety, simple structure, and ease of stacking to increase output voltage. To improve the performance of the batteries solid electrolytes with high lithium ion conductivities are necessary. Although sulfide-based solid electrolytes1,2 have received considerable attention for their high lithium ion conductivities, oxide-based solid electrolytes are attractive for better stability and safety. Various lithium-ion-conducting solid oxides,3–7 including La_{2}O_{3}–Li_{2}O–TiO_{2}8) Li_{5}B_{2}O_{7}Ti_{2}–(PO_{4})_{3}9) and Li_{3}La_{2}Zr_{2}O_{12.10) have been discovered and studied intensively. However, other promising compounds may still exist.

In this study, we focused on lithium chloroboracite, Li_{4}B_{7}O_{12+x}Cl (x = 0–1).11–15) The unit cell structures of the end members (x = 0 and 1) are shown in Fig. 1. These compounds belong to the cubic crystal system. Their unit cell consists of eight subcells, and each subcell contains a Cl^{-} ion surrounded by several Li^{+} ions and negatively-charged B-O framework. The x = 1 compound (Li_{4}B_{2}O_{5}Cl) belongs to the space group no. 196, F23.15) In this compound the eight subcells are classified into two types of subcells stacked alternately. These two types of subcells have fully-occupied Li sites with different positions. In the x = 0 compound (Li_{4}B_{2}O_{5}Cl), in contrast, these subcells are equivalent (differ only in chirality) and the Li sites are not fully occupied. For the x = 0 compound there exists two different structural models based on the space groups no. 196, F2313) and no. 219, F43c.12,14) The ionic conductivity of these compounds has been measured for polycrystalline pellets17,19) and single crystals.14) The conductivity of Li_{4}B_{2}O_{5}Cl is ~10^{-6} S cm^{-1} at room temperature.15,17,18) The conductivity of Li_{4}B_{2}O_{5}Cl is much lower than that of Li_{4}B_{2}O_{5}Cl because of the ordering and full occupancy of the Li sites. These chloroboracites have been synthesized by heat treatment in a sealed glass tube,11,13,18) hydrothermal synthe-

---

1) Corresponding author: K. Kajihara; E-mail: kkaji@tmu.ac.jp

---

DOI http://doi.org/10.2109/jcersj2.16318
with SiC papers to \(~0.8–1.2\) mm thick, polished to 1200 grit, and sputtered with gold electrodes \((\phi = 0.6\) cm) on both faces. In the high-temperature cell carbon clothes were placed on the gold sputtered with gold electrodes \((\text{gold})\) for improved electrical contact to stainless steel electrodes of the sample to improve electrical contact to stainless steel electrodes of the cell.

3. Results

Figure 2 (left) shows photograph of a precursor glass prepared at \((x_1, x_2) = (3.0, 1.4)\). The precursor glass was transparent. However, it became opaque after heat treatment for 3 h at \(600^\circ\text{C}\) as shown in Figure 2 (right). The shape of the sample was nearly identical before and after the heat treatment. Figure 3(a) shows a SEM image of polished surface of a heat-treated sample. The surface of the sample was relatively smooth. Cross-sectional SEM images are shown in Figs. 3(b) and 3(c). The sample exhibited good macroscopic homogeneity over the cross-section. The magnified image shows that the sample consisted of aggregated flaky or rod-like particles as large as \(~1–5\) \(\mu\)m and a small amount of voids between the particles. The relative density of the sample was \(~0.90\) and was much higher than values reported for polycrystalline pellets prepared by sintering at \(700^\circ\text{C}\) \((0.56–0.59^{(29)})\) or \(750^\circ\text{C}\) \((0.85^{(19)})\).

Figure 4 shows TG and DTA curves of precursor glass prepared at \((x_1, x_2) = (3.0, 1.4)\). The DTA curve exhibited glass transition at \(~460^\circ\text{C}\) \((T_g)\) and two exothermic peaks above \(~500^\circ\text{C}\). The onset temperatures of the exothermic peaks were \(~505^\circ\text{C}\) \((T_{50})\) and \(~605^\circ\text{C}\) \((T_{50})\). The weight loss of the sample during heating to \(700^\circ\text{C}\) was less than 2%. However, a notable weight loss was observed at \(T_{50}\).

Figure 5(a) shows XRD patterns of precursor glass prepared at \((x_1, x_2) = (3.0, 1.4)\), and samples derived from the glass by different heat treatment conditions. The precursor glass was amorphous. The main crystal phase formed by heat treatment at \(500^\circ\text{C}\) was \(\text{Li}_3\text{B}_2\text{O}_5\). Prolonged heat treatment at \(500^\circ\text{C}\) improved the crystallinity, whereas \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) remained as a minor phase. The sample was crystallized almost completely at or above \(600^\circ\text{C}\), although a small amount of amorphous phase remained. At \(600^\circ\text{C}\) and \(700^\circ\text{C}\) \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) was the main phase. At \(800^\circ\text{C}\) \(\text{Li}_2\text{B}_4\text{O}_7\) and \(\text{LiBO}_2\) appeared and \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) was no longer the main phase. Table 1 summarizes the weight fractions of crystalline phases \((\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}, \text{Li}_2\text{B}_4\text{O}_7, \text{and LiBO}_2)\) evaluated by the Rietveld refinement of the XRD patterns. At \(600^\circ\text{C}\) the fraction of \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) increased with an increase in heating time along with the consumption of \(\text{Li}_2\text{B}_4\text{O}_7\). The conversion from \(\text{Li}_2\text{B}_4\text{O}_7\) into \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) was nearly completed at \(3\) h. At \(700^\circ\text{C}\), in contrast, the fraction of \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) decreased with time, suggesting that \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) is not stable at this temperature.

Figure 5(b) shows XRD pattern of the precursor glass and curves of broad components derived by the Rietveld refinement for glass-ceramics heat treated at or below \(600^\circ\text{C}\). In this study the degree of crystallinity was defined as \(1 - I_b/I_{b0}\), where \(I_b\) and \(I_{b0}\) denote the intensities of the broad components of the glass-ceramics and precursor glass, respectively. These values are also listed in Table 1. The conventional definition of crystallinity, \(L_x/(L_x + I_b)\), where \(I_b\) denotes the intensity of sharp diffraction peaks, would not be suitable because the small 20 range of the present XRD data may cause an underestimation of \(L_x\). The crystallinity increased by increasing the temperature and time of heat treatment at or below \(600^\circ\text{C}\), whereas slightly decreased after heat treatment for 6 h at \(700^\circ\text{C}\) and 1 h at \(800^\circ\text{C}\). From these observations we concluded that crystallization for 3 h at \(600^\circ\text{C}\) was the best condition and employed in the following experiments.

Figure 5(c) shows XRD patterns of glass-ceramics prepared at \((x_1, x_2) = (3.0, 1.0–1.6)\) and \((4.0, 1.4)\). The intensity of the diffraction peaks of \(\text{Li}_2\text{B}_4\text{O}_7\) decreased with an increase in \(x_2\). In the sample prepared at \(x_2 = 4.0\) the diffraction peak at \(\sim 26^\circ\) attributable to the 111 diffraction of \(\text{Li}_2\text{B}_4\text{O}_7\) was clearly seen. This peak originates from the ordering of the two types of subcells in \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\) and is absent for \(\text{Li}_5\text{B}_7\text{O}_{12}\text{Cl}\). This peak was also seen in the sample prepared at \((x_1, x_2) = (3.0, 1.6)\), although the intensity was very weak.

To decompose the impurity phase \(\text{Li}_2\text{BO}_2\), the amount of LiCl \((x_2)\) was increased. The total amount of Li in the precursor powder was maintained at \(x_1 + x_2 = 4.4\). Figure 6 shows the result of Rietveld refinement for the powder XRD pattern of glass-ceramics prepared at \((x_1, x_2) = (2.8, 1.6)\). The degree of crystallinity of this sample was as high as \(~0.96\). The refined structure parameters are listed in Table 2. The fractional coordinates of \(\text{Li}_2\text{BO}_2\) were fixed at the values reported in Ref. 24. Analysis with the space group \(P43c\) gave a good agreement between the observed and simulated patterns. In the preceding papers Li1 was
placed at the 24c site, located at the midpoint between neighboring Cl atoms.\(^{12,14}\) However, the agreement was improved by allowing the displacement of Li toward Cl atoms and splitting the site into two \(^{48}\) sites. Such displacement of Li atoms is consistent with the structural models based on the space group \(F\overline{2}3.\)\(^{13,15}\) The weight fraction of Li\(_4\)B\(_7\)O\(_{12}\)Cl in the crystalline part was >0.98 and the highest among samples prepared in this study. The occupancy of Cl in the Li\(_4\)B\(_7\)O\(_{12}\)Cl phase was >1.

Because of the large resistivity of the samples conductivity was measured by heating samples up to 200°C. Figure 7 shows the temperature dependence of Nyquist plots of the glass-ceramics prepared at \((x_1, x_2) = (2.8, 1.6)\). The resistance at each temperature was evaluated from the intersection to the \(Z_B\) axis. Curves recorded at or below 80°C exhibited a semicircle and capacitance associated with the semicircle was >3 \(\times 10^{-11}\) F. The resistance significantly decreased with an increase in temperature. Conductivity was calculated from the resistance, thickness, and area of gold electrodes. Figure 8 summarizes Arrhenius plots of the ac conductivities of glass-ceramics prepared in this study. The conductivity of samples prepared at \(x_1 = 2.8\) and 3.0 was much higher than that of samples prepared at \(x_1 = 4.0\). For the samples prepared at \(x_1 = 3.0\) conductivity was the highest at \(x_2 = 1.4\). The best conductivity (\(>4.6 \times 10^{-5}\) S cm\(^{-1}\)) was recorded at 200°C for the sample prepared at \((x_1, x_2) = (2.8, 1.6)\). The activation energy of the conductivity of samples prepared at \(x_1 = 3.0\) was

---

**Table 1.** Variation of weight fractions of crystalline phases in the crystalline part and degree of crystallinity with time and temperature of crystallization

| Temperature/°C | Time/h | Weight fractions of crystalline phases\(^a\) | Degree of crystallinity |
|---------------|--------|--------------------------------------------|------------------------|
| 500           | 1      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.034, Li\(_2\)B\(_4\)O\(_7\): 0.966, LiBO\(_2\): 0  | 0.26                   |
|               | 6      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.018, Li\(_2\)B\(_4\)O\(_7\): 0.982, LiBO\(_2\): 0  | 0.54                   |
| 600           | 1      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.495, Li\(_2\)B\(_4\)O\(_7\): 0.505, LiBO\(_2\): 0  | 0.76                   |
|               | 3      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.737, Li\(_2\)B\(_4\)O\(_7\): 0.263, LiBO\(_2\): 0  | 0.88                   |
|               | 6      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.745, Li\(_2\)B\(_4\)O\(_7\): 0.255, LiBO\(_2\): 0  | 0.91                   |
| 700           | 1      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.796, Li\(_2\)B\(_4\)O\(_7\): 0.204, LiBO\(_2\): 0  | 0.94                   |
|               | 3      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.749, Li\(_2\)B\(_4\)O\(_7\): 0.251, LiBO\(_2\): 0  | 0.96                   |
|               | 6      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.735, Li\(_2\)B\(_4\)O\(_7\): 0.265, LiBO\(_2\): 0  | 0.95                   |
| 800           | 1      | Li\(_4\)B\(_7\)O\(_{12}\)Cl: 0.389, Li\(_2\)B\(_4\)O\(_7\): 0.509, LiBO\(_2\): 0.102 | 0.93                   |

\(a\) Residual amorphous phases were excluded from the calculation.

---

![Fig. 3.](image1) Surface (a) and cross-sectional (b and c) SEM images of glass-ceramics prepared at \((x_1, x_2) = (3.0, 1.4)\) with crystallization for 3 h at 600°C.

![Fig. 4.](image2) TG (left) and DTA (right) curves of precursor glass prepared at \((x_1, x_2) = (3.0, 1.4)\).

---

![Fig. 5.](image3) (a) Powder XRD patterns of precursor glass prepared at \((x_1, x_2) = (3.0, 1.4)\) and glass-ceramics derived from the glass by different crystallization conditions. (b) Powder XRD pattern of the precursor glass shown in the panel (a) and curves of broad components derived by the Rietveld refinement for glass-ceramics derived from the glass with crystallization at or below 600°C. (c) Powder XRD patterns of glass-ceramics prepared at different \(x_1\) and \(x_2\) values with crystallization for 3 h at 600°C. Simulated patterns for Li\(_4\)B\(_7\)O\(_{12}\)Cl and Li\(_5\)B\(_7\)O\(_{12.5}\)Cl were calculated using structural parameters reported in Refs. 13 and 15, respectively.
ductivity. The activation energy for the sample prepared at \( x_1, x_2 = (2.8, 1.6) \) was \( \sim 0.52 \) eV and was smaller than those for samples prepared at \( x_1 = 3.0 \). The abrupt drops of conductivities due to transition into low-symmetry phases, which are observed in single crystals at 348 and 310 K, were not recorded.

As shown in Fig. 4 the DTA curve of the precursor glass exhibited two exothermic peaks at \( \sim 500 \) and \( \sim 600^\circ \)C. Figure 5(a) shows that the main crystal phases precipitated in the samples treated at 500 and 600°C were \( \text{Li}_2\text{B}_4\text{O}_7 \) and \( \text{Li}_4\text{B}_7\text{O}_{12}\text{Cl} \), respectively. Thus, these peaks are attributed to the formation of \( \text{Li}_2\text{B}_4\text{O}_7 \) and \( \text{Li}_4\text{B}_7\text{O}_{12}\text{Cl} \), respectively. At 600°C the fraction of \( \text{Li}_4\text{B}_7\text{O}_{12}\text{Cl} \) decreased with time as listed in Table 1, suggesting that \( \text{Li}_2\text{B}_4\text{O}_7\text{Cl} \) is formed by the reaction between \( \text{Li}_2\text{B}_4\text{O}_7 \) and residual amorphous phases containing chlorine. Indeed, a significant amount of amorphous phase remained after 1 h at 600°C, and the formation of \( \text{Li}_2\text{B}_4\text{O}_7\text{Cl} \) slowed down along with an increase in the degree of crystallinity at \( \geq 3 \) h.

Furthermore, as shown in Figs. 5(c) and 6, the fraction of \( \text{Li}_2\text{B}_4\text{O}_7 \) decreased with an increase in the amount of \( \text{LiCl} \), \( x_2 \), beyond the stoichiometric composition \( (x_2 = 1.0) \). This observation suggests that \( \text{LiCl} \) is...

### Table 2. Refined structure parameters for the calculated XRD pattern shown in Fig. 6(a)

| Atom | Site | Occupancy | \( x \) | \( y \) | \( z \) | \( U_{eq}/\text{Å}^2 \) |
|------|------|-----------|-----|-----|-----|-------------------|
| Li1  | 48g  | 0.465(4)  | 0.0312(8) | 1/4 | 1/4 | 0.036(2) |
| Li2  | 32e  | 0.303(4)  | 0.3616(8) | 0.3616(8) | 0.3616(8) | 0.036(2) |
| B1   | 24d  | 1/4       | 0        | 0 | 0 | 0.0161(6) |
| B2   | 32e  | 1/4       | 0.1004(1) | 0.1004(1) | 0.1004(1) | 0.0161(6) |
| O1   | 96b  | 0.0222(1) | 0.0993(1) | 0.1820(1) | 0.0169(3) |
| Ci1  | 8b   | 0.997(2)  | 1/4 | 1/4 | 1/4 | 0.0313(5) |
| Phase 2: \( x_1, x_2 = (2.8, 1.6) \) | \( \text{Li}_2\text{B}_4\text{O}_7 \) | 2.1 wt% |
| Li1  | 16b  | 1/4       | 0.1507 | 0.1679 | 0.8512 | 0.036(2) |
| B1   | 16h  | 1/4       | 0.1686 | 0.0860 | 0.2032 | 0.0161(6) |
| O1   | 16b  | 1/4       | 0.9461 | 0.1118 | 0.0831 | 0.0161(6) |
| O2   | 16h  | 1/4       | 0.2814 | 0.1371 | 0.2679 | 0.0169(3) |
| O3   | 16h  | 1/4       | 0.0671 | 0.1778 | 0.1561 | 0.0169(3) |
| O4   | 1a   | 1/4       | 0.1552 | 0.9420 | 0.1381 | 0.0169(3) |

a) \( R \)-values: \( R_p = 9.13 \% , R_B = 6.90 \% , R_w = 14.66 \% , R_s = 6.82 \% , S = 1.34 \). Phase 1: \( R_I = 3.75 \% , R_F = 3.36 \% . \) Phase 2: \( R_I = 28.54 \% , R_F = 9.96 \% . \)

b) Space group \( F43c \) (no. 219), \( Z = 8 \). Lattice parameter: \( a = 12.1548(1) \text{Å} \).

c) Space group \( B4c2d \) (no. 110), \( Z = 8 \). Lattice parameters: \( a = 9.4809(3) \text{Å} , c = 10.295(3) \text{Å} \).

---

**Fig. 6.** Observed (dots), calculated (line), and difference (bottom line) XRD patterns of the sample prepared at \( x_1, x_2 = (2.8, 1.6) \) with crystallization for 3 h at 600°C. Vertical bars indicate the positions of allowed Bragg reflections of contributing phases, \( \text{Li}_4\text{B}_7\text{O}_{12}\text{Cl} \) (upper) and \( \text{Li}_2\text{B}_4\text{O}_7 \) (lower).

**Fig. 7.** Nyquist plots of glass-ceramics prepared at \( x_1, x_2 = (2.8, 1.6) \) with crystallization for 3 h at 600°C. The inset shows a magnification near the origin.

**Fig. 8.** Arrhenius plots of ac conductivities of glass-ceramics prepared in this study. Solid lines are drawn by least-squares fitting to the conventional Arrhenius-type dependence of conductivity \( \sigma \) on absolute temperature \( T \) (where \( \sigma_0, E_a, k \) denote the preexponential factor, activation energy, and Boltzmann constant, respectively. Data taken from a single crystal of \( \text{Li}_4\text{B}_7\text{O}_{12}\text{Cl} \) and polycrystalline samples (Ref. 18 and the best data in Ref. 20) are also shown. The abrupt conductivity changes at 348 and 310 K observed in the single crystal sample are due to the phase transitions between two high-temperature cubic phases \( \gamma (F43c) \) and \( \beta (F43c) \), and low-temperature rhombohedral phase \( \alpha (R3) \).
partly lost during melting and compensation for the lack of LiCl is necessary to enhance the conversion of Li$_2$B$_2$O$_3$ into Li$_4$B$_7$O$_{12}$Cl. It also seems likely that weight loss at $T_{2s}$ is due to the removal of chlorine unused for the formation of Li$_4$B$_7$O$_{12}$Cl. Thus, a sufficient supply of Cl is necessary to increase the fraction of Li$_4$B$_7$O$_{12}$Cl and the conductivity of glass-ceramics, as typically demonstrated by the $(x_1, x_2)$ = (2.8, 1.6) sample. However, excess incorporation of LiCl along with an increase in the total amount of Li, $x_1 + x_2$, is harmful as the conductivity of the $(x_1, x_2)$ = (3.0, 1.6) sample was smaller than that of the $(x_1, x_2)$ = (3.0, 1.4) sample as shown in Fig. 8. This conductivity decrease is explained by the formation of the low conductivity phase, Li$_4$B$_7$O$_{12.5}$Cl, as a result of an increase in the Li/B ratio. The decrease in the fraction of Li$_4$B$_7$O$_{12}$Cl at or above 700°C is due to the thermal decomposition into Li$_2$B$_2$O$_3$ and LiBO$_2$, and amorphization.

In the Nyquist plots shown in Fig. 7 semicircles were observed at 40 and 80°C. The capacitance associated with semicircles was as small as 3 x 10$^{-11}$ F. Thus, the semicircles are attributable to the bulk component.

The result of Rietveld refinement shown in Fig. 6 and Table 2 for the glass-ceramics prepared at $(x_1, x_2)$ = (2.8, 1.6) indicates that the weight fraction of Li$_4$B$_7$O$_{12}$Cl in the crystalline part was 0.58 and Cl deficiency was negligible. The crystallization temperature of Li$_4$B$_7$O$_{12}$Cl (~600°C) was lower than the decomposition temperature (~700°C). The low crystallization temperature makes it possible to increase the relative density (~0.90) compared with the polycrystalline pellets prepared by conventional solid-state sintering (0.56–0.59$^{30}$) and 0.85$^{30}$), where the low decomposition temperature prevents to densify samples by increasing sintering temperature. It is most likely that the aggregated flaky or rod-like particles shown in Fig. 3(c) are crystalline phases including Li$_4$B$_7$O$_{12}$Cl and residual amorphous phases are present in the grain boundaries.

Because of the high phase purity and relatively high density, the conductivity of the glass-ceramic sample was larger than that of sol–gel-derived Li$_4$B$_7$O$_{12}$Cl polycrystalline ceramics (~9 x 10$^{-5}$ S cm$^{-1}$ at 200°C$^{20}$). However, the conductivity was still lower than that reported for a Li$_4$B$_7$O$_{12}$Cl single crystal,$^{14}$ probably because of the presence of grain boundaries and residual porosity. The conductivity of the glass-ceramics was also lower than the value reported in Ref. 18 for polycrystalline pellets of Li$_4$B$_7$O$_{12}$Cl, but the reason is unclear. Nevertheless, room temperature conductivity was comparable between the glass-ceramics and single crystal because of the absence of abrupt conductivity change in the glass-ceramics. This observation suggests that the high temperature cubic phase is stable in the glass-ceramics at room temperature. Since the phase transition responsible for the abrupt conductivity change is also not observed for polycrystalline samples,$^{18}$ the polycrystalline nature shown in Fig. 3(c) may be a reason for the absence of the phase transition. Residual amorphous phases probably located at the grain boundaries may also participate in the suppression of the phase transition. The conductivity may be further increased by element substitution.

5. Conclusions

The almost fully-crystallized glass-ceramics of lithium chloroboracites, Li$_{4+x}$B$_{12-2x}$O$_{2x+2}$Cl (x = 0–1), were successfully obtained by melt-quench-crystallization method from the Li$_2$O–B$_2$O$_3$–LiCl ternary system. This procedure enables rapid and facile synthesis of relatively dense and nearly single-phase lithium chloroboracite ceramics applicable to solid electrolytes. This method also avoids difficulties in the densification of lithium chloroboracites by conventional solid-state sintering, where the low decomposition temperature (~700°C) prevents to increase the sintering temperature. The ac conductivity of Li$_4$B$_7$O$_{12}$Cl (x = 0) was much higher than that of Li$_4$B$_7$O$_{12}$Cl (x = 1). The main crystalline impurity phase was Li$_2$B$_2$O$_3$ and was decomposed by increase the amount of LiCl. However, an excess incorporation of LiCl along with an increase in the total amount of Li led to the formation of the low-conductive Li$_4$B$_7$O$_{12}$Cl phase and lowered conductivity. The conductivity and the activation energy of the best sample were ~4.6 x 10$^{-4}$ S cm$^{-1}$ at 200°C and ~0.52 eV, respectively.

Acknowledgment This work was supported by ALCA-SPRING project of JST.

References

1) M. Matsunisago, M. Nagao and A. Hayashi, J. Asian Ceram. Soc., 1, 17–25 (2013).
2) N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama and R. Kanno, Nat. Mater., 10, 682–686 (2011).
3) A. D. Robertson, A. R. West and A. G. Ritchie, Solid State Ionics, 104, 1–11 (1997).
4) V. Thangadurai and W. Weppner, Ionics, 12, 81–92 (2006).
5) V. Thangadurai, S. Narayanan and D. Pinzaru, Chem. Soc. Rev., 43, 4714–4723 (2014).
6) Y. Ren, K. Chen, R. Chen, T. Liu, Y. Zhang and C.-W. Nan, J. Am. Ceram. Soc., 98, 3603–3623 (2015).
7) J. C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano and Y. Shao-Horn, Chem. Rev., 116, 140–162 (2016).
8) Y. Inaguma, C. Liqun, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta and M. Wakahara, Solid State Commun., 86, 689–693 (1993).
9) H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka and G. Adachi, J. Electrochem. Soc., 136, 590–591 (1989).
10) R. Murugan, V. Thangadurai and W. Weppner, Angew. Chem., Int. Ed., 46, 7778–7781 (2007).
11) A. Levasseur, C. Fouassier and P. Hagenmuller, Mater. Res. Bull., 6, 15–22 (1971).
12) W. Jeitschko and T. A. Bither, Z. Naturforsch., B: Chem. Sci., 27B, 1423 (1972).
13) A. Levasseur, D. J. Lloyd, C. Fouassier and P. Hagenmuller, J. Solid State Chem., 8, 318–324 (1973).
14) W. Jeitschko, T. A. Bither and P. E. Bierstedt, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 33, 2767–2775 (1977).
15) M. Vlasse, A. Levasseur and P. Hagenmuller, Solid State Ionics, 2, 33–37 (1981).
16) K. Momma and F. Izumi, J. Appl. Cryst., 44, 1272–1276 (2011).
17) J.-M. Réau, A. Levasseur, G. Magniez, B. Calès, C. Fouassier and P. Hagenmuller, Mater. Res. Bull., 11, 1087–1090 (1976).
18) B. Calès, A. Levasseur, C. Fouassier, J. M. Réau and P. Hagenmuller, Solid State Commun., 24, 323–325 (1977).
19) K. Byrappa and K. V. K. Shekar, J. Mater. Res., 8, 864–870 (1993).
20) T. Nagase, K. Sakane and H. Wada, J. Sol-Gel Sci. Technol., 13, 223–227 (1998).
21) W. Soppe, F. Aldenkamp and H. W. Hartog, J. Non-Cryst. Solids, 91, 351–374 (1987).
22) F. Izumi and K. Momma, Diffus. Defect Data Solid State Data Pt. B Solid State Phenom., 130, 15–20 (2007).
23) R. D. Goodwin, J. Phys. Chem. Ref. Data, 18, 1565–1636 (1989).
24) J. Krogh-Moe, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 24, 179–181 (1968).