Preparation and ionic conductivity of transparent glass-ceramics containing a large quantity of lithium-mica

Seiichi TARUTA*, Maki SUZUKI, †Tomohiko YAMAKAMI, Tomohiro YAMAGUCHI and Kunio KITAJIMA

Department of Chemistry and Materials Engineering, Faculty of Engineering, Shinshu University, 4-17-1, Wakasato, Nagano-shi, Nagano, 380-8553, Japan
†Technical Division, Faculty of Engineering, Shinshu University, 4-17-1, Wakasato, Nagano-shi, Nagano, 380-8553, Japan

*Corresponding Author
Seiichi TARUTA
Department of Chemistry and Materials Engineering, Faculty of Engineering, Shinshu University, 4-17-1, Wakasato, Nagano-shi, Nagano, 380-8553, Japan
TEL: +81-26-269-5416
FAX: +81-26-269-5424
E-mail: staruta@shinshu-u.ac.jp
Abstract

In order to crystallize a large quantity of the lithium-mica in glass-ceramics, 5.1 mass% MgF₂ was added to the starting materials of the parent glasses having chemical compositions of LiₙMg₃AlSi₃O₁₀₋₆.₅xF₂ (x=0.5 and 1.0). Transparent glass-ceramics, in which a large quantity of lithium-mica with particle size of < 50 nm was separated, could be prepared from the MgF₂-added parent glass with x=0.5. While the parent glass, which had a binodal phase separation structure, did not exhibit electrical conductivity, the transparent glass-ceramic was given conductivity by the formation of an interlocking structure of mica. As the separated mica formed a tighter interlocking structure, the conductivity increased and reached a value of 2.0 × 10⁻³ S/cm at 600°C. The MgF₂-added parent glass with x=1.0 was not transparent because of coarse spinodal phase separation. The conductivity was 4.3× 10⁻⁴ S/cm at 600°C but was significantly decreased by the separation of mica.

PACS codes: 81.05.Pj  (Glass-based composites, vitroceramics)

Keyword: Crystallization C290; Glass Ceramics G160; Ionic Conductivity I250
1. Introduction

Glass-ceramics are transparent when the crystals are small enough, low enough in birefringence, or well matched in refractive index with the residual glass [1]. Such transparent glass-ceramics have been developed and practically used in many application fields. We succeeded in preparing novel transparent and machinable mica glass-ceramics from parent glasses having chemical compositions of Li_{(1+x)}Mg_3AlSi_3O_{10+6.5x}F_2 (x=0.15-1.2) [2]. The separated micas were lithium-micas in which the interlayer cation is lithium ion. Thus, the novel mica glass-ceramics have potential for applications not only as machinable ceramics and optical materials but also as lithium ion conductors.

Micas have the potential to be ionic conductors because they are layered compounds having interlayer cations. The ionic conductivity is caused by the movement of the cations in the interlayer. That is, the conductive mechanism is the same as that of β-alumina, which is well known as an ionic conductor. K-type fluorophlogopite (KMg_3AlSi_3O_{10}F_2), of which the interlayer cation is K^+ ion, is a representative synthetic mica. However, the electrical resistance is very high. The mica glass-ceramics are well known as machinable ceramics and are also very good electrical insulators [3]. One of the reasons why K-type fluorophlogopite and mica-type glass-ceramics are not ionic conductors but electrical insulators may be that the size of K^+ ion in the interlayer is large. If so, micas with smaller interlayer cations, e.g. Li- or Na-type fluorophlogopite (LiMg_3AlSi_3O_{10}F_2 or NaMg_3AlSi_3O_{10}F_2), should have a higher likelihood of being ionic conductors. In fact, we found that the electrical conductivity of porous Na-type fluorophlogopite polycrystalline is 1.2×10^{-6} S/cm at 650°C [4]. Therefore, we thought that if the lithium-micas of which the interlayer cation is the smaller Li^+ ion form the interlocking microstructure in the glass-ceramic, the resulting glass-ceramic should
exhibit higher conductivity.

Transparent lithium-mica glass-ceramics were prepared in the previous study but they contained only a small quantity of lithium-mica [2]. In this study, in order to crystallize a large quantity of lithium-mica in the glass-ceramics, 5.1 mass% MgF₂ was added to the starting materials of the parent glasses having chemical compositions of Li_{(1+x)}Mg₃AlSi_{3(1+x)}O_{10+6.5x}F₂ (x=0.5 and 1.0). Sellaite (MgF₂) is an intermediate product in the crystallization process of micas and is a component of chondrodite (Mg₄(Si₄O₁₂)·MgF₂) and norbergite (Mg₂SiO₄·MgF₂), both of which are also intermediate products in the crystallization process [5-7]. Thus, the influence of MgF₂ addition on the crystallization of mica and microstructure development in the glass-ceramic was investigated and the ionic conductivity of the obtained glass-ceramic was estimated.

2. Experimental procedure

The reagents of MgO, Al₂O₃, SiO₂, Li₂CO₃ and MgF₂ were mixed in the chemical compositions corresponding to 94.9 mass% Li_{(1+x)}Mg₃AlSi_{3(1+x)}O_{10+6.5x}F₂ (x=0.5 and 1.0) + 5.1 mass% MgF₂. The two specimens with x=0.5 and 1.0 are shown as LSM150 and LSM200, respectively, in this paper. The mixtures were calcined at 900°C for 1 h, melted in a sealed platinum container at 1450°C for 2 h, and then cooled outside of the furnace. The obtained glasses were annealed at about 20°C higher temperatures than their glass-transition temperatures and cooled at 2°C/min to eliminate strain. The parent glasses prepared by such a method were cut to dimensions of about 5 mm × 5 mm × 1 mm and were heated at 600-800°C for 1-6 h to be crystallized. The heating rate was 10°C/min.

The thermal change of the parent glasses was analyzed using an X-ray diffraction (XRD) analyzer and a differential thermal analyzer (DTA). The microstructure
development was observed using a field-emission type scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM). For the FE-SEM observation, specimens polished with diamond slurries and chemically etched with 5 mass% hydrofluoric acid were used. The coordination number of Li\(^+\) ion in the glass-ceramic was determined using a \(^7\text{Li}\) magic angle spinning nuclear magnetic resonance (\(^7\text{Li}\) MAS NMR) spectroscope.

The machinability was qualitatively evaluated using a bench-drilling machine. The drill was made of conventional high-speed steel and the rotational frequency was 620 rpm. Specific electrical resistance of the specimens was measured at 100-600\(^\circ\)C by a four-probe method using an impedance analyzer in a frequency range of 4 to 10\(^6\) Hz. For this measurement, samples with dimensions of about 20 mm × 5 mm × 5 mm were used.

3. Results

3.1. Phase separation of parent glasses

The LSM150 parent glass was transparent and colorless while the LSM200 parent glass was white opaque. Crystals were not detected in the LSM150 and LSM200 parent glasses by XRD analysis. SEM photographs of the polished and etched surfaces of the parent glasses are shown in Fig.1. In the LSM150 parent glass, the separation of droplet-like phase with size of 60-70 nm was observed. This may be a binodal phase separation. In the LSM200 parent glass, two continuous phases, of which one was a dissolved phase by etching and another was the remaining phase with a width of 200-300 nm, were observed. This is a spinodal phase separation. Such binodal and spinodal phase separations were observed in the previous parent glasses having
chemical compositions of Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2 (x=0.15-1.2) and these glasses were transparent [2]. Because the LSM200 parent glass had the coarser spinodal phase separation, it became white opaque. The addition of 5 mass% MgF_2 resulted in coarser phase separation structure in both parent glasses.

3.2. Phase change by heating

The phase change in the LSM150 specimen by heating is shown in Fig. 2 and Fig. 3. Chondrodite was first separated at 600°C. Next, mica was separated at 700°C for 1 h though the diffraction peaks in the XRD pattern were very small. The quantity of separated mica increased with heating time at 700°C. The glass-ceramic heated at 700°C for 1-4 h remained transparent throughout the time period. A large quantity of β-eucryptite was crystallized at 800°C (This β-eucryptite was β-eucryptite solid solution [2]). Compared with the previous specimen [2] having chemical composition of Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2 (x=0.5), the LSM150 specimen separated a large quantity of mica at 700°C for 2-6 h.

The phase change in the LSM200 specimen by heating at 600-800°C was almost the same as that in the previous specimen [2] having chemical composition of Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2 (x=1.0).

The DTA curves of the previous parent glass having chemical compositions of Li_{(1+x)}Mg_3AlSi_{3(1+x)}O_{10+6.5x}F_2 (x=0.5 and 1.0), the LSM150 parent glass, and the LSM200 parent glass are shown in Fig. 4. These glasses were heated at 10°C/min during the measurement. Each DTA curve shows three or four exothermic peaks. According to the XRD analysis, the exothermic peak which appears at the lowest temperature for each glass and represented by C_1, C_2, C_3 and C_4 in the figure is attributed to the crystallization of chondrodite. The next exothermic peak for each glass, represented by
M1, M2, M3 and M4, and the third exothermic peak, represented by E1, E2, E3 and E4, are attributed to the crystallization of mica and β-eucryptite, respectively. The fourth exothermic peak, observed only for the LSM200 parent glass and represented by S4, is attributed to the crystallization of β-spodumene. The three exothermic peaks (C2, M2, and E2) of the LSM150 parent glass appeared at lower temperatures compared with the corresponding three exothermic peaks (C1, M1, and E1) of the previous parent glass with composition of \( \text{Li}(1+x)\text{Mg}_3\text{AlSi}_{3(1+x)}\text{O}_{10+6.5x}\text{F}_2 \) \((x=0.5)\). This indicates that the addition of 5.1 mass% MgF2 led to the crystallization of chondrodite, mica and β-eucryptite at lower temperatures. On the other hand, the crystallization of chondrodite in the LSM200 parent glass and the previous parent glass with composition of \( \text{Li}(1+x)\text{Mg}_3\text{AlSi}_{3(1+x)}\text{O}_{10+6.5x}\text{F}_2 \) \((x=1.0)\) took place at almost the same temperature. Additionally, the crystallization of mica in both parent glasses also took place at almost the same temperature. That is, the addition of 5.1 mass% MgF2 did not have an effect on the crystallization of chondrodite and mica in the LSM200 specimen because the LSM200 specimen contained a larger quantity of SiO2 and Li2O components. However, the addition did lead to the crystallization of β-eucryptite at much lower temperatures.

The basal spacing \((c \cdot \sin\beta; c \text{ and } \beta \text{ are lattice constants})\) and lattice constant \(b\) of the mica separated in the heat treated LSM150 and LSM200 specimens were measured and found to be independent of the heating condition. The obtained basal spacing and lattice constant \(b\) are shown in Fig. 5. In addition, the reported basal spacing and lattice constant \(b\) of trisilicic type mica [8,9], tetrasilicic type mica [10-12], and mica in the previous specimens [2] are plotted as a reference in Fig. 5. In general, the basal spacing, which is the distance between basal planes in the vertical direction relative to the layer, depends mainly on the size of the interlayer ion and the electrostatic repulsion between layers. Furthermore, the lattice constant \(b\) is a standard for determining whether the
mica is of the tetrasilicic or trisilicic type and the b of tetrasilicic type mica is shown to be smaller than that of trisilicic type mica. This figure shows that mica in the LSM150 and LSM200 specimens had intermediate compositions between tetrasilicic and trisilicic type mica. The basal spacing of mica in the LSM150 and LSM200 specimens was smaller than that of mica in the previous specimens [2]. This suggests that Li⁺ ions in the layer of mica in the LSM150 and LSM200 specimens fell into hexagonal holes formed by the basal oxygen of the tetrahedral sheet.

³⁷Li MAS NMR spectra of the LSM150 specimen, heated at 700°C for 4 h, and K-type taeniolite (KMg₂LiSi₄O₁₀F₂) are shown in Fig. 6. The K-type taeniolite which was synthesized by the melting method [11,13] and refined by elutriation was used as a reference specimen for the estimation of the coordination number of Li⁺ ion. Li in the K-type taeniolite is located in the octahedral sheet and the spectrum of K-type taeniolite showed a resonance due to the Li in the octahedral sheet at a chemical shift (δ) of about -0.7 ppm from LiCl. In the spectra of the LSM150 specimen, two resonances were observed at δ of about -0.7 ppm and -1.2 ppm which were due to the Li in the octahedral sheet and the Li in the interlayer, respectively. That is, the Li⁺ ion was located both in the octahedral sheet and in the interlayer of mica. The above results indicate that the structural formula of mica in the LSM150 and LSM200 specimens was shown as Li(Mg₂⁺yLi₁−y)(Al₁−ySi₄+y)O₁₀F₂ (0<y<1).

3.3. Microstructure development

TEM photographs of the LSM150 specimen heated at 700°C for 1, 2 and 4 h and at 750°C for 4 h are shown in Fig. 7. The droplet phase of glass was observed faintly at 700°C for 1 h and the very fine spherical particles with size of < 10nm were observed around the droplet phase. These particles were chondrodite crystals. Fig. 7 (a) suggests
that chondrodite was formed in the matrix phase and/or at the boundary between droplet and matrix phases. The flake-like particles which are denoted by the arrow in Fig. 7(a) must be mica crystal. While only some mica was separated at 700°C for 1 h, many mica crystals with size of < 50 nm were observed at 700°C for 2 h. A larger quantity of mica formed a tight interlocking microstructure at 700°C for 4 h. Spherical particles with sizes of 100-200 nm appeared in the mica matrix at 750°C for 4 h. They must be β-eucryptite solid solution, according to the XRD analysis (The XRD pattern is not shown in this paper). This photograph indicates that the nuclei of the β-eucryptite solid solution generated in the mica matrix and the β-eucryptite solid solution grew spherically as it consumed the mica. The mica crystals grew only by a small amount.

SEM photographs of the LSM200 specimen heated at 650°C and 700°C for 1 h are shown in Fig. 8. The microstructure development was similar to that of the previous specimen [2] having chemical composition of Li_{1+x}Mg_{3}\text{AlSi}_{3(1+x)}O_{10+6.5x}F_2 (x=1.0). The finer particles and the coarser particles were observed in the specimen and were the mica crystallites and glass phase, respectively.

3.4. Properties

The photograph of the drilling test for the LSM150 specimen heated at 700°C for 4 h is shown in Fig. 9. It is clear from this figure that this specimen was transparent. The LSM150 specimen remained transparent because a large quantity of the fine mica with size of < 50 nm was separated uniformly in the specimen, as shown in Fig. 7 (b) and (c). The specimen was machined using a drill made by conventional high-speed steel but large amount of chipping was observed on the bottom side of the specimen. While a large quantity of mica formed a tight interlocking structure, the mica size was so small that the specimen did not exhibit better machinability [5].
While the electrical resistance of the LSM150 parent glass was so high that the conductivity could not be measured at room temperature to 600°C, the conductivity of LSM150 specimen heated at 700°C for 2 h and 4 h was $5.8 \times 10^{-4}$ S/cm and $2.0 \times 10^{-3}$ S/cm, respectively, at 600°C. That is, the separation of mica gave the LSM150 specimen the conductivity and the conductivity increased with an increase in the content of mica. The conductivity of the LSM200 parent glass was $2.8 \times 10^{-4}$ S/cm at 600°C but the LSM200 specimen heated at 700°C for 1 h exhibited much lower conductivity ($1.8 \times 10^{-7}$ S/cm, at 600°C) than the parent glass. The conductivity of the LSM200 specimen was lowered by the separation of mica.

4. Discussion

4.1. Effect of addition of MgF$_2$ on crystallization process

The SiO$_2$-B$_2$O$_3$-Al$_2$O$_3$-MgO-K$_2$O-F glass shows a phase separation consisting of a SiO$_2$- and F-rich K$_2$O-B$_2$O$_3$-SiO$_2$-F droplet phase and a MgO- and Al$_2$O$_3$-rich K$_2$O-MgO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ matrix phase; the first crystalline phase is a chondrodite-like phase which is crystallized in the matrix phase at 650°C and undergoes dendritic growth; the second phase is norbergite which is formed at 750°C; mica is then formed at 850°C, entirely consuming the norbergite [6]. On the other hand, SiO$_2$-Al$_2$O$_3$-MgO-Na$_2$O-K$_2$O-F-Cl glass exhibits a phase separation consisting of a glassy Mg- and F-rich droplet phase and a glassy matrix phase; the first crystalline phase is norbergite which is crystallized at 730°C; mica is then separated from norbergite at 780°C [7]. In this study, the LSM150 parent glass showed binodal phase separation and chondrodite was first separated at 600°C. That is, the LSM150 parent glass might have the F-rich droplet and the MgO-rich matrix phases such as the
SiO$_2$-B$_2$O$_3$-Al$_2$O$_3$-MgO-K$_2$O-F glass. So chondrodite was separate in the matrix phase and/or at the boundary between the droplet and matrix phases, though it was different from that in the SiO$_2$-B$_2$O$_3$-Al$_2$O$_3$-MgO-K$_2$O-F glass in composition and shape. Mica in the LSM150 specimen was formed consuming the chondrodite but not through norbergite.

The addition of 5.1 mass% MgF$_2$ might result in the formation of MgO-richer matrix phase and F-rich droplet phase in the LSM150 parent glass. Moreover, the addition caused the separation of a large quantity of chondrodite at lower temperatures and the stabilization of chondrodite at 600-700ºC, as shown in Fig. 2 and 4. A large number of chondrodite particles acted as nuclei for mica, which resulted in the crystallization of a large number of mica particles with size of <50 nm. The mica grew by a small amount during heating because the structure of the lithium-mica is unstable and the large quantity of mica was formed uniformly. Consequently, the LSM150 specimen heated at 700ºC for 1-4 h remained transparent throughout the time period. On the other hand, in the previous parent glass to which 5.1 mass% MgF$_2$ was not added, not enough MgO and F was in the matrix and droplet phases, respectively, to form a large amount of chondrodite. The separated chondrodite formed mica immediately, as shown in Fig. 4 and only a small amount of chondrodite formed mica.

The addition of 5.1 mass% MgF$_2$ led to the separation of a large quantity of chondrodite in the LSM150 specimen at lower temperatures. A large number of chondrodite particles acted as nuclei for mica formation. Consequently, a large number of finer mica particles were separated and formed an interlocking structure, which resulted in a transparent and machinable mica glass-ceramic.

4.2. Mechanism of ionic conductivity
The temperature (T) dependence of the conductivity (σ) for the LSM150 specimen heated at 700ºC for 2 h and for 4 h, the LSM200 parent glass, and the LSM200 specimen heated at 700ºC for 1 h over the temperature range from 100 to 600ºC, is shown in Fig. 10. The dotted lines in the figure were drawn according to the method of least squares. The plots of log(σT) against 1/T for the LSM150 specimen were found to be linear over the temperature range and fitted the Arrhenius equation shown in equation (1):

$$\sigma T = A \exp\left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (1)

Where A is pre-exponential factor, Ea is the activation energy for the conductivity and k is the Boltzmann constant. In accordance with the Arrhenius equation, the activation energy was determined. The activation energy of the LSM150 specimen heated at 700ºC for 2 h and for 4 h was about 0.78 eV. This indicates that the conductivity mechanism of the LSM150 specimen heated 700ºC for 2-4 h was the same. The conductivity was caused by the formation of the interlocking structure of mica and it increased as the interlocking structure became tighter with heating time. These results suggest that the conductive ion and path were Li⁺ ion and interlayer of mica, respectively.

On the other hand, the plots of log(σT) against 1/T for the LSM200 parent glass and the LSM200 specimen heated at 700ºC for 1 h showed a knee at 200ºC and 450ºC, respectively, and were divided into two linear regions. The activation energy of the LSM200 parent glass was 0.97 eV at 200 to 600ºC. The LSM200 parent glass had a spinodal phase separation which consisted of two continuous glass phases. Li⁺ ion which was the conductive ion may have concentrated in one of the two continuous phases and moved through the continuous phase. It is known that the isolated SiO₄ tetrahedral units with 3-4 non-bridging oxygen atoms per silicon atom, such as SiO₄⁴⁻ and Si₂O₇⁶⁻ ions, contribute to the high Li⁺ ion conductivity of Li₂O-SiO₂ glasses [14].
The continuous glass phase in which Li$^+$ ion was concentrated might have contained the isolated SiO$_4$ tetrahedral units, which contributed to Li$^+$ ion conductivity in the LSM200 parent glass. The conductivity of the LSM200 specimen heated at 700°C for 1 h was lower than that of the parent glass. The activation energy was higher (Ea=1.74 eV) at 450 to 600°C though the mica was separated. Judging from the activation energy, the conductive mechanism was not due to mica. The separated mica did not form a sufficient continuous phase, as shown in Fig. 8 (b). In addition, the separation of mica consumed not only the glass phase, in which Li$^+$ ion was concentrated, but also another glass phase, which varied not only the structure of the spinodal phase separation but also the composition of the glass phases. The content of Li$^+$ ion and the isolated SiO$_4$ tetrahedral units decreased in the continuous glass phase as the mica crystals were separated, which caused the decrease in the conductivity and the increase in the activation energy.

5. Conclusions

In order to crystallize a large quantity of the lithium-mica in the glass-ceramics, 5.1 mass% MgF$_2$ was added to the starting materials of the parent glasses having chemical compositions of Li$_{(1+x)}$Mg$_3$AlSi$_{(1+x)}$O$_{10+6.5x}F_2$ (x=0.5 and 1.0).

The transparent and machinable glass-ceramic in which a large quantity of mica was separated was obtained from the MgF$_2$-added parent glass with x=0.5. The addition of MgF$_2$ led to the separation of a large number of chondrodite at lower temperatures and the chondrodite particles acted as nuclei for mica, which resulted in the crystallization of a large quantity of mica at lower temperatures. The separated mica crystals, with a size of < 50 nm, formed an interlocking microstructure in the glass-ceramic and had the
structural formula of $\text{Li(Mg}_{2+y}\text{Li}_{1-y})(\text{Al}_{y}\text{Si}_{4-y})\text{O}_{10}\text{F}_2$ $(0<y<1)$. The conductivity of the transparent glass-ceramic became higher as the mica formed a tighter interlocking structure. The conductivity was $2.0 \times 10^{-3} \text{ S/cm}$ at $600^\circ\text{C}$. Such results indicate that the conductive ion and path were Li$^+$ ion and the interlayer of mica, respectively.

On the other hand, the MgF$_2$-added parent glass with $x=1.0$ lost the transparency due to the formation of a coarser spinodal phase separation. Because the parent glass contained a larger quantity of SiO$_2$ and Li$_2$O components, the addition of MgF$_2$ did not have an effect on the formation of nuclei such as chondrodite and did not promote the crystallization of mica. The parent glass exhibited Li$^+$ ion conductivity through the one continuous glass phase of spinodal phase separation and the conductivity was $2.8 \times 10^{-4} \text{ S/cm}$ at $600^\circ\text{C}$. However, when the mica crystals were separated and did not form a sufficient interlocking microstructure, the conductivity was significantly lower. The crystallization of mica led to the decrease in the content of Li$^+$ ion and isolated SiO$_4$ tetrahedral units in the continuous glass phase which, in turn, caused the decrease in conductivity.
References


**Figure legends**

**Fig. 1.** SEM photographs of polished and chemically etched surfaces of the parent glasses: (a) LSM150 and (b) LSM200 specimens.

**Fig. 2.** XRD patterns of (a) LSM150 parent glass and LSM150 specimen heated at (b) 600°C, (c) 650°C, (d) 700°C, (e) 750°C and (f) 800°C for 1 h.

**Fig. 3.** XRD patterns of LSM150 specimen heated at 700°C for (a) 1 h, (b) 2 h, (c) 4 h and (d) 6 h.

**Fig. 4.** DTA curves of (a) previous parent glass with composition of Li_{(1+x)}Mg_{3}AlSi_{3(1+x)}O_{10+6.5x}F_{2} (x=0.5), (b) LSM150 parent glass, (c) previous parent glass with composition of Li_{(1+x)}Mg_{3}AlSi_{3(1+x)}O_{10+6.5x}F_{2} (x=1.0) and (d) LSM200 parent glass.

**Fig. 5.** Relationship between basal spacing ($c \cdot \sin \beta$) and lattice constant (b) of mica crystals showing: mica in the (☉) LSM150 and (☉) LS200 specimens.

Micas in the previous study [2]: x = (◆) 0.115, (■) 0.5, (▲) 1.0 and (●) 1.2.

Trisilicic type mica: (▽)[8], ◐[9]) K-phlogopite (KMg_{3}(AlSi_{3}O_{10})F_{2})

Tetrasilicic type mica: (○)[10], □[11]) K-taeniolite (KMg_{2}Li(Si_{4}O_{10})F_{2}), (◇)[10]) Na-taeniolite (NaMg_{2}Li(Si_{4}O_{10})F_{2}), and (☆)[12]) K-tetrasilisic mica (KMg_{2.5}(Si_{4}O_{10})F_{2}).

**Fig. 6.** $^7$Li MAS NMR spectra (ref. LiClaq) of (a) LSM150 specimen heated at 700°C for 4 h and (b) K-taeniorite.
**Fig. 7.** TEM photographs of the heated LSM150 specimen. Heat treatment: (a) 700°C, 1 h, (b) 700°C, 2 h, (c) 700°C, 4 h and (d) 750°C, 4 h.

**Fig. 8.** SEM photographs of polished and chemically etched surfaces of the heated LSM200 specimen. Heat treatment: (a) 650°C, 1 h and (b) 700°C, 1 h.

**Fig. 9.** Photograph of drilling test for LSM150 specimen heated at 700°C for 4 h.

**Fig. 10.** Temperature (T) dependence of the conductivity (σ) for the LSM150 specimen heated at 700°C for (●) 2 h and (○) 4 h, (◆) LSM200 parent glass and (◇) LSM200 heated at 700°C for 1 h over the temperature range from 100 to 600°C.
Fig. 1. SEM photographs of polished and chemically etched surfaces of the parent glasses: (a) LSM150 and (b) LSM200 specimens.
Fig. 2. XRD patterns of (a) LSM150 parent glass and LSM150 specimen heated at (b) 600°C, (c) 650°C, (d) 700°C, (e) 750°C and (f) 800°C for 1 h.
Fig. 3. XRD patterns of LSM150 specimen heated at 700°C for (a) 1 h, (b) 2 h, (c) 4 h and (d) 6 h.
Fig. 4. DTA curves of (a) previous parent glass with composition of \( \text{Li}_{(1+x)}\text{Mg}_3\text{AlSi}_3(1+x)\text{O}_{10+6.5x}\text{F}_2 \) \((x=0.5)\), (b) LSM150 parent glass, (c) previous parent glass with composition of \( \text{Li}_{(1+x)}\text{Mg}_3\text{AlSi}_3(1+x)\text{O}_{10+6.5x}\text{F}_2 \)
Fig. 5. Relationship between basal spacing \((c \cdot \sin \beta)\) and lattice constant \((b)\) of mica crystals showing: mica in the (○) LSM150 and (⊗) LS200 specimens.

Micas in the previous study [2]: x = (◆) 0.115, (■) 0.5, (▲) 1.0 and (●) 1.2.

Trisilicic type mica: (▽[8], ◯[9]) K-phlogopite \((\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2)\)

Tetrasilicic type mica: (○ [10], □ [11]) K-taeniolite \((\text{KMg}_3\text{LiSi}_4\text{O}_{10}\text{F}_2)\), (◇ [10]) Na-taeniolite \((\text{NaMg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2)\), and (☆ [12]) K-tetrasilisic mica \((\text{KMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2)\).
Fig. 6. $^7$Li MAS NMR spectra (ref. LiCl) of (a) LSM150 specimen heated at 700°C for 4 h and (b) K-taeniorite.
Fig. 7. TEM photographs of the heated LSM150 specimen. Heat treatment: (a) 700°C, 1 h, (b) 700°C, 2 h, (c) 700°C, 4 h and (d) 750°C, 4 h.
Fig. 8. SEM photographs of polished and chemically etched surfaces of the heated LSM200 specimen. Heat treatment: (a) 650°C, 1 h and (b) 700°C, 1 h.
Fig. 9. Photograph of drilling test for LSM150 specimen heated at 700°C for 4 h.
Fig. 10. Temperature (T) dependence of the conductivity (σ) for the LSM150 specimen heated at 700°C for (●) 2 h and (○) 4 h, (◆) LSM200 parent glass and (◇) LSM200 heated at 700°C for 1 h over the temperature range from 100 to 600°C.