

Title

**New synthetic method and ionic conductivity of
Na-4-mica**

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Abstract

If interlayer cations of micas can move in the interlayer, the micas show ionic conductivity. However, K-type fluorophlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) which is the representative synthetic mica and the main crystal of mica ceramics is known as an electrical insulator. If interlayer cations of micas are smaller than K^+ ion which is the interlayer cation of K-type fluorophlogopite and a larger amount of cation is stuffed in the interlayer, the micas have a higher possibility as ionic conductors. As one of such micas, highly charged sodium fluorophlogopite mica ($\text{Na}_4\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4 \cdot x\text{H}_2\text{O}$) which is called "Na-4-mica" is nominated. But there are no studies on its ionic conductivity. In this study, Na-4-mica could be synthesized by new and simple method which consisted of mixing of MgO , Al_2O_3 , SiO_2 and NaF , calcination, sieving, compaction and firing in a sealed platinum container. The conductivity of the obtained Na-4-mica increased with an increase in temperature and reached 4.3×10^{-4} S/cm at 650°C .

Keywords; Na-4-mica; Interlayer ion; Ionic conductivity; Solid-state reaction

1. Introduction

Micas have a possibility as ionic conductors because they are a layered compound having interlayer cations. The ionic conductivity of the micas will be caused by the movement of the cations in the interlayer. That is, the conductive mechanism is the same with that of β -alumina which is well known as the ionic conductor. K-type fluorophlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$), of which the interlayer cation is K^+ ion, is the representative synthetic mica. However, the electrical resistance is very high. For the single crystal, the electrical resistance of the vertical direction relative to the layer is 10^{11} - 10^{12} $\Omega\cdot\text{cm}$ and that of the parallel direction relative to the layer is 10^6 - 10^7 $\Omega\cdot\text{cm}$ even at 500°C [1]. And mica-type glass-ceramics are well known as machinable ceramics and are also very good electrical insulators [2]. One of the reasons why K-type fluorophlogopite and mica-type glass-ceramics are electrical insulators but not ionic conductors may be that the size of K^+ ion in interlayer is large. If so, micas with smaller interlayer cations, e.g. Li- or Na-type fluorophlogopite ($\text{LiMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$ or $\text{NaMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$), have a higher possibility as the ionic conductors. In addition, highly charged sodium fluorophlogopite mica ($\text{Na}_4\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4\cdot x\text{H}_2\text{O}$) which is called “Na-4-mica” may have much higher conductivity because its interlayer contains twice as many Na^+ ions as that of the ordinary Na-type fluorophlogopite contains.

On the other hand, the Na-4-mica has theoretically high ion-exchange capacity. So it has been synthesized by using natural materials such as augite [3] or kaolinite [6,8-10,11,13], by sol-gel method [4,5] or by using NaCl melt [12] and its cation exchange properties have been investigated [4-10,13]. However, there are no studies on its ionic conductivity.

In this study, in order to make novel ionic conductive materials, new and simple synthetic method of Na-4-mica was investigated and electrical conductivity of the obtained micas was measured.

2. Experimental procedure

The reagents of MgO , Al_2O_3 , SiO_2 , NaF and MgF_2 were mixed in the chemical compositions corresponding to $\text{Na}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{20}\text{F}_4$ and $\text{Na}_4\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4$ which are chemical formulas of Na-type fluorophlogopite and anhydrous Na-4-mica, respectively, per unit cell. These two specimens are shown as Na2 and Na4 specimens, respectively, in this paper. MgF_2 was not used for the Na4 specimen. The mixtures were calcined, passed through a 100-mesh sieve, compacted by a cold isostatic pressing at 98 MPa and then fired in a sealed platinum container at 700 - 1250°C for 2 h. Crystalline phases were immediately analyzed using an X-ray

diffraction (XRD) after the powdered specimens were dried at 150°C. Morphology of micas was observed using a scanning electron microscopy (SEM). Specific electrical resistance of the specimens was measured at 100-650°C by four-probe method using an impedance analyzer in a frequency range of 4 to 10⁶ Hz.

3. Results and discussion

XRD patterns of the Na₂ and Na₄ specimens are shown in Fig. 1 and Fig. 2, respectively. For the Na₂ specimen, mica, quartz and unknown were observed at 950°C. Though quartz disappeared at 1000°C and the peak intensity of the mica became stronger with an increase in temperature, the small peaks of unknown remained at the temperature range of 1000 to 1200°C. The lattice spacings of the mica formed at 950-1200°C almost corresponded to those of Na-type fluorophlogopite (NaMg₃AlSi₃O₁₀F₂) shown in JCPDS card No. 25-842. The (001) reflection of a hydrated Na-type fluorophlogopite with a single sheet of interlayer water was observed at $d = 12.17 \text{ \AA}$ for the Na₂ specimen heated at 950°C and 1000°C [5] though the specimens dried at 150°C were used for the analysis. For the Na₄ specimen, a very small amount of mica was formed at 800°C and a single phase of the mica was obtained at 900-1000°C. And the small peaks of unknown were observed again at 1100-1150°C. The lattice spacings of the mica formed at 900-1150°C almost corresponded to those of anhydrous Na-4-mica synthesized by Paulus et al.[4], Franklin and Lee [5], Komarneni et al. [6,9] and Kodama et al [6-8,10,11]. That is, Na-4-mica could be obtained by new and simple method which was the solid-state reaction of the mixtures of MgO, Al₂O₃, SiO₂ and NaF in the sealed container, and besides, it was synthesized at about the same firing temperature (900°C) for shorter firing time, comparing with that obtained by other methods [3-13]. SEM photographs of fracture surfaces of the Na₄ specimen fired at 900°C and 1100°C are shown in Fig. 3. Plate-like particles with size of <5 μm, which were identified as Na-4-mica, were observed at 900°C and grew up to ~10 μm at 1100°C. And it is clear that the fired Na₄ specimen was porous but not densified. Though Na-type fluorophlogopite and Na-4-mica are swelled even by the moisture in air, there were no changes in the appearance of the fired Na₂ and Na₄ specimens in air.

In this method, the starting materials, particularly fluorine and/or fluorides, were difficult to be evaporated and were not lost during firing because they were fired in the sealed container. On the other hand, when Na₂CO₃ and MgF₂ were used as sodium and fluorine sources instead of NaF, Na-4-mica and Na-type fluorophlogopite were very difficult to be formed by the same method. Therefore, the atmosphere in the sealed container was very suitable for the formation of Na-4-mica and Na-type fluorophlogopite during firing when NaF was used as sodium and fluorine sources. The evaporated fluorine and/or fluorides in the sealed container might play a

significant role on the formation of such micas.

The temperature dependence of the electrical conductivity of the Na2 specimen fired at 1200°C for 2 h and the Na4 specimen fired at 1150°C for 2 h is shown in Fig. 4. The conductivity of the Na2 specimen was 8.3×10^{-8} S/cm at 500°C, which is larger than that (10^{-12} - 10^{-13} S/cm) of the vertical direction relative to the layer of the single crystal K-type fluorophlogopite at 500°C and is about the same with that (10^{-7} - 10^{-8} S/cm) of the parallel direction relative to the layer [1]. Because the Na2 specimen was porous and polycrystalline, the result indicates that Na-type fluorophlogopite have higher conductivity than K-type fluorophlogopite and suggests that micas with smaller interlayer cations have higher conductivity. And it is clear that the conductivity of Na-4-mica was higher than that of Na-type fluorophlogopite, which suggests that micas with a larger amount of interlayer cation have higher conductivity. Though the electrical resistance of the Na4 specimen was too high at $\leq 200^\circ\text{C}$ to be measured, it increased with an increase in temperature and reached 4.3×10^{-4} S/cm at 650°C. This result indicates that Na-4-mica is ionic conductor at higher temperatures. On the other hand, Na-4-mica did not show as high conductivity as β and β'' -alumina single crystals have (10^{-3} - 10^{-1} S/cm, at room temperatures [14]). If micas with a larger amount of Na^+ ion in the interlayer than Na-4-mica can be prepared, oriented and much more densified, they have much higher conductivity. In addition, Na^+ ions in the interlayer of micas is exchanged for other kinds of cation in solutions at room temperatures [4-8,10,13] while those in β and β'' -alumina can be exchanged for other cations in molten salts at high temperatures [15,16]. So we expect that proton, lithium and multivalent cation conducting micas will be easy to be fabricated by the ion exchange.

4. Conclusions

In this study, Na-4-mica could be synthesized by new and simple method which was the solid-state reaction of the mixtures of MgO, Al_2O_3 , SiO_2 and NaF in a sealed platinum container. The method consisted of just five processes, which were mixing, calcinations, sieving, compaction and firing in the sealed container. The obtained Na-4-mica showed ionic conductivity at higher temperatures. The conductivity was 4.3×10^{-4} S/cm at 650°C.

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Figure legends

Fig. 1. XRD patterns of Na₂ specimen fired at (a) 950°C, (b) 1000°C, (c) 1100°C and (d) 1200 °C for 2 h. (◆): mica, (●): Quartz, no-mark: unknown. The numerals on the top of peaks are values of the lattice spacing. The unit is Å.

Fig. 2. XRD patterns of Na₄ specimen fired at (a) 800°C, (b) 900°C, (c) 1000°C , (d) 1100°C and (e) 1150°C for 2 h. (◆): mica, (○): α-alumina, no-mark: unknown. The numerals on the top of peaks are values of the lattice spacing. The unit is Å.

Fig. 3. SEM photographs of fracture surfaces of Na₄ specimen fired at (a) 900°C and (b) 1100°C for 2 h.

Fig. 4. Temperature dependence of electrical conductivity of (●) Na₂ specimen fired at 1200°C for 2 h and (◆) Na₄ specimen fired at 1150°C for 2 h.

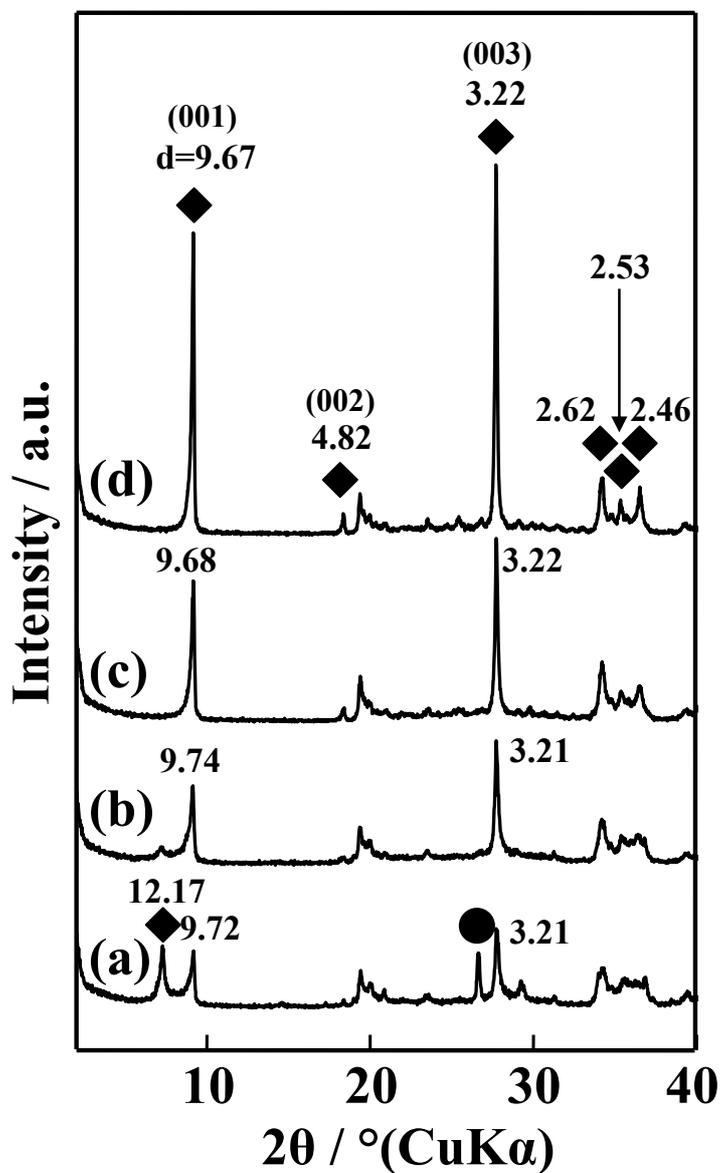


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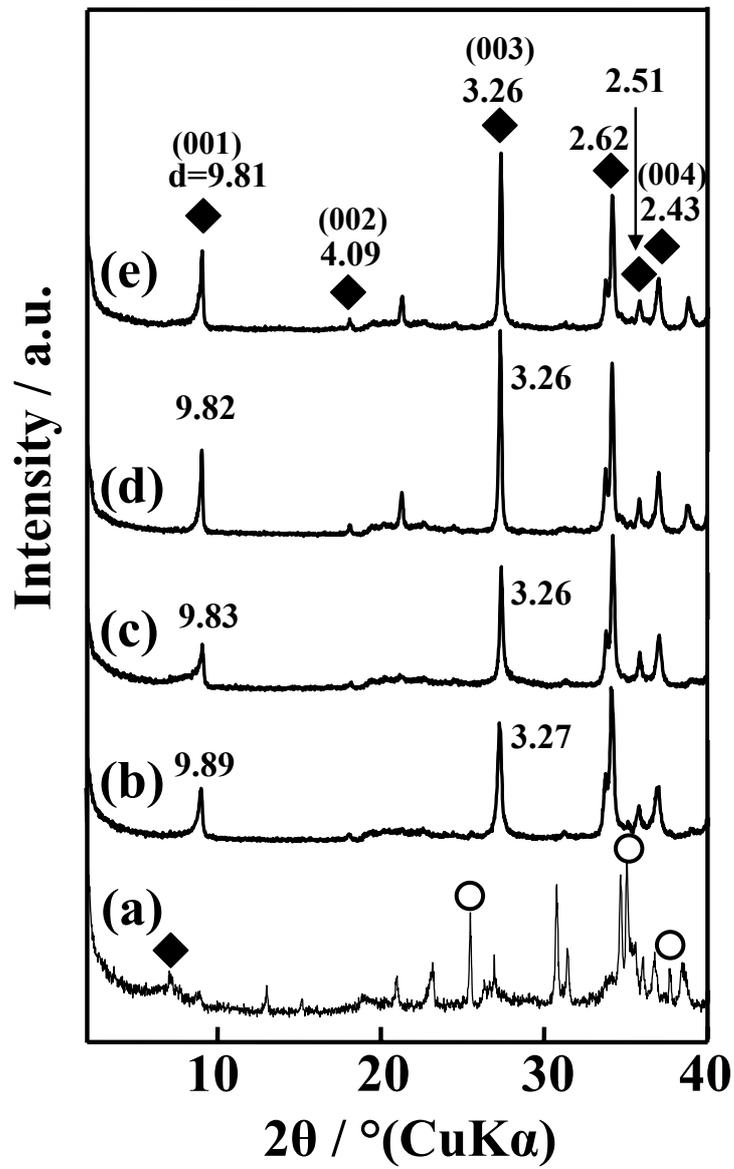


Fig. 2. XRD patterns of Na₄ specimen fired at (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C and (e) 1150°C for 2 h. (◆): mica, (○): α-alumina, no-mark: unknown. The numerals on the top of peaks are values of the lattice spacing. The unit is Å.

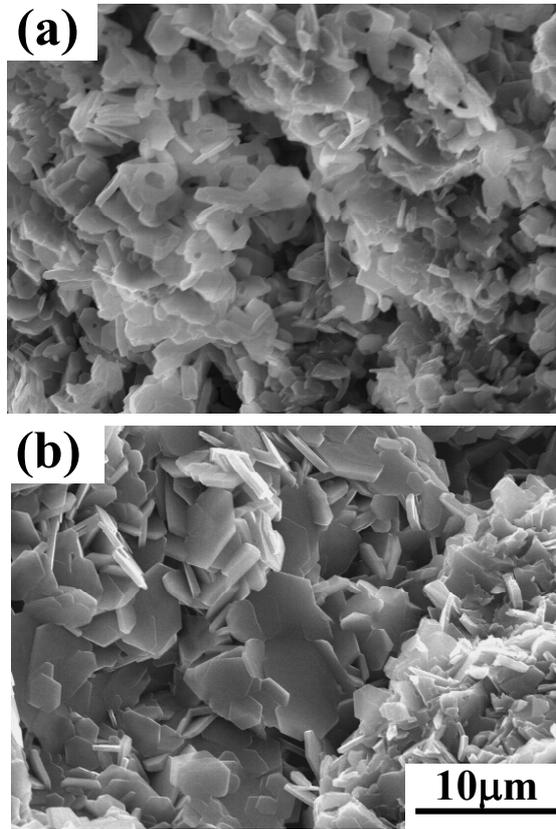


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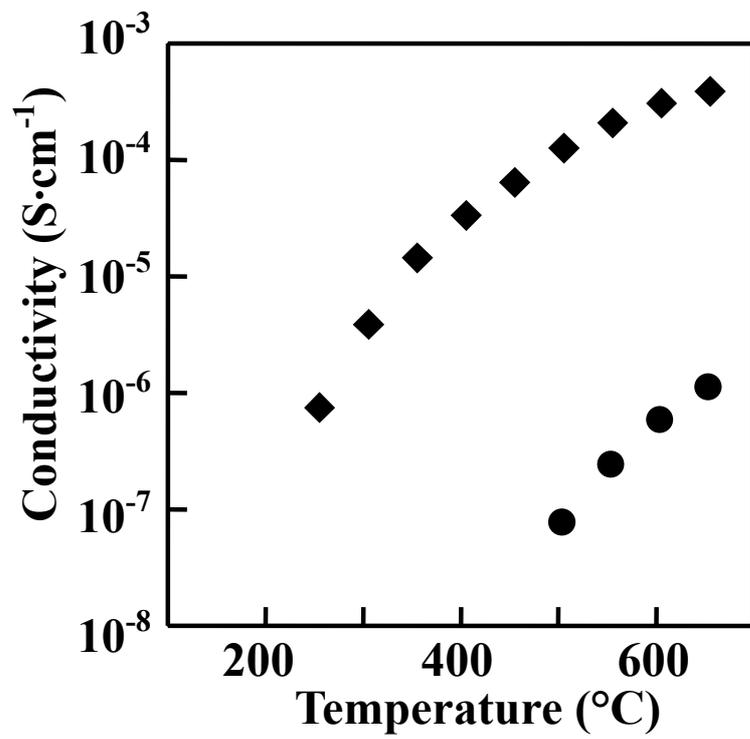


Fig. 4. Temperature dependence of electrical conductivity of (●) Na2 specimen fired at 1200°C for 2 h and (♦) Na4 specimen fired at 1150°C for 2 h.