JOURNAL OF MATERIALS SCIENCE 27 (1992) 5045–5051

Ionic conductivity in $Na_5YSi_4O_{12}$-based ceramics with and without additives

Y. SADAOKA, M. MATSUGUCHI, Y. SAKAI, K. KOMATSUBARA
Department of Applied Chemistry, Faculty of Engineering, Ehime University, Bunhyo-cho, Matsuyama 790, Japan

Addition of Na_2O–Y_2O_3–SiO_2 glass to $Na_5YSi_4O_{12}$ during the sintering process induced enhancements in conductivity and decrease in its activation energy. The highest conductivity and activation energy were 1.3×10^{-1} S cm^{-1} at 300 °C and 0.21 eV, respectively, for $Na_5YSi_4O_{12}$ with about 20 wt% Na_2O–Y_2O_3–SiO_2 glass which was sintered at 1000 °C. This improvement may be caused by the formation of a $Na_5YSi_4O_{12}$ phase from the added glass. Such an improvement in the electrical characteristics was not achieved by the addition of 10 wt% or more Na_2O–Al_2O_3–$4SiO_2$ glass or α-alumina in which the conductivity decreased monotonically with an increase in the amount of additive.

1. Introduction

Recently, there has been considerable interest in glass–ceramic ionic conductors [1] because a dense ionic conductor is a preferable material for solid-state batteries and chemical sensors. Hunter and Ingram [2] have examined sodium ion conduction in glasses including silicates, borates etc., and found that the conductivity increases with the basicity of the material while the activation energy in conduction falls toward an apparent limiting value of about 0.52 eV; no further improvement in conductivity could be achieved, even by the use of special additives such as NaCl, NaF or Al_2O_3. With regard to the cationic conduction mechanism in silica-based glasses. Anderson and Stuart [3] have tried to estimate the activation energy of ionic conduction based on the classical ideas of ionic crystal theory and elasticity theory. While this model to estimate the activation energy was based on several assumptions, the estimated activation energy in sodium ion conduction (~ 0.7 eV) was consistent with the reported values for sodium silicate and aluminosilicate systems (0.5–0.75 eV).

More recently, sodium silicate glasses and glass–ceramics with some cation modifiers such as Y^{3+} and Sn^{4+} were examined as ionic conductors [4–6]. The activation energy could not be lowered by these modifications to 0.5 eV or below. Previously, it had been reported that the conductivity of $Na_3Zr_2Si_2PO_{12}$ was enhanced and its activation energy was lowered by the addition of a proper amount of sodium aluminosilicate glass. Furthermore, the densification was also enhanced [7]. More recently, increases in conductivity were achieved for lithium titanium phosphate by the addition of lithium salts such as Li_3PO_4, Li_3BO_3 and Li_2SO_4, while the porosity was considerably decreased by utilization of a binder [8, 9]. It is expected that proper amounts of glassy additives induce densification and improvements in ionic conductivity of a crystal-based ionic conductor, with a lower activation energy for the conduction.

This paper will present the results of a study of composites of $Na_5YSi_4O_{12}$ with other materials (glass or crystal) to prepare dense sodium-ion conductors.

2. Experimental procedure

As starting materials, reagent-grade Na_2CO_3, SiO_2 and Y_2O_3 were used. Na_2O–Y_2O_3–SiO_2 glass (6.69:1.00:9.95 in molar ratio) was prepared by melting the compressed powder and then quickly pouring the molten liquid on to a room-temperature copper plate. Powdered glass was obtained by ball-milling. Na_2O–Al_2O_3–$4SiO_2$ glass was also prepared. Four kinds of sodium yttrium silicate ceramic were prepared by sintering a mixture of Na_2CO_3, Y_2O_3 and SiO_2 in the prescribed mole ratio at 1000 °C for 24 h in air and then milling. Pellets were prepared by sintering the disc compressed at 200 kg cm^{-2}. The composites of $Na_5YSi_4O_{12}$ and the other materials in the prescribed weight ratio were compressed at 200 kg cm^{-2} and sintered at some temperature in air for 3 h. The sintered discs were polished with 400-grade emery paper and Pikal metal polish and then cleaned by acetone for surface observation. The prepared pellets were 10 mm in diameter and 0.5 mm thick. Gold electrodes, 4 mm × 4 mm, were applied to opposite faces of the pellet by vacuum evaporation.

The electrical properties were measured using a multi-frequency LCR meter in the frequency range of 100 Hz–100 kHz (Yokogawa Hewlett-Packard, 4274A) in flowing N_2 (50 ml min^{-1}) from room temperature to 600 °C. The crystalline phases were identified at room temperature by X-ray diffraction. The

0022-2461

microstructure was examined using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Observations using scanning electron microscopy

Fig. 1 shows the surface microstructure of the sintered $Na_5YSi_4O_{12}$ alone using SEM. It is confirmed that the densification goes almost to completion by sintering at 1000 °C, but the closed pores could not be completely removed. The addition of Na_2O–Y_2O_3–SiO_2 glass to $Na_5YSi_4O_{12}$ is effective for preparing a denser material as shown in Fig. 2. In the sample with 5 wt % glass, grain boundaries and closed pores were detected, but the number of these pores and grain boundaries was drastically decreased for the $Na_5YSi_4O_{12}$ with 10 wt % Na_2O–Y_2O_3–SiO_2 glass sintered at 1000 °C. Microphotographs of sintered $Na_5YSi_4O_{12}$ with Na_2O–Al_2O_3–$4SiO_2$ glass or α-alumina are shown in Figs 3 and 4, respectively. It seems that the densification was only partially completed. It implies that the addition of 10 wt % or more Na_2O–Y_2O_3–SiO_2 glass is more effective for preparing a dense ceramic.

3.2. Conductivity determination

To determine the conductivity component, complex-plane impedance analysis was used. In the lower temperature region, the low-frequency result was represented by a nearly straight line and the high-frequency one by an arc which passed through the origin. With an increase in the measuring temperature, the arc was diminished and only a quasi-straight line caused by the electrolyte–electrode behaviour was observed for all samples. As an example, the results for $Na_3YSi_3O_9$ are shown in Fig. 5. From these observed results the conductivity was determined by an extrapolation to zero reactance of the complex impedance plot. It is well known that for a compressed powder the equivalent total conductivity is composed of several components. Nevertheless, in these measurements we could not determine the individual conductive components such as the intergranular and intragranular (bulk) components, since the depression angle for most of the arcs was 10° or less. The total conductivity data were parametrized by the Arrhenius equation

$$GT = G_0 \exp(-E/kT) \qquad (1)$$

where G is the conductivity. G_0 is the pre-exponential factor, E is the activation energy, k is the Boltzmann constant and T is the absolute temperature. The activation energy and conductivity at 300 °C of some ceramics sintered at 1000 °C were the following: 0.69 eV and 2×10^{-6} S cm^{-1} for $NaYSiO_4$, 0.68 eV and 6×10^{-6} S cm^{-1} for $Na_3YSi_2O_7$, 0.90 eV and 7.5×10^{-6} S cm^{-1} for $Na_3YSi_3O_9$, and 0.30 eV and 7×10^{-2} S cm^{-1} for $Na_5YSi_4O_{12}$. The highest

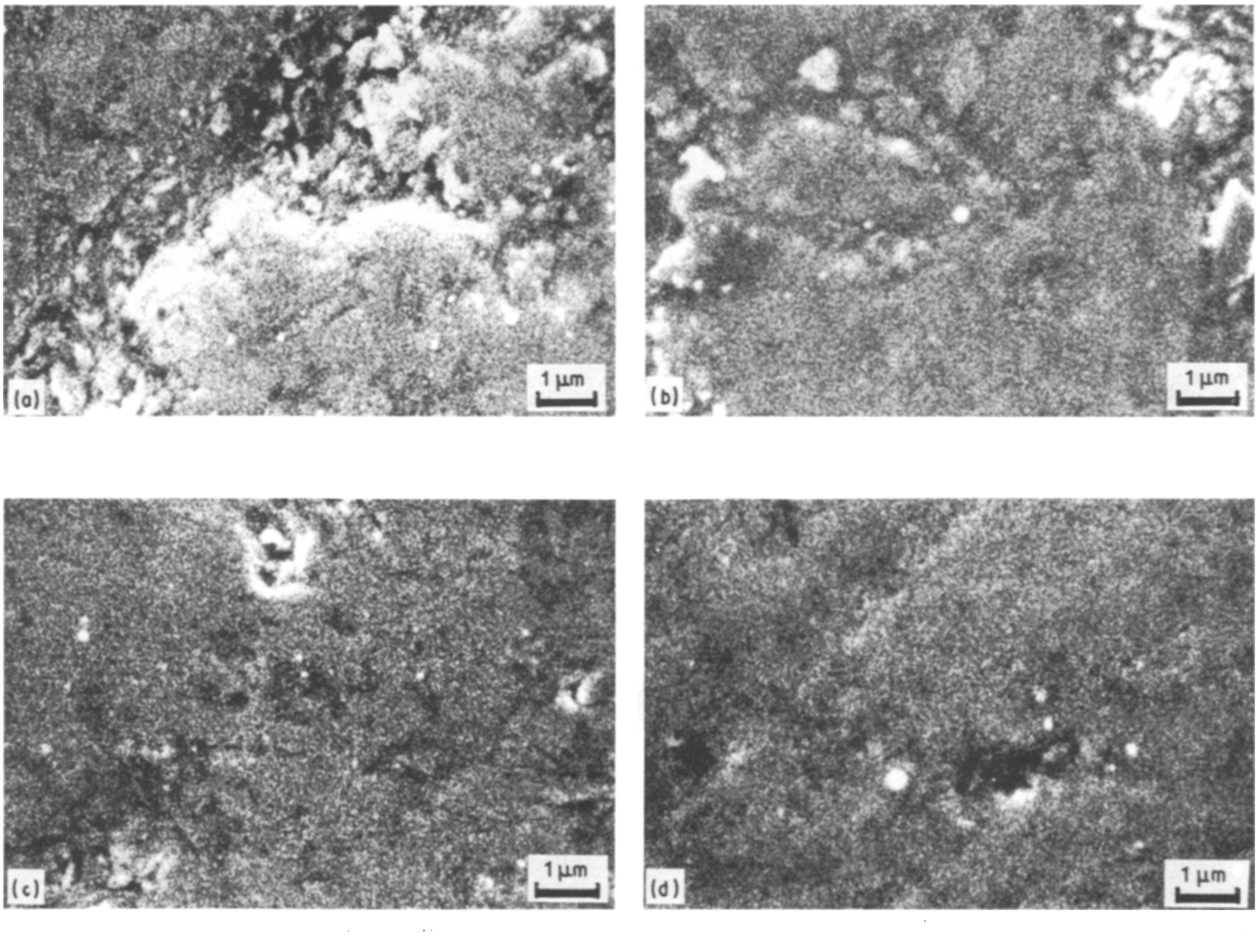


Figure 1 Scanning electron micrographs of $Na_5YSi_4O_{12}$. Sintering temperature: (a) 500 °C for 3 h, (b) 700 °C for 3 h, (c) 1000 °C for 3 h, (d) 1000 °C for 8 h.

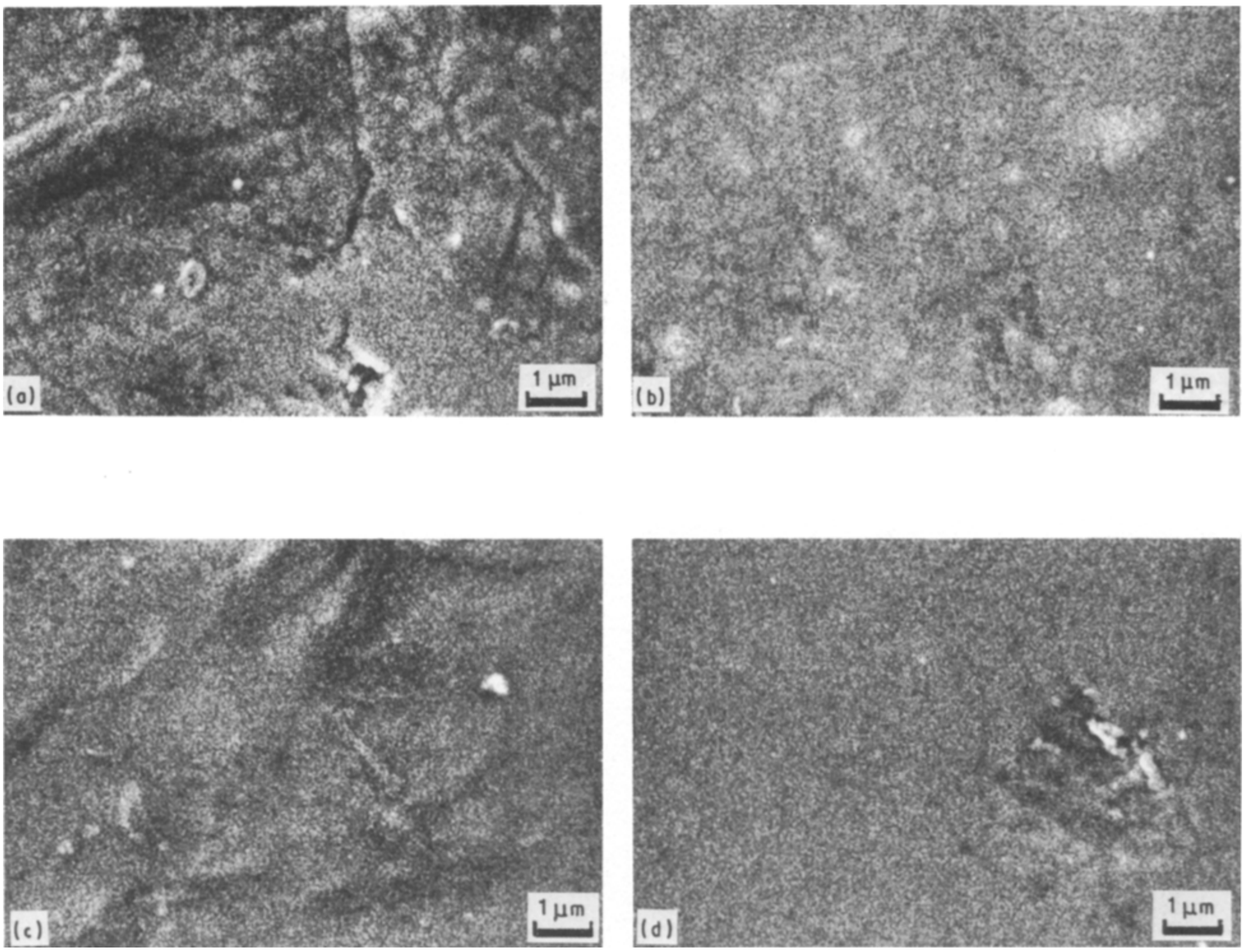
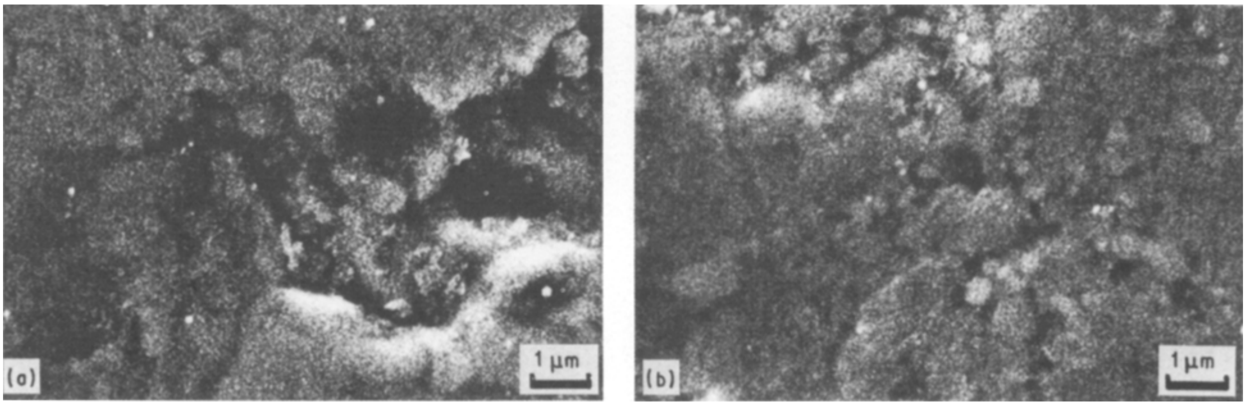


Figure 2 Scanning electron micrographs of $Na_5YSi_4O_{12}$ composite with Na_2O–Y_2O_3–SiO_2 glass sintered at 1000 °C. Glass content (wt %): (a) 5, (b) 9, (c) 17, (d) 28.



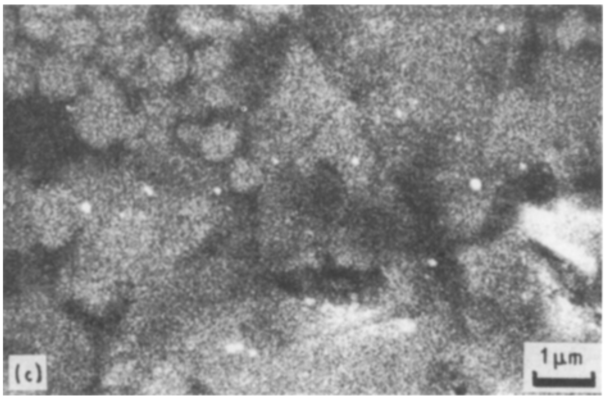
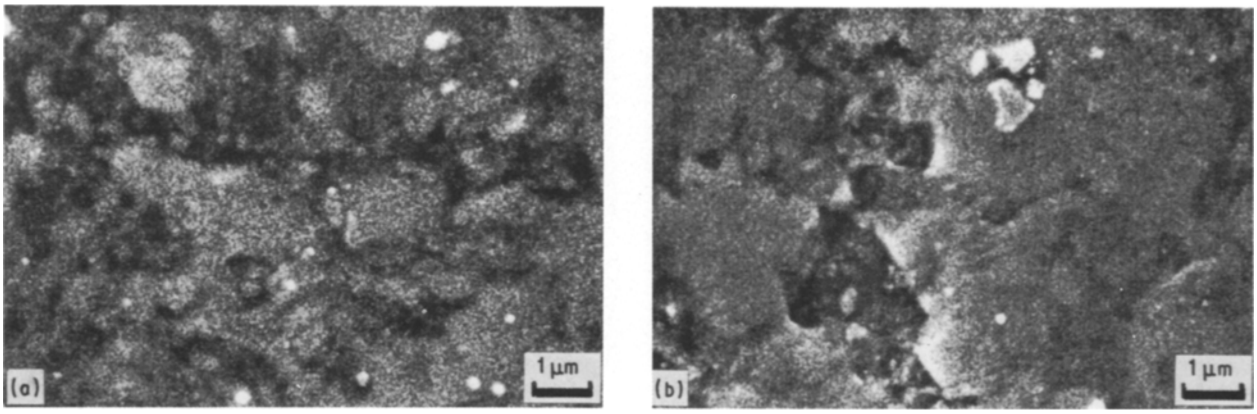


Figure 3 Scanning electron micrographs of $Na_5YSi_4O_{12}$ composite with Na_2O–Al_2O_3–$4SiO_2$ glass sintered at 1000 °C. Glass content (wt %): (a) 5, (b) 9, (c) 13.

conductivity and the lowest activation energy were observed in $Na_5YSi_4O_{12}$. Therefore, for the glass–ceramic composite, $Na_5YSi_4O_{12}$ powder was used as the parent material.

The temperature dependence of the conductivity for some samples is shown in Fig. 6. The conductivity of the $Na_5YSi_4O_{12}$ sample with and without the Na_2O–Y_2O_3–SiO_2 glass was higher than that of the glass alone. It is seen in the Arrhenius plots of $Na_5YSi_4O_{12}$-based samples that the lines drawn for



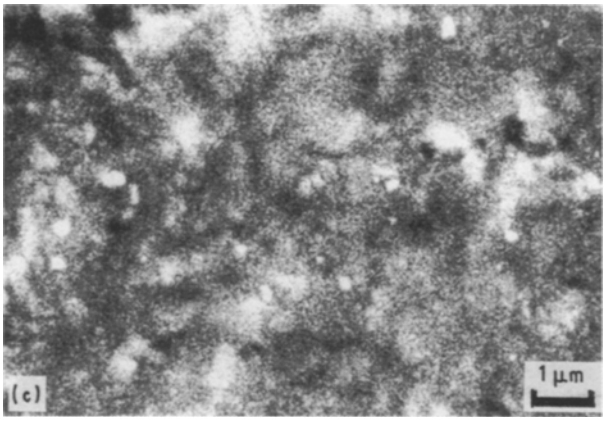


Figure 4 Scanning electron micrographs of $Na_5YSi_4O_{12}$ composite with α-alumina sintered at 1000 °C. α-alumina content (wt %) (a) 5, (b) 9, (c) 17.

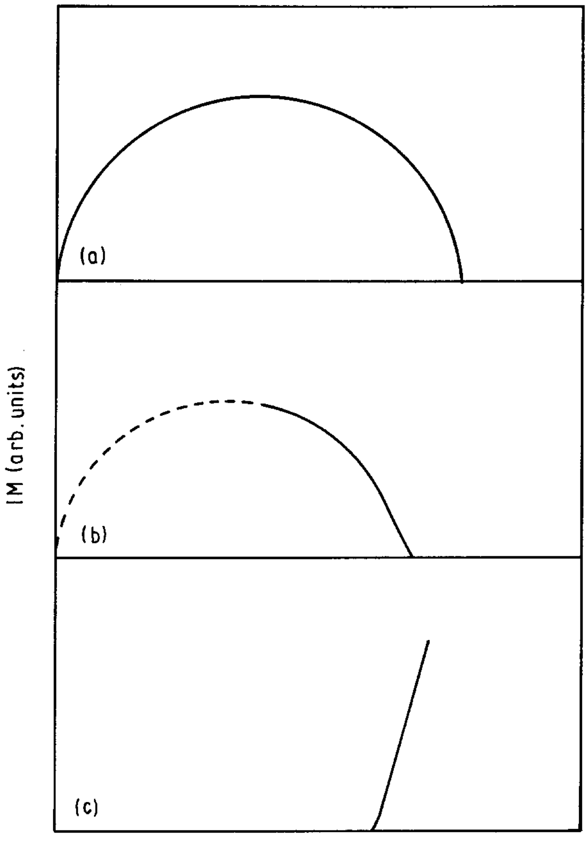


Figure 5 Cole–Cole impedance plots for $Na_3YSi_3O_9$: RE = real, IM = imaginary component. Temperature: (a) 160 °C, (b) 250 °C, (c) 490 °C. The results, measured in the frequency range 100 Hz to 100 kHz, were shown by the solid.

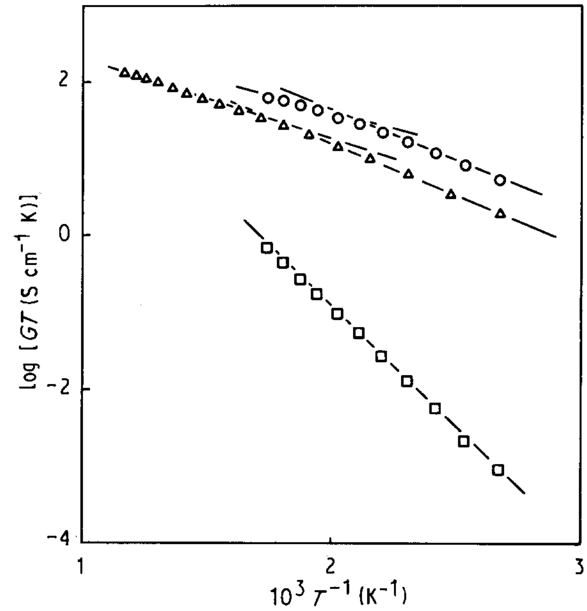


Figure 6 Temperature dependence of conductivity for sample sintered at 1000 °C for 3 h: (□) Na_2O–Y_2O_3–SiO_2 glass, (○) $Na_5YSi_4O_{12}$ composite with 17 wt % of Na_2O–Y_2O_3–SiO_2 glass, (△) $Na_5YSi_4O_{12}$.

the conductivity are bending downwards and the inflection points are at around 200 °C, which is slightly dependent on the sample components and the sintering conditions. In this work, the conductivity and its activation energy determined in a higher-temperature region (> 200 °C) are denoted by G_h and E_h and those in a lower region by G_l and E_l, respectively. In addition, G and E are the respective values determined in the whole temperature region in which the line is straight.

3.3. Effects of sintering temperature on conductivity

The correlation between the conductive characteristics and the sintering temperature of the Na_2O–Y_2O_3–SiO_2 glass is shown in Fig. 7. The conductivity increased monotonically with sintering temperature and its activation energy decreased. The

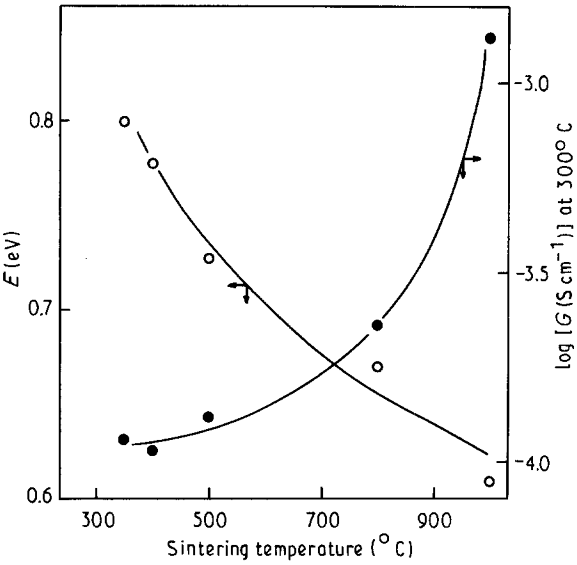


Figure 7 Sintering temperature dependences of (●) conductivity at 300 °C and (○) activation energy for $Na_2O–Y_2O_3–SiO_2$ glass.

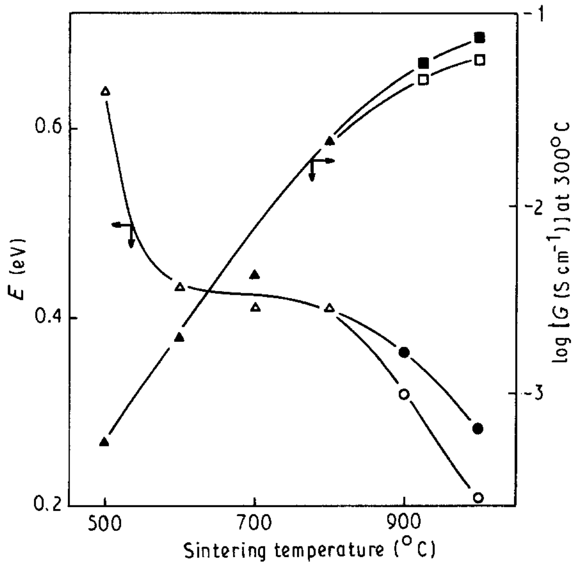


Figure 8 Sintering temperature dependences of (▲, ■, □) conductivity at 300 °C and (△, ●, ○) activation energy for $Na_5YSi_4O_{12}$: (■) G_l, (□) G_h, (●) E_l, (○) E_h.

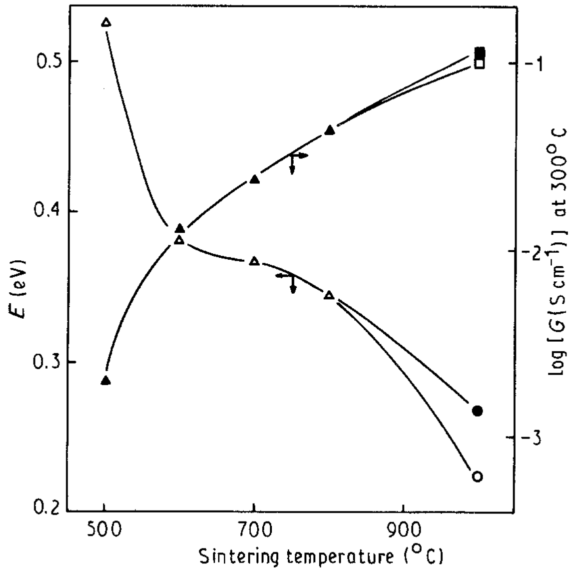


Figure 9 Sintering temperature dependences of (▲, ■, □) conductivity at 300 °C and (△, ●, ○) activation energy for $Na_5YSi_4O_{12}$ composite with 9 wt % $Na_2O–Y_2O_3–SiO_2$ glass: (■) G_l, (●) E_l, (□) G_h, (○) E_h.

activation energy for the glass alone sintered at 1000 °C for 3 h was estimated to be 0.61 eV and was comparable to the value (0.55 eV) for the same glass reported by Alexander [4]. The results for $Na_5YSi_4O_{12}$ are indicated in Fig. 8. The conductivity and activation energy of $Na_5YSi_4O_{12}$ are preferable to those of the glass. The sintering at 600 °C induced a decrease of 0.2 eV in the activation energy, while sintering at up to approximately 800 °C did not result in any drastic decrease. In this plateau region accompanying an increase in the conductivity with sintering temperature, densification may occur. For samples sintered at 900 °C or higher, the temperature dependence of the conductivity changed, i.e. the line in the Arrhenius plot drawn for the conductivity was bending downward and the inflection point was around 200 °C. The value of E_h ($\sim$ 0.2 eV) is slightly less than that of E_l which is comparable to that of $Na_5YSi_4O_{12}$ alone (0.31 eV) reported by Shannon *et al.* [10].

While the conductivity of the glass is considerably less than that of $Na_5YSi_4O_{12}$ alone, the addition of the glass to $Na_5YSi_4O_{12}$ induced an increase in conductivity and a decrease in activation energy. The conductivity and its activation energy are plotted in Fig. 9 against sintering temperature for the composite $Na_5YSi_4O_{12}$ with 9 wt % $Na_2O–Y_2O_3–SiO_2$ glass. In Fig. 10 the correlation between the logarithm of conductivity at 300 °C and its activation energy is shown for $Na_5YSi_4O_{12}$ alone, $Na_5YSi_4O_{12}–(Na_2O–Y_2O_3–SiO_2)$ glass composite and $Na_2O–Y_2O_3–SiO_2$ glass. The conductivity was in the order: $Na_5YSi_4O_{12}$ with glass > $Na_5YSi_4O_{12}$ > $Na_2O–Y_2O_3–SiO_2$ glass, and increased with a decrease in activation energy. Furthermore, a good linear relationship was observed while the slope of this line was less than $1/kT\,(\mathrm{eV}^{-1})$, and could be expressed as follows instead of using Equation 1:

$$GT = G_0^* \exp(E/kT^*) \exp(-E/kT) \qquad (2)$$

where G_0^* is the new pre-exponential factor and T^* is a characteristic temperature. This is an empirical relationship and is well known as the Meyer–Neldel rule [11–14]. While at this stage a detailed physical explanation of this relationship cannot be derived, the idea of the equivalent circuit of the continuous-time random walk (CTRW) approximation [15], in which the resistances are assumed to be thermally activated with a distribution of activation energy while the corresponding capacitances are equal, is applicable.

3.4. Effect of additives on electrical characteristics

The electrical characteristics for the $Na_5YSi_4O_{12}$ composites with $Na_2O–Y_2O_3–SiO_2$ glass, $Na_2O–Al_2O_3–4SiO_2$ glass or α-alumina with 1 μm mean diameter were examined as a function of the additive

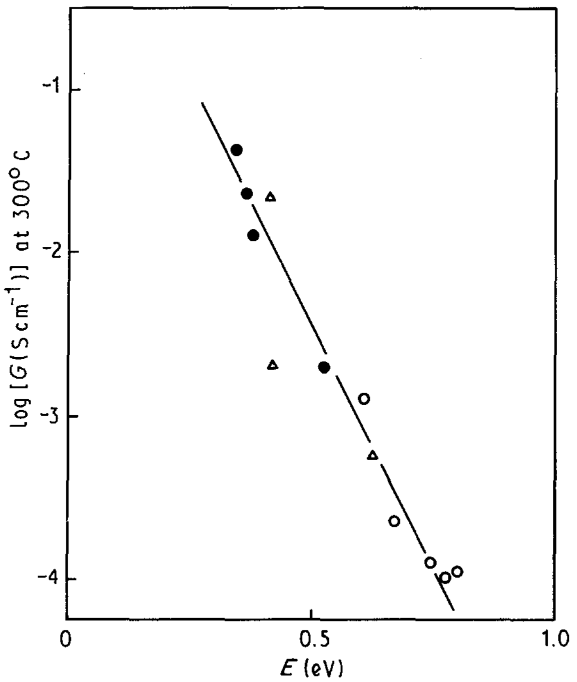


Figure 10 Correlation between activation energy and conductivity at 300 °C for samples sintered at several temperatures: (○) $Na_2O–Y_2O_3–SiO_2$ glass, (●) $Na_5YSi_4O_{12}$ with 9 wt % $Na_2O–Y_2O_3–SiO_2$ glass, (△) $Na_5YSi_4O_{12}$. The slope of the solid line is $-5.0\ eV^{-1}$.

TABLE I Conductivity at 300 °C and activation energy for $Na_5YSi_4O_{12}$–X composites

X-species content	NaYSi glass[a]		NaAlSi glass[b]		α-Al_2O_3	
(wt %)	E(eV)	G($S\,cm^{-1}$)	E(eV)	G($S\,cm^{-1}$)	E(eV)	G($S\,cm^{-1}$)
0	0.24	8.9×10^{-2}				
3					0.22	6.2×10^{-2}
5	0.22	1.0×10^{-1}	0.20	9.0×10^{-2}		
9	0.22	1.2×10^{-1}	0.28	4.7×10^{-2}	0.30	2.4×10^{-2}
13					0.37	8.6×10^{-4}
17	0.21	1.3×10^{-1}	0.26	2.0×10^{-2}	0.73	3.3×10^{-5}
23	0.21	1.2×10^{-1}	0.32	8.0×10^{-3}	0.73	2.1×10^{-5}
28	0.21	1.2×10^{-1}	0.54	7.0×10^{-4}		

[a] $Na_2O–Y_2O_3–SiO_2$ glass,
[b] $Na_2O–Al_2O_3–4SiO_2$ glass.

content. The results are listed in Table I. The decrease in the activation energy was achieved by adding 5 wt % or less additive. For the sample with 10 wt % or more additive, except for the first composite, the activation energy increased and the conductivity decreased with additive content.

The glass ($Na_2O–Y_2O_3–SiO_2$) content dependence on the activation energy is shown in Fig. 11 for the sample sintered at 1000 °C. The addition of glass up to approximately 25 wt % induced decreases in the activation energy determined in each of two temperature regions separated by ~ 200 °C. Excess addition of the glass induced an increase in activation energy, and the conductivity at 300 °C was decreased as shown in Fig. 12. In this case the conductivity at 300 °C, corresponding to the results observed below 200 °C, was estimated by the extrapolation technique.

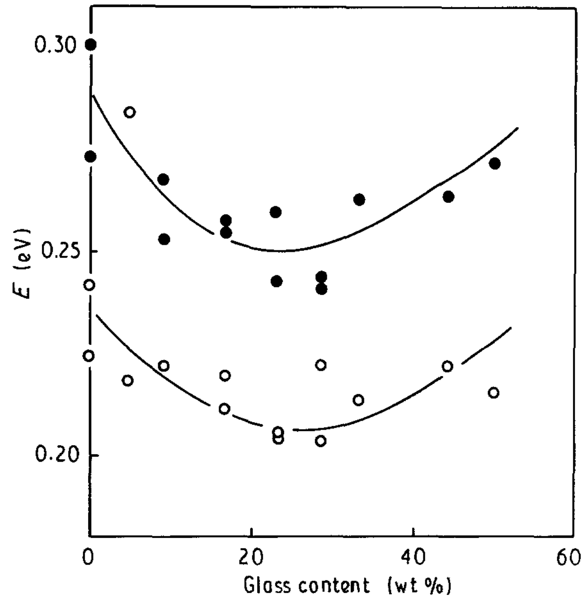


Figure 11 Glass content dependence of activation energy for $Na_5YSi_4O_{12}$ composite with $Na_2O–Y_2O_3–SiO_2$ glass sintered at 1000 °C: (○) E_h, (●) E_l.

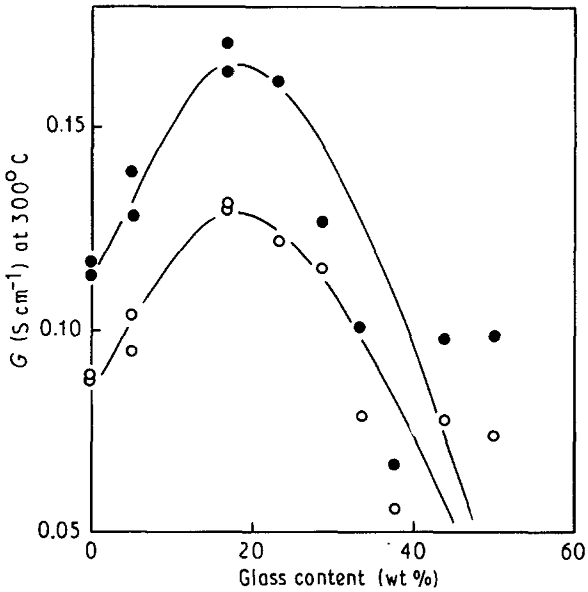


Figure 12 Glass content dependence of conductivity at 300 °C for $Na_5YSi_4O_{12}$ composite with $Na_2O–Y_2O_3–SiO_2$ glass sintered at 1000 °C: (○) G_h, (●) G_l.

In Fig. 13 the correlation between the conductivity at 300 °C and the activation energy is shown for the sample sintered at 1000 °C. It was very difficult to determine the relationship with good accuracy, but the slopes determined for the results observed in both temperature regions are the same (~ $8.6\ eV^{-1}$) and nearly equal to $1/kT$ (theoretical value: $8.8\ eV^{-1}$ at 300 °C). This coincidence implies that the conductivity is mainly controlled by the activation energy, and the pre-exponential factor is hardly influenced by the glass content for the sample sintered at 1000 °C.

To understand the additive effects on the conductivity of the composite in which the conductivity of the additive is considerably lower than that of the parent

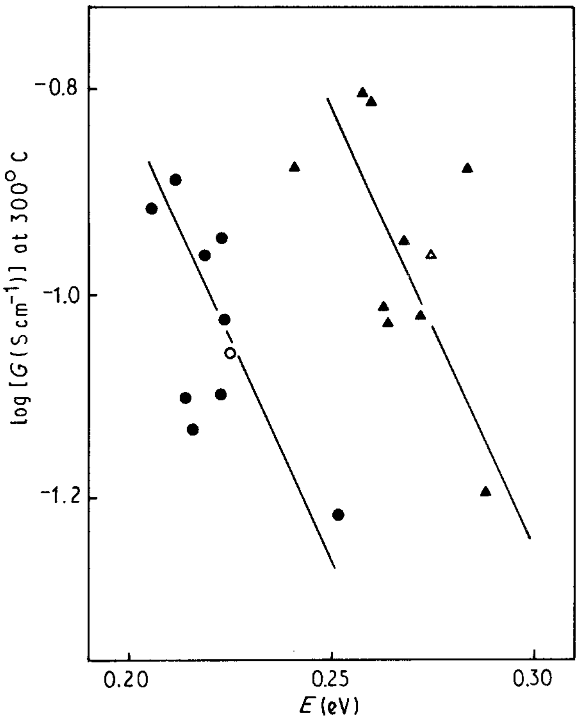


Figure 13 Correlation between activation energy and conductivity at 300 °C for samples sintered at 1000 °C: (●, ▲) $Na_5YSi_4O_{12}$ composite with 33 wt % or less $Na_2O–Y_2O_3–SiO_2$ glass, (○, △) $Na_5YSi_4O_{12}$; (●, ○) G_h, (▲, △) G_l. The slope of the solid lines is $-8.6\ eV^{-1}$.

materials, some models such as effective media theories and mixing rules have been proposed [16]. These models may be applied to the composite with $Na_2O–Al_2O_3–4SiO_2$ glass or α-alumina, but not to the composite with $Na_2O–Y_2O_3–SiO_2$ glass since the conductivity increases with $Na_2O–Y_2O_3–SiO_2$ glass content up to about 25 wt %. One possibility, of the formation of $Na_5YSi_4O_{12}$ in the intergranular region, may be considered for the composites with $Na_2O–Y_2O_3–SiO_2$ glass, since the activation energy of the glass sintered at 1000 °C for 12 h or longer was about 0.30 eV or less but a geometrical transformation was produced during the sintering process. X-ray diffraction analysis was applied to these samples. The absolute intensity of the diffraction peaks assigned to $Na_5YSi_4O_{12}$ was hardly influenced by additive contents up to at least 25 wt %, and the broad band caused by the glass phase was not enhanced.

While the formation of phases such as $Na_3YSi_2O_{12}$ and $Na_3YSi_3O_9$ is possible, peaks assigned to these compounds were not detected. Formation of $Na_5YSi_4O_{12}$ phase from the additive accompanying densification is considered to be the origin of the enhancement of the conductivity of the sintered $Na_5YSi_4O_{12}$ composite with $Na_2O–Y_2O_3–SiO_2$ glass.

References

1. E. BANKS and C. H. KIM, *J. Electrochem. Soc.* **132** (1985) 2617.
2. C. C. HUNTER and M. D. INGRAM, *Solid State Ionics* **14** (1984) 32.
3. O. L. ANDERSON and D. A. STUART, *J. Amer. Ceram. Soc.* **37** (1954) 573.
4. M. G. ALEXANDER, *Solid State Ionics.* **22** (1987) 257.
5. C. H. KIM, B. QIU and E. BANKS, *J. Electrochem. Soc.* **132** (1985) 1340.
6. M. G. ALEXANDER and B. RILEY, *Solid State Ionics* **18/19** (1987) 478.
7. Y. SADAOKA, M. MATSUGUCHI and Y. SAKAI, *J. Mater. Sci.* **24** (1989) 1299.
8. H. AONO, E. SUGIMOTO, Y. SADAOKA, N. IMANAKA and G. ADACHI, *Chem. Lett.* (1990) 331.
9. *Idem, J. Electrochem. Soc.* **137** (1990) 1023.
10. R. D. SHANNON, B. E. TAYLOR, T. E. GIER, H.-Y. CHEN and T. BERZINS, *Inorg. Chem.* **17** (1978) 958.
11. W. MEYER and H. NELDEL, *Z. Tech. Phys.* **12** (1937) 588.
12. R. DEWSBERRY, *J. Phys. D: Appl. Phys.* **8** (1975) 1797.
13. G. J. DIENS *J. Appl. Phys.* **21** (1950) 189.
14. D. O. ALMOND and A. R. WEST, *Solid State Ionics* **23** (1987) 27.
15. J. C. DYRE, *J. Phys. C: Solid State Phys.* **21** (1988) 2431.
16. D. S. McLACHLAN, M. BLASZKIEWICZ and R. E. NEWNHAM, *J. Amer. Ceram. Soc.* **73** (1990) 2187.

Received 22 May
and accepted 27 September 1991