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Superionic conducting $Na_5SmSi_4O_{12}$-type glass-ceramics: Crystallization condition and ionic conductivity

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Abstract

Glass-ceramics of the phosphorus-containing $Na_5RSi_4O_{12}$ (N5)-type (R = rare earth element; Sm) Na^+-superionic conductors (NaRPSi) were prepared by crystallization of glasses with the composition $Na_{3.9}Sm_{0.6}P_{0.3}Si_{2.7}O_9$. The optimum conditions for crystallization were discussed with respect to the conduction properties and the preparation of uncracked N5-type glass-ceramics. Most of the N5-type NaSmPSi compounds were obtained as uncracked glass-ceramics when the heating time for nucleation was more than 6 h. Also studied were the microstructural effects on the conduction properties, which were dependent upon the heating conditions of crystallization. Large enhancement of electrical conductivity was observed in the glass-ceramics as the grain growth was promoted with the increase of the heating time for crystallization. The ionic conductivity of the glass-ceramic $Na_{3.9}Sm_{0.6}P_{0.3}Si_{2.7}O_9$ heated at 900 °C for 42 h was 9.07×10^{-2} S/cm at 300 °C.

Keywords: Glass; Crystallization; Glass-ceramics; Ionic conductivity

1. Introduction

Glass-ceramics are polycrystalline materials which are produced by controlled crystallization of glasses.[1] In addition to their easy fabrication into desired shapes, glass-ceramics generally have advantages over conventional sintered ceramics in mechanical properties and chemical durability because of their pore-free and small grained (<1 μm) microstructure.[1] Glass-ceramics of Na^+-superionic conductors are therefore expected to overcome the difficulties in the fabrication of practical devices such as tubes for Na/S secondary batteries. The conventional Na^+-superionic conductors, however, have not yet been produced in the form of glass-ceramics. The present authors have successfully prepared a new family of the phosphorus-containing $Na_5RSi_4O_{12}$ (N5)-type (R = rare earth element)[2,3] Na^+-superionic conductors (NaRPSi)[4] by crystallization of glasses with the composition formula, $Na_{3+3x-y}R_{1-x}P_ySi_{3-y}O_9$.[5–9] These materials are reportedly comparable to the conventional ceramic Na^+-conductors such as NASICON, β- and β″- aluminas (e. g., $NaAl_{11}O_{17}$ and $NaAl_5O_8$). The R elements have a significant effect on the crystallization of glasses, as well as on the conduction properties.[2] To date, polycrystalline N5-type NaRPSi has been obtained with Sc, Y, Gd or Sm as the R element. In the following, these NaRPSi compounds will be referred to as NaScPSi, NaYPSi, NaGdPSi and NaSmPSi, respectively. The size of the R ions has been expected to have a significant effect on the crystallization of the phase. Although the precise structural analysis of the silico-phosphate N5-type NaRPSi has not yet been completed, it is currently assumed from the analogy with $Na_5YSi_4O_{12}$[10] that all the R ions can be octahedrally coordinated with the non-bridging oxide ions of the (SiO_4, PO_4)-tetrahedra of the 12-membered rings. The reported results on the silicate ceramics[2] show that the conductivity of the N5-type NaRPSi increases with increasing size of its R ions, giving the order NaSmPSi > NaGdPSi > NaYPSi > NaScPSi.

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It can be expected that NaSmPSi is the most conductive. However, this order was not always true in glass-ceramics.[11] Although most of the NaRPSi compounds were obtained as uncracked glass-ceramics, NaSmPSi was difficult to prevent from cracking during crystallization. It was found that uncracked NaGdPSi with larger Gd^{3+} ions was the most conductive; however, NaSmPSi with the largest Sm^{3+} ions was less conductive than NaYPSi with medium Y^{3+} ions.

In the present study, the N5-type NaSmPSi ionic conductors were prepared by crystallization of glasses. The optimum conditions for crystallization were discussed with reference to the conduction properties and the preparation of uncracked N5-type glass-ceramic NaSmPSi. The microstructure of glass-ceramics, including neck growth among grains as well as grain size, is generally affected by the crystallization process.[1] As the above mentioned devices utilize dc conduction properties of Na^+-superionic conductors, another aim was to study the microstructural effects on the conduction properties of whole glass-ceramics.

2. Experimental procedure

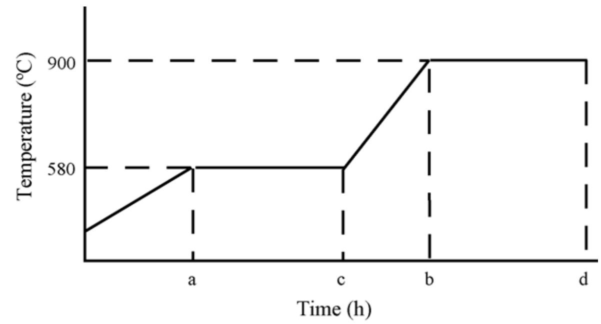
2.1. Preparation of glasses and glass-ceramics

The precursor glasses were prepared from reagent-grade oxides of anhydrous Na_2CO_3, Sm_2O_3, $NH_4H_2PO_4$ and SiO_2; the mechanically mixed powders according to the composition formula $Na_{3+3x-y}Sm_{1-x}P_ySi_{3-y}O_9$ with the parameters $x = 0.4$ and $y = 0.3$ were melted at 1350 °C for 1 h after calcinations at 900 °C for 1 h, in the air. The melts were quickly poured into cylindrical graphite, and then annealed at 500 °C for 3 h, giving NaSmPSi glasses.

Fig. 1 shows the program of temperature and time for the production of glass-ceramic NaSmPSi employed in the present work. Bulk glasses were heated with an increasing rate of 75 °C/h to 580 °C above ca. 50 °C of the glass transition point, which had been determined in advance by differential thermal analysis (DTA). This pretreatment was done in order to obtain homogeneous nucleation.[1] After the annealing for 1–10 h, specimens were heated at 900 °C for 2–42 h, thereafter slowly cooled in a furnace with a decreasing rate of 150 °C/h to room temperature. These glass-ceramic specimens were polished down with 0.5 μm diamond paste, thereafter subjected to the conductivity measurements.

2.2. Measurements and characterization

Ionic conductivities were measured by the complex impedance method on cylindrical glass-ceramics of typically 15 mm in diameter and 2 mm in thickness. Electrodes were prepared by sputtering of gold on polished surfaces. The applied ac field ranged from 5 to 10 MHz in frequency. The temperature dependence of the conductivity was measured in a similar way at several temperatures ranging from room temperature to 350 °C. The complex impedance or admittance loci of glass-ceramics were analyzed by an equivalent circuit.



	a-b	b-c	c-d
(A)	1	7	17
(B)	3	8	10
(C)	6	8	5
(D)	6	8	8
(E)	6	8	25
(F)	6	8	42
(G)	10	8	2

a-b: nucleation c-d: crystal growth

Fig. 1. The programs of temperature and time for the production of glass-ceramics.

Crystalline phases of glass-ceramic specimens were identified by X-ray diffraction (XRD) method. Glass-ceramic NaSmPSi were subjected to scanning electron microscope (SEM) for microstructural analysis.

3. Results and discussion

3.1. Preparation of uncracked glass-ceramics: crystallization condition

The N5 single phase NaSmPSi ionic conductors with the $Na_{3.9}Sm_{0.6}P_{0.3}Si_{2.7}O_9$ composition were successfully produced by crystallization of glasses. The glass samples heated by the program pattern (A) shown in Fig. 1 broke during crystallization and the glass-ceramic NaSmPSi obtained by the pattern (B) was difficult to prevent from cracking during crystallization. Most of the NaSmPSi compounds by the patterns (C)–(G) (i.e. longer nucleation time) were obtained as uncracked glass-ceramics.

Fig. 2 shows SEM photographs of microstructure of the NaSmPSi glass-ceramics obtained by the patterns (C), (F) and (G). The grain sizes of the specimens by the patterns (C) and (F) were about 6 and 10 μm, respectively. The grain growth is promoted with increase of heating time for crystallization. The glass samples broke during crystallization when the heating time for crystallization was more than 42 h. Although grain growth may cause high conductivity, it was difficult

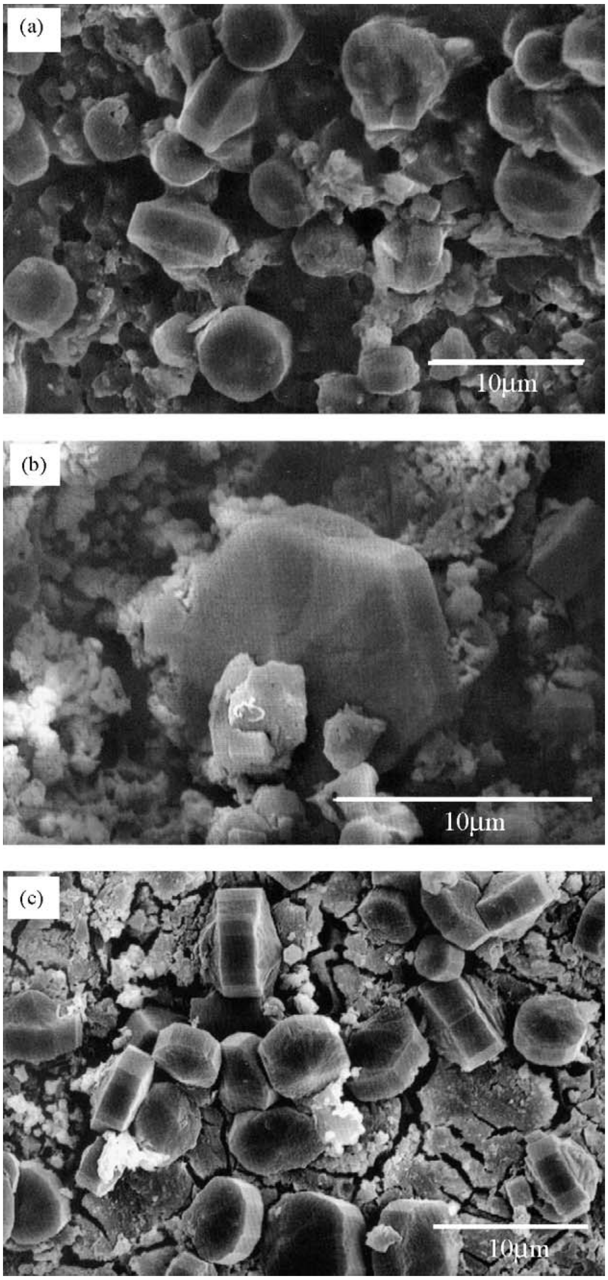


Fig. 2. SEM photographs of the glass-ceramics: (a) pattern (C); (b) pattern (F); (c) pattern (G).

to prevent the sample heated for a long time from cracking during crystallization. The microstructure of the specimen by the pattern (G) was denser and the grain size was about 5 μm. The glass samples broke during crystallization when the heating time was over 2 h.

3.2. Conduction properties of grains and grain boundaries

Fig. 3 shows the complex admittance diagrams of the glass-ceramic NaSmPSi crystallized by the program pattern (F). Those admittance diagrams were analyzed with the equivalent circuit shown in Fig. 4. The complex admittances of the measured glass-ceramic specimens consisted of two semicircles below 300 °C. The two intercepting points on the real axis are interpreted as the resistance of crystallized grains (R_G) and the total resistance of grains and remaining glassy grain boundaries (R_{GB}).

Shown in Fig. 5 are examples of the temperature dependence Arrhenius plots made on the basis of the calculated

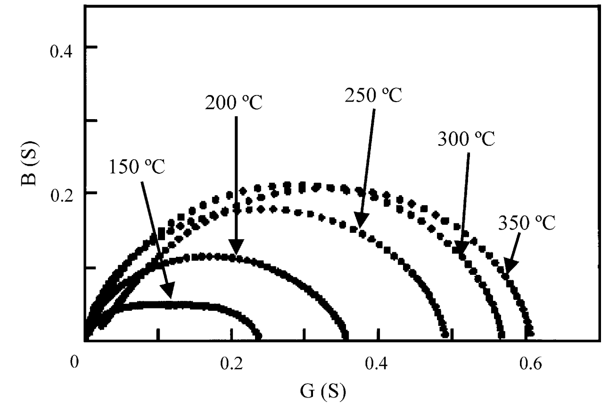


Fig. 3. Complex admittance diagrams of the glass-ceramics crystallized by the pattern (F).

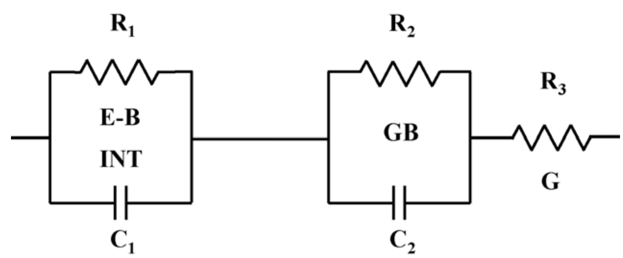


Fig. 4. Equivalent circuit employed for the admittance analysis. E-B INT, GB and *G* represent the electrode-bulk interface, grain boundaries and grains, respectively, and (R_1, C_1), (R_2, C_2) and R_3 are their resistances and capacitances.

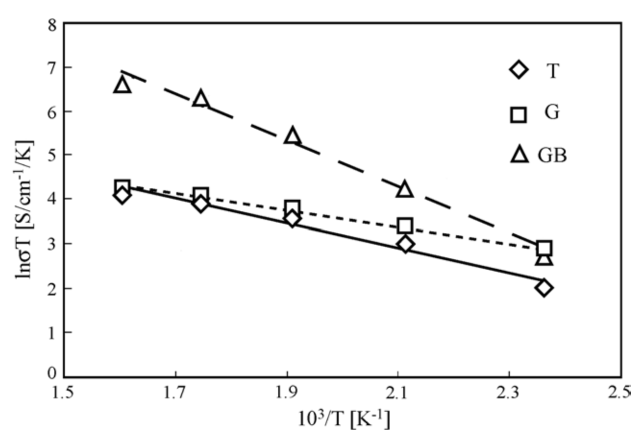


Fig. 5. Arrhenius plots of conductivities of grains (*G*), grain boundaries (GB) and total bulk (*T*) for the glass-ceramics crystallized by the pattern (F).

Table 1
Conduction properties of the glass-ceramics

Program pattern	σ_{300} (10^{-2} S/cm)	E_a (kJ/mol)		
		T	*G*	GB
(C)	6.59	22.77	14.36	44.65
(D)	7.39	20.78	13.57	42.02
(E)	7.57	21.56	14.92	46.61
(F)	9.07	22.34	14.75	44.22
(G)	3.10	22.43	20.77	23.88

σ_{300}: conductivity at 300 °C. E_a: activation energy (*T*: total; *G*: grain; GB: grain boundary).

conductivity values of grains and grain boundaries of the glass-ceramic NaSmPSi, in which the geometrical ratios of thickness to surface area for grains were also used for convenience for those of grain boundaries because of their indefinable shapes. The conductivity of the total bulk (*T*) is as close as to that of grains (*G*) at higher temperatures, while the resistance of grain boundaries (GB) dominates the whole conductance at lower temperatures. It should be noted that, concerned with the conduction properties of grain boundaries, only the activation energies are significant, since the conductivity of grain boundaries were calculated using the geometry ratio of surface area to thickness of the whole glass-ceramic bulk.

Table 1 summarizes the measured conductivities at 300 °C (σ_{300}) and the calculated activation energies (E_a) of the glass-ceramic NaSmPSi specimens. The samples crystallized by the program patterns (C) and (F) showed the ionic conductivities of 6.59×10^{-2} and 9.07×10^{-2} S/cm, respectively. It was found that the conductivity increased with the grain growth. The samples crystallized by the pattern (G) showed much lower conductivity of 3.10×10^{-2} S/cm.

It was found that uncracked NaSmPSi with the largest Sm^{3+} ions was more conductive than NaYPSi with medium Y^{3+} ions; however, NaSmPSi was less conductive than NaGdPSi. Further grain growth can expect the increase in the conductivity of NaSmPSi.

As R_{GB} decreases rapidly with increasing temperature because of high $(E_a)_{GB}$ to a comparable value with R_G at 300 °C (Fig. 5), the total conductivities ($R_G + R_{GB}$) are dominated by grain boundary conductivity. The grain size-dependence of σ_{300} is therefore explained by the decrease in the number of poorly conductive grain boundaries with grain size.

The conduction properties of grain boundaries were strongly dependent on the annealing conditions, although those of the grains were little changed by annealing temperature and time. Glass-ceramics are generally composites consisting of crystallized grains and small amounts of residual glass (<1%).[1]

4. Conclusions

The uncracked N5-type NaSmPSi glass-ceramics were successfully produced by crystallization of glasses with the composition $Na_{3.9}Sm_{0.6}P_{0.3}Si_{2.7}O_9$. The main features of this work are as follows:

1. Grain growth cause high conductivity.
2. The grain growth is promoted with increase of heating time for crystallization.
3. Conduction properties of these glass-ceramics were strongly dependent upon the crystallization conditions.
4. Complex admittance analysis confirmed that this dependence was attributed to the conduction properties of grain boundaries.
5. The ionic conductivity of the glass-ceramic NaSmPSi heated at 900 °C for 42 h was 9.07×10^{-2} S/cm at 300 °C.

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