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Synthesis and Conduction Properties of New Na^+-conducting Glass-ceramics of Sodium Yttrium Silicophosphate

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Na^+ superion conducting glass-ceramics were obtained in the system Na_2O-Y_2O_3-P_2O_5-SiO_2. The compounds with the crystal structure of $Na_5YSi_4O_{12}$ was found to be the most conductive and exhibit the ionic conductivity as 8.0×10^{-2} S/cm at 300 °C with the activation energy of 22.8 kJ/mol.

Glass-ceramics of Na^+ superion conductors (NASICON) can be expected to have the advantage over the conventional ceramic NASICON such as β- and β''-aluminas in the fabrication of various shapes. Generally, it is also approved[1)] that the crystallization of glasses improve their chemical durability and mechanical properties. Taking account of these advantages, glass-ceramic NASICON has been investigated. Recently, we have successfully produced a new kind of glass-ceramics in the system Na_2O-Y_2O_3-P_2O_5-SiO_2. Our materials have the advantage of lower melting point (<1200 °C) in addition to those mentioned above. In this report, the procedures of synthesis and ionic conduction properties will be presented.

Preceding the finding of the present materials, we have also synthesized new types of Na^+ superion conducting silicophosphate compounds in the system Na_2O-Y_2O_3-P_2O_5-SiO_2.[2-4)] Those crystalline compounds will be referred hereafter to as NYPS. Those NYPS compounds were the derivatives from the silicates $Na_3YSi_3O_9$, $Na_5YSi_4O_{12}$, and $Na_9YSi_6O_{18}$ in the family of $Na_{24-3x}Y_xSi_{12}O_{36}$.[5,6)] The present glass-ceramic materials (named glass-ceramic NYPS) were produced according to the phase-composition relationship for NYPS.[4)] At present, the crystal structure of those silicophosphate compounds have been assumed to be analogous to the respective mother silicates. The ionic conductivity and activation energy of the NYPS compounds were strongly dependent upon the composition and the type of structure. The values were in the range of 10^{-1} and 10^{-6} S/cm at 300 °C and of 20 and 70 kJ/mol, respectively. Of the three kinds of NYPS, $Na_5YSi_4O_{12}$-type NYPS (named N_5YPS) was superior to the other two (named N_3YPS and N_9YPS, respectively) in the electrical properties. Accordingly, glass-ceramic N_5YPS has been mainly studied in our work. In this report, glass-ceramic N_9YPS will be also introduced for comparison.

Starting materials were prepared by mixing of anhydrous Na_2CO_3, Y_2O_3, $(NH_4)_2HPO_4$, and SiO_2. The mixture was melted at 1300 °C for 1 h and rapidly quenched in a cylindrical graphite mould. Glass specimens thus obtained were annealed for several hours at an optimum temperature (ca. 25 °C below the glass transition temperature (T_g)) determined by DSC analysis. Shown in Fig. 1 are the DSC results of typical specimens A and B listed in Table 1. The temperatures employed for nucleation (T_N) and crystallization (T_C) of glass specimens were also determined by the results of DSC analysis (Fig.1). As an example, the temperatures were chosen as follows: T_N=570 °C and T_C=900-1050 °C for specimen A, and T_N=600 °C and T_C=1000 °C for specimen B. Figure 2 shows the program of temperature and time for the production of glass-ceramic NYPS employed in the present work. From the XRD analysis, it was clarified that the highly conducting phase of N_5YPS

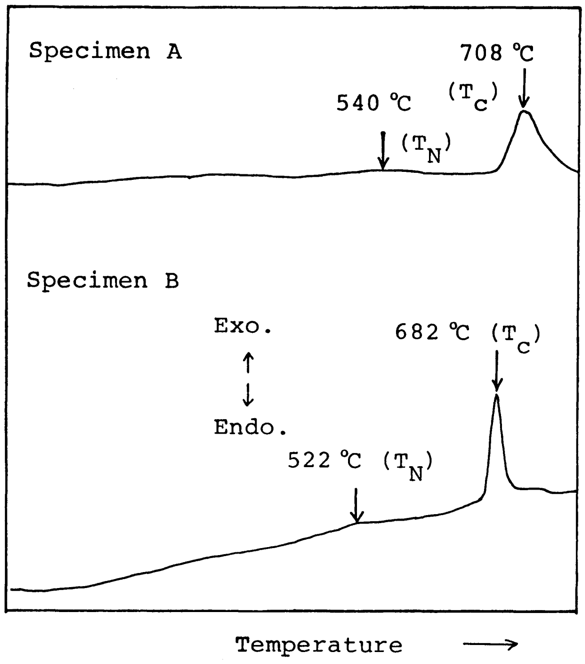

Fig.1. DSC results of specimens A and B.

Table 1. Composition of specimens A and B

Specimen	Composition (mol%)			
	Na_2O	Y_2O_3	P_2O_5	SiO_2
A	38.24	5.88	2.94	52.94
B	42.23	3.88	4.37	49.52

was formed in specimen A, while N_3YPS-type phase with lesser conductivity appeared in specimen B.

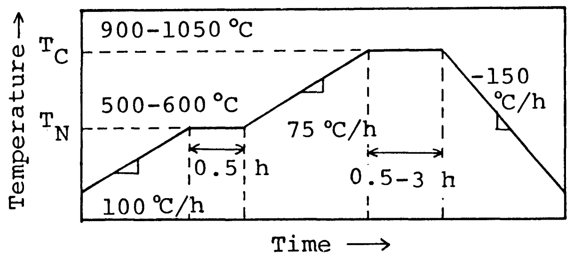

Fig.2. T-t program for crystallization.

The ionic conductivity was determined by the complex impedance analysis. The measurements were performed by the ac 2-probe method on the cylindrical specimens (ca. 10 mm in diameter and 1 mm in thickness). Sputtered gold was used as the blocking electrode. As an example, shown in Fig. 3 are the complex admittance diagrams of the two kinds of specimens A crystallized at different temperatures. It is seen in the figure that two semicircles constructed the diagrams, and that the ratio of the radii of the two is varied with T_C. These diagrams were analysed by the equivalent circuit inserted in Fig. 3. The conductivities (σ_T) at a temperature T (T=150 and 300 °C) and the activation energies (Ea) thus determined are summarized with those of specimen B in Table 2. It is seen in the table that the total value of σ_{300} of specimen A is comparable to those of β-alumina and $Na_5YSi_4O_{12}$, while that of specimen B is much inferior. There is still a matter to be improved concerning the microstructural effect on the conduction properties. By comparison with the two kinds of the results of specimen A, it is seen that the conduction properties of glass-ceramic NYPS is affected by the condition of thermal treatment. The total conductivity of a specimen seems to be enhanced by thermal treatment at a higher temperature. Those results arise from the fact that the two components is related to the microstructure of the specimen. The σ value of component 1

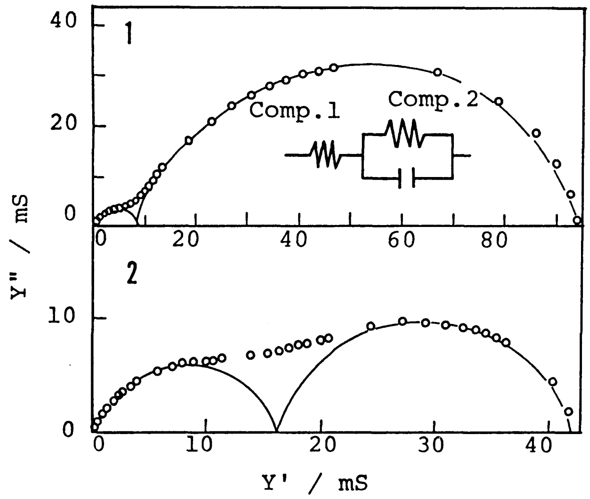

Fig.3. Complex admittance diagrams measured at 150 °C. (1): specimen A heated at 1050 °C, (2): specimen A heated at 950 °C.

was consistent with that of $Na_5YSi_4O_{12}$.[4,5] On the other hand, Ea of component 2 were close to those of precursor glasses (ca.60 kJ/mol). At present, components 1 and 2 are assumed to be attributed to the crystallized grains and glassy parts still remaining, respectively.

Table 2. Ionic conductivities and activation energies of glass-ceramic NYPS

Specimen	Component 1		Component 2		Total
	σ_{150}/S cm^{-1}	Ea/kJ mol^{-1}	σ_{150}/S cm^{-1}	Ea/kJ mol^{-1}	σ_{300}/S cm^{-1}
A[a)]	9.5×10^{-3}	28.3	7.3×10^{-3}	69.2	4.3×10^{-2}
A[b)]	1.7×10^{-2}	22.8	1.5×10^{-3}	89.5	8.0×10^{-2}
B	2.4×10^{-6}	68.4			2.4×10^{-4}

a), b) Thermally treated at 950 °C for 0.5 h (a)) and at 1050 °C for 0.5 h (b)).

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