Electrical Conductivity of the System $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$

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$\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ 系の電気伝導度

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The effect of substitution of Ge for Si in the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ on the phase and electrical conductivity was investigated. The compositions $x=0.17$ and 1.0 gave rhombohedral structure below 1100°C , with the shifts of X-ray diffraction lines to lower diffraction angles as compared with $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_4\text{Zr}_2\text{Si}_2\text{O}_{13}$, respectively. However, a difference in the diffraction patterns of $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{13}$ and NASICON ($\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{13}$) was recognized. Arrhenius plots of σT for $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{13}$ sintered at 1000°C broke in two straight lines indicating activation energies of 8.3-9.2 and 13.4-14.2 kcal/mol in high (500°C - 320°C) and low (320°C - 230°C) temperature regions respectively. The system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ showed lower electrical conductivity and higher activation energy than the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$.

[Received January 16, 1988 ; Accepted March 24, 1988]

Key-words : $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ system, $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ system, Nasicon, Sodium ion conductor, Electrical conductivity, Activation energy

1. Introduction

The system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ is well known as a fast sodium ion conductor and its conductivity is comparable to that of β -alumina. The ionic conductivity of the system reaches a maximum ($\approx 0.2 \text{ S}\cdot\text{cm}^{-1}$ at 300°C) at the composition $x=0.67$ and the compound is named NASICON^(1),2). However, there are large differences in the migration mechanism of sodium ion and the sintering temperature between nasicon and β -alumina. The skeleton structures in β -alumina and nasicon provide two and three dimensional sodium ion transport, respectively. For the fabrication of dense β -alumina polycrystalline high sintering temperature above 1600°C is required. On the other hand, nasicon ceramics can be fabricated below 1250°C . The ionic conductivity is affected by the interaction between the mobile ion and the static lattice. This interaction in a cation conductor is modified by exchanging the mobile ion or by altering the size of diffusion channels through replacements of the framework cations. The crystal data of the ion-exchanged $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{13}$ are reported by Hong⁽²⁾. This letter describes the effect of substitution of Ge for Si in the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ on the phase and conductivity. The experimental results suggest that the substitution of Ge for Si with an increase in ion radius increases the migration energy of sodium ion.

2. Experimental procedures

The powders of the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ were synthesized from mixtures of Na_2CO_3 , ZrO_2 , GeO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ through the following calcination steps in Al_2O_3 crucibles: $200^\circ\text{C}(2\text{h}) \rightarrow 900^\circ\text{C}(2\text{h}) \rightarrow 1000^\circ\text{C}(4\text{h})$. Sodium carbonate added was 5% in excess of the calculated amount on the premise of loss of Na_2O by heating. After the heating at each calcination step, the powders were ground in an agate mortar. The powders calcined at 1000°C were compacted to disks (ca. 10 mm in diameter and 2-3 mm thickness) by isostatic pressing at 3000 kg/cm^2 after a preliminary uniaxial pressing at 500 kg/cm^2 and then sintered at 1000°C - 1100°C for 4 h in air. Bulk densities of green compacts and sintered bodies were calculated from their dimensions measured with a microscope ($\pm 0.01 \text{ mm}$). The crystal structure of the sintered body was examined with X-ray diffraction (Rigaku Cat No. 2013, $\text{CuK}\alpha$). Electrical conductivity of the sintered body was measured with a conventional A. C. bridge circuit (YHP 4262A) at 0.12, 1 and 10 kHz between 140°C and 500°C in dried N_2 flow. Electrical contact was made via platinum plates in pressure contact with platinum electrodes formed by firing a platinum paste on the surface of the sample at 850°C .

3. Results and discussion

3.1 Phases and sintering in the system

$\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$

Figure 1 shows the X-ray diffraction patterns of the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ sintered at 1070°C for 4 h. Comparison of the diffraction patterns between the two systems of $\text{M}=\text{Si}$ and $\text{M}=\text{Ge}$ in $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{M}_x\text{O}_4)_3$ indicates that the compounds with $x=0.17$ and 1.0 in the system $\text{M}=\text{Ge}$ have rhombohedral structure being similar to $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$, respectively. These replacements of P ($x=0.17$) and Si ($x=1.0$) by Ge caused the shifts of the diffraction lines to lower angles of diffraction owing to the increase of ion radius from 0.31 Å for P^{5+} ion or 0.40 Å for Si^{4+} ion to 0.53 Å for Ge^{4+} ion. However, the phases produced in the compositions $x=0.33$, 0.50 and 0.67 in the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ differ from those for $x=0$, 0.67 and 1.0 in the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$. Although free ZrO_2 was not detected in these compositions, the composition $x=0.33$ contained the phase being similar to $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and unidentified phase(s). The structures of these unknown phases will be analyzed in detail.

All the green compacts were sintered at 1000°–1100°C. The sample with composition $x=0.67$ melted completely at 1100°C, i.e. lower by 200°C than the lowest temperature where complete melting of nasicon has been observed³⁾. Composition dependence of the sintered density reflected mainly the variation in the density of green compact with composition. Little densification occurred in the composition $x=0$, whereas the densities in the compositions above $x=$

0.33 increased abruptly when the firing temperature was elevated from 1050° to 1070°C. This densification behavior in the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ may be related to the formation of glass or liquid phase containing GeO_2 . Incidentally the lowest eutectic temperature of the system $\text{P}_2\text{O}_5\text{--GeO}_2$, $\text{Na}_2\text{O--P}_2\text{O}_5$ and $\text{Na}_2\text{O--GeO}_2$ are 955°, 552° and 790°C, respectively⁶⁾. Densities of samples sintered at 1070°–1090°C were 2.36 ± 0.01 g/cm³ for $x=0$, 3.08 ± 0.01 g/cm³ for $x=0.17$, 3.41 ± 0.01 g/cm³ for $x=0.33$, 3.73 ± 0.04 g/cm³ for $x=0.50$, 3.59 ± 0.03 g/cm³ for $x=0.67$, and 3.30 ± 0.02 g/cm³ for $x=1.0$.

3.2 Electrical conductivity**3.2.1 Electrical conductivity of $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$**

Figure 2 shows the complex impedance diagram observed for $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$ at 230°–500°C. The impedance diagram corresponds to the following equivalent circuit Z^7 ; $Z=R(\text{sample resistance})+Zp(\text{electrode impedance})=R+K(j\omega)^{-p}$, where K and p are independent of ω , $|p|<1$. Figure 3 shows the temperature dependence of the electrical conductivity for $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$, calculated from the real axis intercept by extrapolation of the impedance data to higher frequency. Arrhenius plots of σT broke in two straight lines independently of the sintered densities. Activation energies in the high-(>320°C) and low-temperature (<320°C) region were 8.7 ± 0.5 kcal/mol and 13.8 ± 0.4 kcal/mol, respectively. On the other hand, the activation energy for migration of sodium ion in sintered

Fig. 1. X-ray diffraction patterns for the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ fired at 1070°C for 4 h.

Fig. 2. Complex impedance plot for $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$ sintered at 1000°C for 4 h.

Fig. 3. Temperature dependence of electrical conductivity for $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$.

Key	Sintering		Bulk density (g/cm^3)
	Temperature	Time	
○	1000°C	4 h	3.33
●	1070°C	4 h	3.56
□	1090°C	4 h	3.62

nasicon is reported to be 4.4–7.0 kcal/mol in rhombohedral structure at temperatures above 200°C and 8.2–10.5 kcal/mol in monoclinic structure for lower temperatures^{3), 4), 8)–11)}. Replacement of Si in nasicon by Ge led to the increase in activation energy, but the similarity of temperature dependence in Arrhenius plots of σT between $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$ and $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$ suggests a possibility of phase transition in $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$. The specific resistivities of $\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$ at 300°C

Fig. 4. Comparison of temperature dependence of electrical conductivity for the two systems of $\text{M}=\text{Ge}$ and $\text{M}=\text{Si}$ in $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{M}_x\text{O}_4)_3$.

Key	M	X	Ref.
●	Ge	0.17	present work
○	Ge	0.33	present work
■	Ge	0.50	present work
▣	Ge	0.67	present work
□	Ge	1.00	present work
A	Si	0.33	9)
B	Si	0.53	9)
C	Si	0.67	8)
D	Si	0.67	9)
E	Si	0.67	4)
F	Si	0.67	11)
G	Si	1.00	9)
H	Si	1.00	4)

were 640, 670 and 720 $\Omega \cdot \text{cm}$ for the sample with density 3.62, 3.56 and 3.33 g/cm^3 , respectively. These values were higher than the resistivity of nasicon by a factor of about 100.

3.2.2 Composition dependence of electrical conductivity

Figure 4 summarizes the temperature dependence of electrical conductivity for the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ sintered at 1070°C for 4 h. Although the analysis of impedance plot by three frequency (0.12, 1 and 10 kHz) limited the possible measurement temperature range of electrical conductivity, little difference in activation energy was observed for the compositions $x=0.33$ and 0.50 (12.1-12.5 kcal/mol). These activation energies are higher than those for $x=0.67$ in the high temperature region. Comparison of the temperature dependence of electrical conductivity on the two systems of $\text{M}=\text{Ge}$ and $\text{M}=\text{Si}$ in $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{M}_x\text{O}_4)_3$ is shown in Fig. 4. The rhombohedral system $\text{M}=\text{Si}$ at temperatures above 200°C has the activation energies of 4.4-8.0 kcal/mol^[3), 4), 8)-11]. Therefore, the system $\text{M}=\text{Ge}$ showed higher activation energy and lower electrical conductivity as compared with the system $\text{M}=\text{Si}$. Only at the composition $x=1$, the electrical conductivity of the system $\text{M}=\text{Ge}$ at 500°C was very close to the extrapolated conductivity^[4), 9] of the system $\text{M}=\text{Si}$.

4. Conclusion

The compositions $x=0.17$ and 1.0 in the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ at temperatures

below 1100°C gave rhombohedral structure being similar to $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$, respectively. The structure of the composition $x=0.67$ ($\text{Na}_3\text{Zr}_2\text{PGe}_2\text{O}_{12}$) differs from that of nasicon ($\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$). The system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Ge}_x\text{O}_4)_3$ showed higher activation energy and lower electrical conductivity as compared with the system $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$.

Acknowledgement This work was supported by the Scientific Research Aid from the Ministry of Education (No. 57750690).

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