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Substitution Effect of Framework Constituents on Electrical Property of Solid Electrolytes with β-$Fe_2(SO_4)_3$-Type Structure, $M_{1+X}Zr_2P_{3-X}Si_XO_{12}$ (M = Li, 1/2Mg, and 1/2Zn)

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An enhancement of electric conductivity was observed by substitution of Si^{4+} for P^{5+} in $LiZr_2(PO_4)_3$, $MgZr_4(PO_4)_6$, and $ZnZr_4(PO_4)_6$ solid electrolytes with a β-$Fe_2(SO_4)_3$-type structure. An increase in the concentration of interstitial Li^+ ion resulted in the conductivity enhancement for the Li compound, whereas an increase in the compactness of sintered specimen for the Mg and Zn compounds.

The electric conductivity (σ) of solid electrolytes can be expressed by the product of the concentration of charge carriers (n), the electric charge (q), and the mobility (μ). If these quantities are increased by some way, the conductivity can be increased. Thus far many super-ionic-conductors with a NASICON-type structure have been reported.[1-3] $Na_3Zr_2PSi_2O_{12}$ is one of the most familiar compounds with this type of structure; this compound has been prepared by substitution of $Na^+ + Si^{4+}$ for P^{5+} in $NaZr_2(PO_4)_3$ [1] which increases the concentration of charge carriers (n). We could obtain only a few ionic conductors with a β-$Fe_2(SO_4)_3$-type structure,[4,5] as compared with those with the NASICON-type one. Furthermore, there has been no reports on the Si^{4+}-substituted compounds of zirconium phosphate framework with this type of structure, e.g. $LiZr_2(PO_4)_3$ [6] and $MgZr_4(PO_4)_6$,[7] having a relatively high conductivity.

In the present study, following systems have been investigated in order to obtain high-conductive solid electrolytes with the β-$Fe_2(SO_4)_3$-type structure; $Li_{1+X}Zr_2P_{3-X}Si_XO_{12}$ (LIZRPSIO) ($0 \leqq X \leqq 0.5$), $Mg_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (MGZRPSIO) ($0 \leqq X \leqq 0.5$), and $Zn_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (ZNZRPSIO) ($0 \leqq X \leqq 0.5$). These compounds are characteristic in that mobile cations have almost the same ionic radius of 0.9 Å [8] but different valence and polarizability.

Sample powder was prepared from reagent grade $ZrOCl_2 \cdot 8H_2O$, $Si(OEt)_4$, $NH_4H_2PO_4$, and $LiNO_3$ (or $Mg(NO_3)_2 \cdot 6H_2O$, or $Zn(NO_3)_2 \cdot 6H_2O$) by using the sol-gel method.[7] The powder obtained was pressed uniaxially under 9.8 MPa and then hydrostatically under 620 MPa to form a tablet. The resulting tablet for LIZRPSIO was sintered at 900 °C for 6 - 24 h in air. (Pure phase with the β-$Fe_2(SO_4)_3$-type structure could not be obtained by sintering at a temperature higher than 900 °C.[6]) The tablets of MGZRPSIO and ZNZRPSIO were sintered at 900 - 1200 °C for 6 - 24 h in air. Sample impedance was measured by an ac method from 100 to 900 °C in a frequency range of 0.2 Hz to 2 MHz in air or flowing Ar of 100 cm^3 s^{-1} using Pt electrodes. Powder X-ray diffraction (XRD) analysis was performed by using Cu-Kα radiation. Lattice constants were determined with α-Al_2O_3 powder as an internal standard.

The lattice constants versus X values for the LIZRPSIO (sintered at 900 °C for 6 h), MGZRPSIO (1200 °C for 6 h), and ZNZRPSIO (1200 °C for 6 h) systems are plotted in Fig. 1. The lattice constants of the LIZRPSIO system increase linearly up to X = 0.3 with the Si^{4+} substitution. In this system no peaks of second phase were observed for $0 \leqq X \leqq 0.5$ with XRD. These results indicate that Si^{4+} can be substituted for P^{5+} within $X \leqq 0.3$ in the LIZRPSIO system.

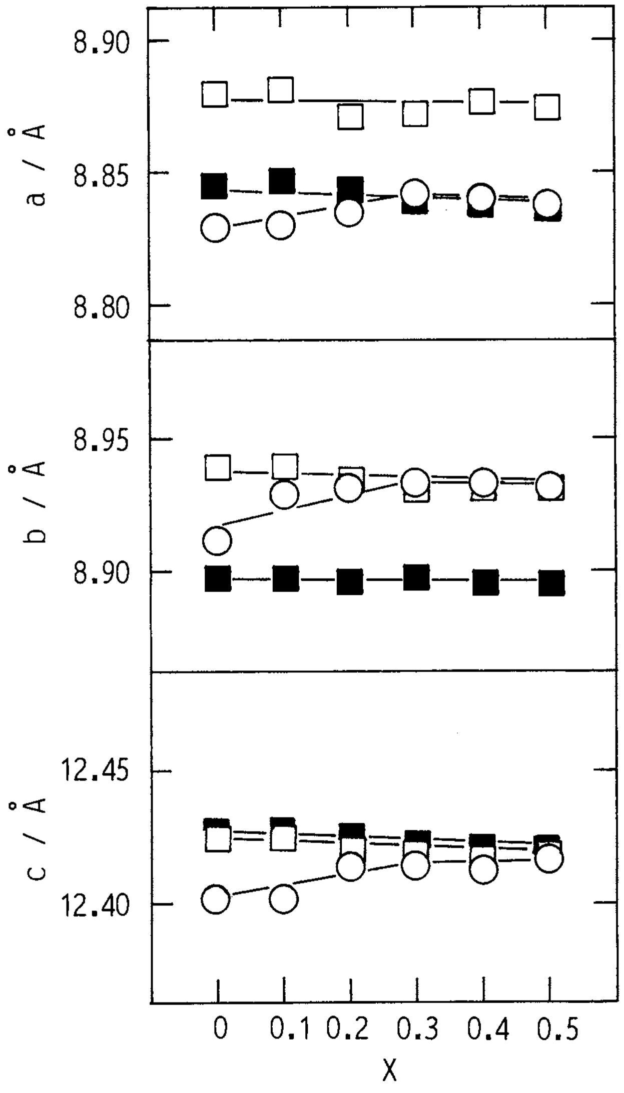

Fig. 1. Lattice constants in relation to X for $Li_{1+X}Zr_2P_{3-X}Si_XO_{12}$ (○), $Mg_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (■), and $Zn_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (□).

On the other hand, the lattice constants in the MGZRPSIO and the ZNZRPSIO systems did not change with the increase of X. The second phase of $Zr_2O(PO_4)_2$ was found for these two systems of $0.1 \leqq X$ with XRD, and the peak intensity increased with the Si^{4+} substitution. Hence, it is inferred that the introduced Mg^{2+} (or Zn^{2+}) ion in the MGZRPSIO (or ZNZRPSIO) system cannot occupy the interstitial site of the β-$Fe_2(SO_4)_3$-type structure. The Mg^{2+} (or Zn^{2+}) ions having higher charge density are expected to cause larger repulsive force between the guest cations, which hinders further incorporation of the guest cations into the framework structure.

The relative density (observed to theoretical, the latter being calculated from the XRD data) of sintered pellets as a function of X for the LIZRPSIO (sintered at 900 °C for 6 h), MGZRPSIO (1200 °C for 6 h), and ZNZRPSIO (1200 °C for 6 h) are shown in Fig. 2. Zirconium phosphate compounds (X = 0.0) showed the lowest relative density for all the systems. The relative density increased with the Si^{4+} substitution; a slight increase was observed in the range of $0 \leqq X \leqq 0.3$ for LIZRPSIO, whereas a considerable increase was noticed for MGZRPSIO and ZNZRPSIO. Higher values of the relative density in MGZRPSIO and ZNZRPSIO can be attributed to their higher sintering temperature and the presence of the second phase.

Figure 3 depicts the total conductivity as a function of X (Si^{4+} substitution) for LIZRPSIO, MGZRPSIO, and ZNZRPSIO at 530 °C. Less than two semi-circles were observed in complex impedance plots for all the compounds; the high frequency one passing almost the origin was assigned to the impedance of solid electrolytes (bulk plus grain boundary) and the low frequency one to that of electrode-solid electrolyte interface.

The conductivity of LIZRPSIO system slightly increased with X and showed the maximum value of 3.3×10^{-2} S cm^{-1} at X of 0.2. Furthermore, the lowering of an apparent activation energy for conduction was observed with Si^{4+} substitution in the LIZRPSIO system for $0 \leqq X \leqq 0.3$. This result also supports the Si^{4+} substitution for P^{5+} in the LIZRPSIO system.

On the other hand, the conductivity of MGZRPSIO and ZNZRPSIO greatly increased by introducing

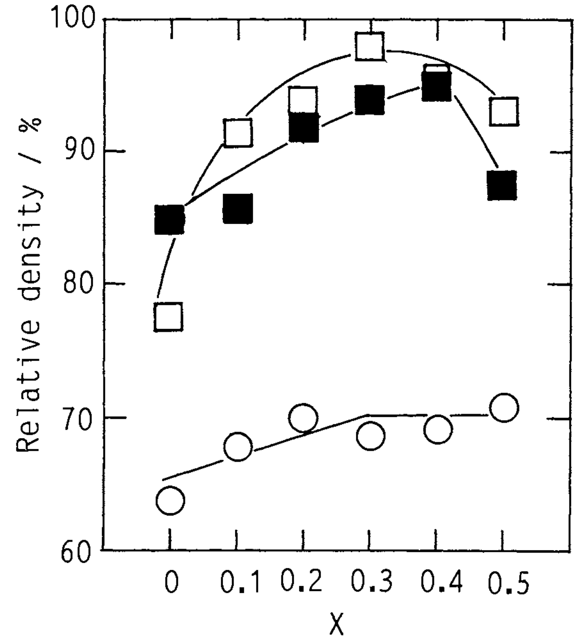

Fig. 2. Relative density in relation to X for $Li_{1+X}Zr_2P_{3-X}Si_XO_{12}$ (○), $Mg_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (■), and $Zn_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (□).

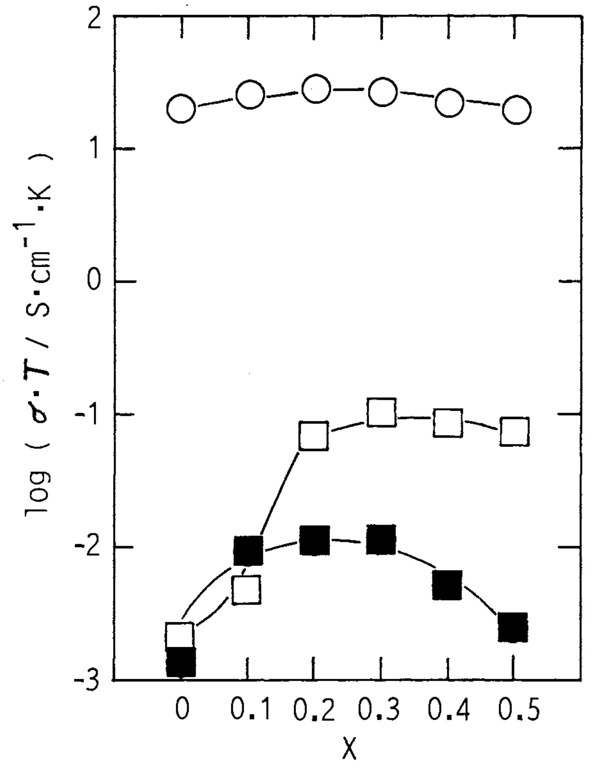

Fig. 3. Total conductivity in relation to X for $Li_{1+X}Zr_2P_{3-X}Si_XO_{12}$ (○), $Mg_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (■), and $Zn_{1+X/2}Zr_4P_{6-X}Si_XO_{24}$ (□) at 530 °C.

Si^{4+} in place of P^{5+} (about one and two orders of magnitude for the Mg and Zn compounds, respectively) and showed the best conductivities of 1.4×10^{-5} and 1.2×10^{-4} S cm^{-1} for the Mg and Zn compounds, respectively, at X of 0.3. These two conductivity changes with X are not in agreement with the variations of their lattice constants (cf. Fig. 1) but do almost with those of their densities (cf. Fig. 2). The higher polarizability of Zn^{2+} may be responsible for the higher conductivity of ZNZRPSIO than that of MGZRPSIO. A similar conductivity enhancement by Li^{+} + M^{3+} for Ti^{4+} has been reported on $Li_{1+X}M_{X}Ti_{2-X}(PO_4)_3$ (M = trivalent cation) systems.[9]

In conclusion, a conductivity enhancement was attained by Si^{4+} substitution in the LIZRPSIO, MGZRPSIO, and ZNZRPSIO systems; the enhancement is expected to be caused by an increase in the interstitial cationic concentration for the LIZRPSIO system but in the compactness of sintered specimens for the MGZRPSIO and ZNZRPSIO systems.

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