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Effects of Al_2O_3 addition on the sinterability and ionic conductivity of nasicon

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The effects Al_2O_3 doping on the sintering behaviour and ionic conductivity of nasicon have been investigated using formulations of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ where Al^{3+} ions were substituted to P^{5+} sites within the range $0 \leqslant x \leqslant 0.2$. The density of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ was increased with increasing amount of Al_2O_3 doping due to the enhanced liquid-phase sintering. The relative density of $Na_{3.4}Zr_2Si_2Al_{0.2}P_{0.8}O_{12}$ reached a maximum value of 96% when sintered at 1200 °C for more than 7 h. The maximum conductivity of 0.24 Ω^{-1} cm^{-1} at 300 °C was obtained for the composition with $x = 0.1$ when sintered at 1200 °C for 10 h.

1. Introduction

Superionic conductors, which possess high ionic conductivity and very low electronic conductivity, have been widely investigated for use in energy storage or conversion systems, and microionic devices such as electrochemical sensors and electrochromic displays [1–3]. In recent years, investigations have been focused on nasicon ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 \leqslant x \leqslant 3$), due to its lower sintering temperature and three-dimensional conductivity, to replace Na-β-alumina which is a potential candidate for a solid electrolyte in Na/S secondary batteries [1–8]. However, phase transformation in the temperature range 200 to 300 °C and poor densification of nasicon may be detrimental to the stability of nasicon as a solid electrolyte in Na/S batteries [2, 9].

Al_2O_3 doping has been reported to enhance the densification of $Na_3Zr_2Si_2PO_{12}$ and $Na_5YSi_4O_{12}$ ceramics at lower sintering temperatures [2, 10]. The ionic conductivity of various solid electrolytes, such as CaF_2 and $Na_5YSi_4O_{12}$, could be improved with Al_2O_3 addition either by the formation of highly conducting paths at the phase boundaries, or by forming a solid solution and modifying the crystal structure [10, 11]. Addition of sodium aluminosilicates to $Na_3Zr_2Si_2PO_{12}$ also increases the conductivity of $Na_3Zr_2Si_2PO_{12}$, although sodium aluminosilicate glass has a much lower conductivity [12].

In this study, the effects of Al_2O_3 doping on the sintering behaviour and ionic conductivity of nasicon have been investigated using formulations of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ where Al^{3+} ions were substituted to P^{5+} sites within the range $0 \leqslant x \leqslant 0.2$.

2. Experimental procedure

The starting powders were reagent-grade Na_2CO_3, $Na_3PO_4 \cdot 12H_2O$, ZrO_2, SiO_2 and Al_2O_3. After drying each powder at 300 °C for 2 h, formulations of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$, $0 \leqslant x \leqslant 0.2$, were weighed and mixed with ethanol in a polyethylene jar using zirconia balls for 16 h. The mixed powder was calcined at 1150 °C for 10 h with heating and cooling rates of 4 °C min^{-1}. The calcined powder was then ball-milled using ethanol and zirconia balls for 16 h and dried. The powder was uniaxially pressed at 100 kg cm^{-2} to form pellets and then isostatically cold pressed at 1500 kg cm^{-2} in a rubber mould. Sintering was conducted in an α-alumina crucible at 1150 or 1200 °C for 1 to 10 h at heating and cooling rates of 4 °C min^{-1}.

Sintered pellets were shaped to 7 mm × 2 mm × 30 mm, polished, and four electrodes of 4 mm × 1 mm were formed by screen-printing of Pt paste on bar-type samples and annealing at 1000 °C for 5 min. Ionic conductivity was measured at 300 °C using the a.c. four-point probe complex impedance method. The densities of sintered samples were measured by the Archimedes method using isobutyl alcohol. Crystalline phases were characterized by X-ray diffraction (XRD) on ground powder of sintered samples, and microstructure was observed using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Sintering behaviour

Fig. 1 shows the relative density of sintered $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics as a function of Al_2O_3 addition. The relative density of sintered samples was calculated by taking 3.27 g cm^{-3}, which is the theoretical density of $Na_3Zr_2Si_2PO_{12}$, as the theoretical value of all compositions. The density of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ was increased with increasing sintering temperature and time. For each sintering condition, more densification could be obtained with higher Al_2O_3 doping due to the enhanced liquid-phase sintering [1, 7]. As shown in Fig. 2, the relative density of $Na_{3.4}Zr_2Si_2Al_{0.2}P_{0.8}O_{12}$ reached a maximum value

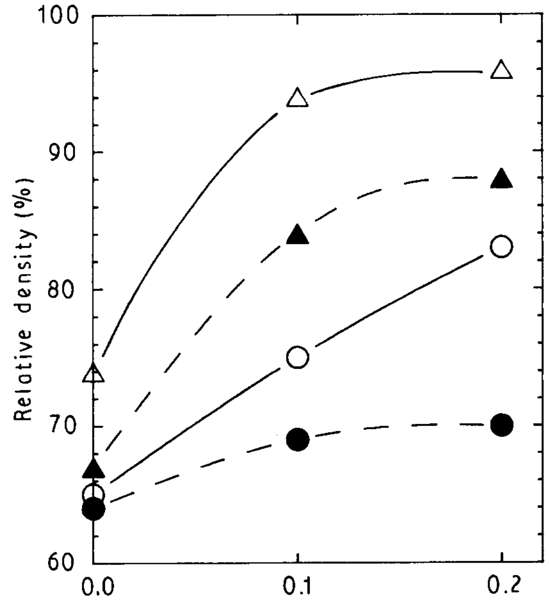

Figure 1 Relative density of sintered $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics as a function of Al_2O_3 doping: (●) 1150 °C/1 h, (○) 1200 °C/1 h, (▲) 1150 °C/10 h, (△) 1200 °C/10 h.

of 96% when sintered at 1200 °C for more than 7 h. The weight loss due to the vaporization of Na and P during sintering was proportional to the sintering time, and was about 2.4% for 7 h sintering.

Al_2O_3 doping to various solid electrolytes, such as nasicon, titzicon and $Na_5YSi_4O_{12}$, is known to enhance the densification at lower sintering temperature [2, 10] and increase the amount of glass phase [1]. The sintering temperature for a relative density of 96% can be lowered to 1050 °C by Al_2O_3 doping for gel-processed nasicon [2, 3]. When processed by the conventional mixed oxide method used in this study, however, the relative density of 96% was obtained only by sintering at 1200 °C for more than 7 h (Fig. 1). This discrepancy of the sintering behaviour with processing methods may be due to the inhomogeneity of the composition for the mixed oxide method [1, 6–8].

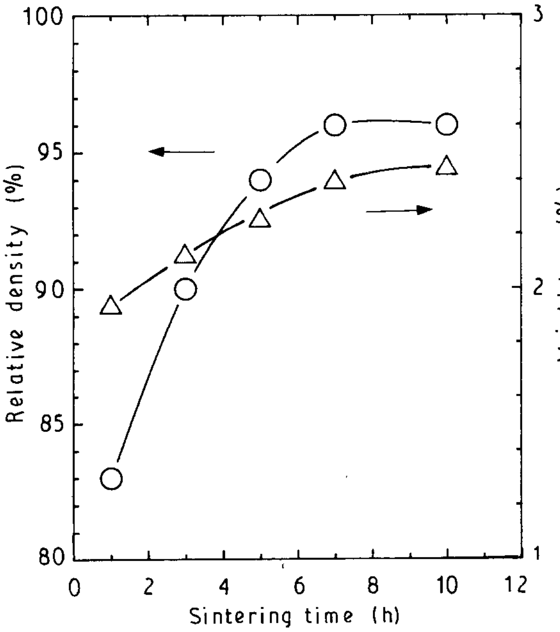

Figure 2 Relative density (○) and weight loss (△) of $Na_{3.4}Zr_2Si_2Al_{0.2}P_{0.8}O_{12}$ ceramics as a function of sintering time at 1200 °C.

Decomposition of nasicon to monoclinic ZrO_2 and glass phase has been found to be accelerated by sintering at higher temperatures [7, 8]. Thus, the precipitation of monoclinic ZrO_2 was suppressed by Al_2O_3 doping of gel-processed nasicon which could be fully densified at 1050 °C [2]. As shown for XRD analysis in Fig. 3, however, $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics, sintered at 1150 or 1200 °C, contain monoclinic ZrO_2 even with Al_2O_3 doping.

3.2. Microstructure

Fig. 4 illustrates the microstructural evolution of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics sintered at 1200 °C for 10 h. For the compositions with $x = 0.1$ and 0.2, the microstructure was composed of nasicon (grey phase), monoclinic ZrO_2 (light phase) and glass phase (dark phase). Although the presence of monoclinic ZrO_2 was detected by XRD analysis for all compositions (Fig. 3), ZrO_2 phase could hardly be observed for $Na_3Zr_2Si_2PO_{12}$. With higher Al_2O_3 doping, more ZrO_2 and glass phase were formed, which may be attributed to the accelerated decomposition of nasicon phase with Al_2O_3 addition [1]. As confirmed by energy-dispersive X-ray analysis, most of the Al_2O_3 doping to nasicon was present in the glass phase, which enhanced liquid-phase sintering with higher Al_2O_3 addition [1, 7].

As shown in Fig. 4c and Fig. 5, the nasicon phase of $Na_{3.4}Zr_2Si_2Al_{0.2}P_{0.8}O_{12}$ ceramic was decomposed to

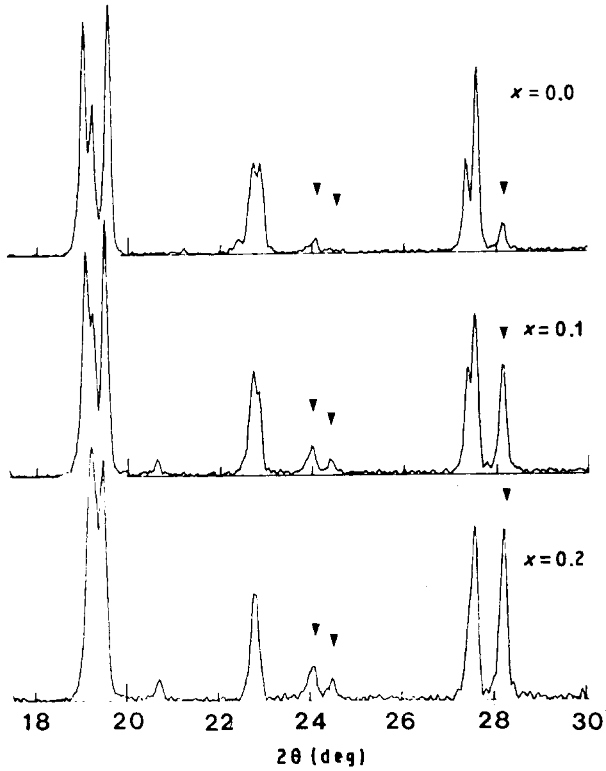

Figure 3 XRD patterns of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics, for $x = 0$, 0.1 and 0.2, sintered at 1200 °C for 10 h. Triangles indicate monoclinic ZrO_2 peaks.

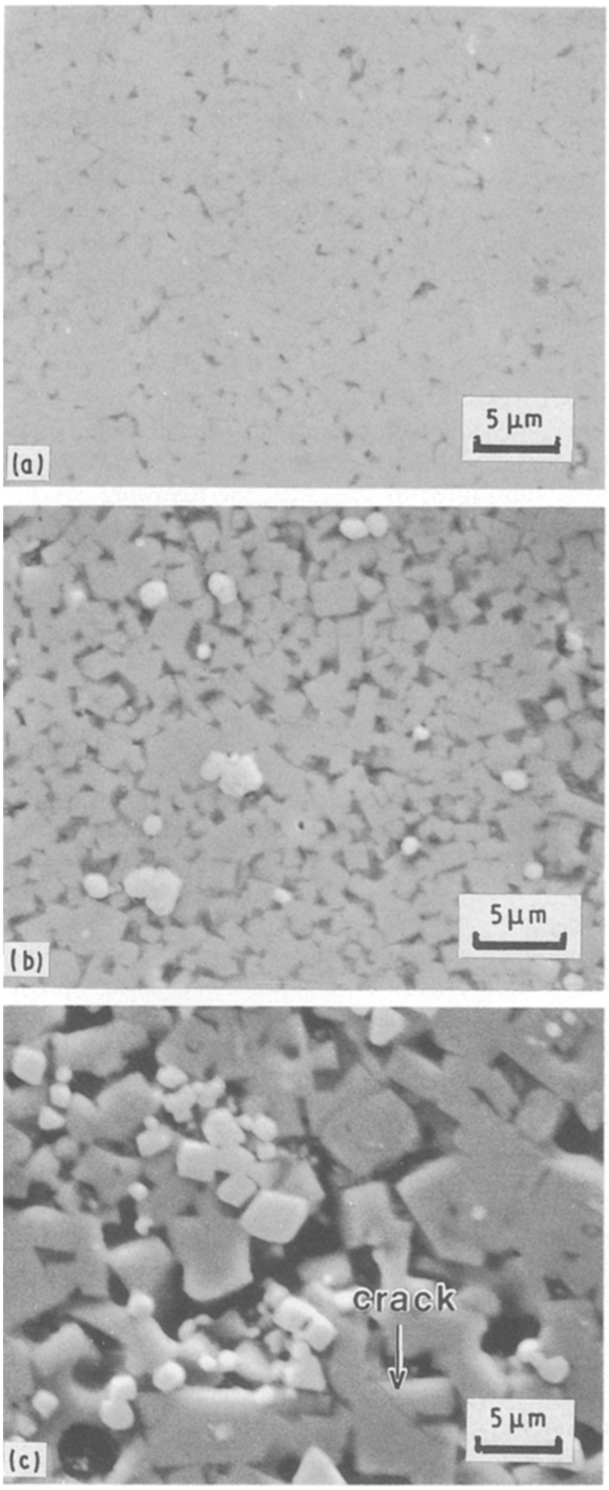

Figure 4 SEM micrographs of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics, sintered at 1200 °C for 10 h, for composition of (a) $x = 0$, (b) $x = 0.1$ and (c) $x = 0.2$.

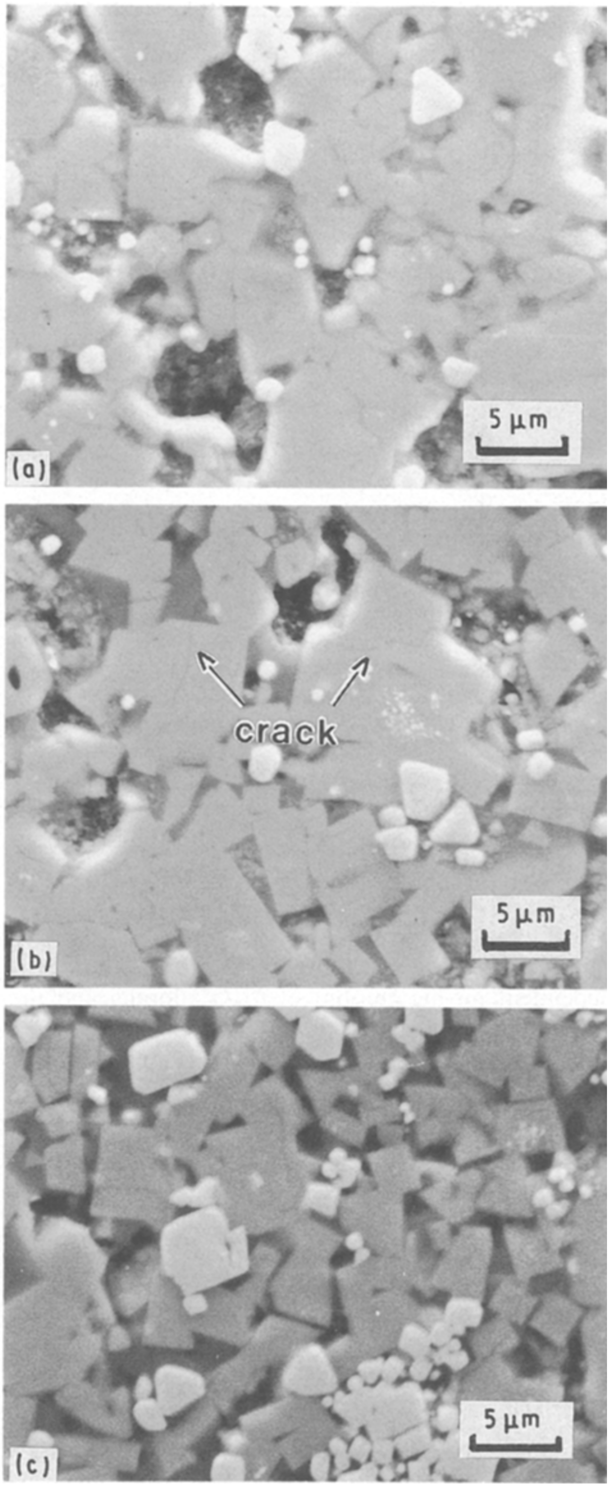

Figure 5 SEM micrographs of $Na_{3.4}Zr_2Si_2Al_{0.2}P_{0.8}O_{12}$ ceramics sintered at 1200 °C for (a) 1 h, (b) 5 h and (c) 7 h.

glass and ZrO_2, and the grain size of nasicon became smaller with longer sintering time at 1200 °C. The glass phase of nasicon is very unstable in water and is rapidly degraded [1, 7]. When the glass phase contains Al_2O_3, furthermore, the reactivity of nasicon with water has been reported to be increased by about four orders of magnitude. To achieve high density and the environmental stability of $Na_{3.4}Zr_2Si_2Al_{0.2}P_{0.8}O_{12}$ ceramics, it can thus be concluded that the dissociation of nasicon to monoclinic ZrO_2 and glass phase should be minimized by taking a shorter sintering time such as 7 h at maximum density.

3.3. Ionic conductivity

It has been reported that Al^{3+} substitution to Si^{4+} sites weakly decreases the conductivity of gel-processed nasicon and lithium-containing solid electrolytes or does not change the value for titzicon [2]. The densification of Al_2O_3-doped nasicon was enhanced

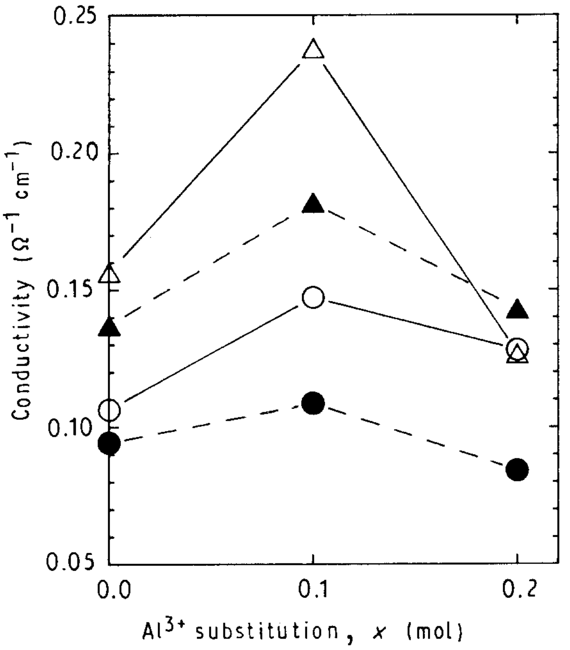

Figure. 6 Ionic conductivity of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics, sintered under various conditions, as a function of Al_2O_3 doping: (●) 1150 °C/1 h, (○) 1200 °C/1 h, (▲) 1150 °C/10 h, (△) 1200 °C/10 h.

with higher Al_2O_3 doping (Fig. 1) and the ionic conductivity of solid electrolytes is generally increased with higher density [10, 13, 14]. When Al^{3+} ions were substituted to P^{5+} sites of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics in this study, however, the conductivity was dependent on the amount of Al_2O_3 doping and the maximum conductivity of 0.24 Ω^{-1} cm^{-1} at 300 °C was obtained with 0.1 mol of Al^{3+} substitution as shown in Fig. 6.

As illustrated by the variation of X-ray peaks at 2θ values of 18–20° and 26–28° in Fig. 3, the crystal structure of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics was gradually changed from monoclinic phase with $x = 0$ to rhombohedral structure at $x = 0.2$ by a higher degree of tetrahedral disorder with the incorporation of Al^{3+} ions into the nasicon framework [2, 13–15]. Such structural change of nasicon with Al_2O_3 doping has also been observed when Al^{3+} ions are substituted to Si^{4+} sites in nasicon, titzicon and lithium-containing solid electrolytes [2]. As the conductivity increases of $Na_{5+x}YAl_xSi_{4-x}O_{12}$ with Al^{3+} substitution up to 0.1 mol [10], the modification of the nasicon framework by the presence of Al^{3+} ions may enhance the mobility of Na^+ ions. Also additional Na^+ ions were brought into the nasicon structure for charge balance with the substitution of Al^{3+} ions to P^{5+} sites [2, 10], which might explain the conductivity increase of nasicon with Al_2O_3 doping up to 0.1 mol.

The ionic conductivity of the $x = 0.2$ composition was lower than the value for the $x = 0.1$ composition without depending on the sintering condition (Fig. 6). As shown in the microstructure (Figs 4 and 5), such a reduction in the ionic conductivity could be attributed to the large amount of ZrO_2 precipitation for the $x = 0.2$ composition, which increased the intergrain resistance [16], and the associated cracking of nasicon grains due to volume expansion during the tetragonal–monoclinic transformation of ZrO_2 particles [1].

Although the composition with $x = 0.2$ has a lower conductivity than the value for the $x = 0.1$ composition, its conductivity (comparable to the value for $Na_3Zr_2Si_2PO_{12}$), high density and rhombohedral structure at room temperature may be advantageous for real application as a solid electrolyte in Na/S secondary batteries, by eliminating the thermal stress problem during phase transformation of nasicon [9].

4. Conclusions

Based on a study of the sintering behaviour and ionic conductivity of Al_2O_3-doped nasicon where Al^{3+} ions were substituted to P^{5+} sites, the following conclusions can be drawn:

1. The sintered density of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$, $0 \leqslant x \leqslant 0.2$, was increased with increasing amount of Al_2O_3 doping due to the enhanced liquid-phase sintering with higher Al_2O_3 addition. The relative density of $Na_{3.4}Zr_2Si_2Al_{0.2}P_{0.8}O_{12}$ reached a maximum value of 96% when sintered at 1200 °C for more than 7 h.
2. In contrast with gel-processed nasicon, where the precipitation of monoclinic ZrO_2 was suppressed by Al_2O_3 doping, the microstructure of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics was composed of nasicon, monoclinic ZrO_2 and glass phase. The amount of ZrO_2 and glass phase was increased with higher Al_2O_3 doping due to the accelerated decomposition of nasicon phase with Al_2O_3 addition. The room-temperature structure of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics was changed from monoclinic to rhombohedral phase for the $x = 0.2$ composition.
3. Although the densification of $Na_{3+2x}Zr_2Si_2Al_xP_{1-x}O_{12}$ ceramics was enhanced with higher Al_2O_3 addition, the maximum conductivity of 0.24 Ω^{-1} cm^{-1} at 300 °C was obtained for the composition with $x = 0.1$ by sintering at 1200 °C for 10 h.

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