

Proton conduction in the system of $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ perovskite oxides

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The phase formation and proton conduction in a BaO doped LaScO_3 with the perovskite structure were studied. $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ was analyzed as a single cubic phase and $\text{La}_{0.9}\text{Ba}_{0.1}\text{ScO}_{3-\delta}$, $\text{La}_{0.8}\text{Ba}_{0.2}\text{ScO}_{3-\delta}$ and $\text{La}_{0.7}\text{Ba}_{0.3}\text{ScO}_{3-\delta}$ were analyzed to consist of two cubic and orthorhombic phases. Below 300°C, all compositions were found to be pure proton conductors in the presence of water vapor. The bulk conductivity of $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ was higher than that of any other composition.

Key words: proton conduction, BaO doped LaScO_3 , perovskite structure, bulk conductivity.

Introduction

Since the discovery of proton conduction in rare earth ions doped SrCeO_3 by Iwahara *et al.* [1], a considerable number of studies of proton conduction in perovskite or its related structures have been reported. Acceptor doped alkali earth cerates and zirconates, which were classified as high temperature proton conductors, exhibited high proton conductivity under water vapor [2, 3]. On the other hand, some studies showed that acceptor doped $\text{LaMO}_{3-\delta}$ compounds (M=Al, Ga, Sc, In, and rare earth ions) of perovskite-related structure were also ionic conductors of protons and oxygen ions [4-7]. Among these materials, oxygen ion conductivity of doped LaAlO_3 with an orthorhombic structure was first studied, but it had too low conductivity to be applicable [4]. Sr^{2+} and Mg^{2+} ions doped LaGaO_3 perovskites exhibited high oxygen ion conductivity at intermediate temperatures [5], so that the application of these materials as electrolytes for reduced-temperature ceramic fuel cell is expected. For Sr^{2+} ion doped LaInO_3 with an orthorhombic structure, p-type and n-type conduction were observed in oxidizing and reducing atmospheres, respectively, and ionic conduction became dominant in the intermediate oxygen partial pressure range [6]. Proton conduction was detected in Sr^{2+} ion doped LaYO_3 below 550°C [7].

A recent investigation into Sr^{2+} and Mg^{2+} ion doped LaScO_3 demonstrated that this material was a mixed conductor of oxygen ion and proton in low oxygen partial pressures; proton conduction was dominant at temperatures below 700°C while above 800°C oxygen ion conduction became increasingly dominant with

temperature [8]. However, most studies of doped LaScO_3 have concentrated on Sr^{2+} ion or Ca^{2+} ion doped compositions showing an orthorhombic structure [8-12]. In this study, the Ba^{2+} ion was selected as the dopant material on the La site so that the phase formation and the electrical conductivity of the compositions $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ could be investigated.

Experimental procedure

10~40 at% BaO doped LaScO_3 compositions, $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$, were prepared by a solid-state reaction method. Commercial La_2O_3 (purity 99.9%), Sc_2O_3 (99.9%) and BaCO_3 (99.95%) powders were used as the starting materials. La_2O_3 and Sc_2O_3 powders were calcined in air at 1100°C for 1 h to remove the absorbed moisture. BaCO_3 powder was heated in a dry oven at 200°C for 24 h to remove the water adsorbed on the powder surface. Powders were weighed in the proper ratio of the required compositions and well mixed in a mortar for two hours. The mixture was pressed into discs before being heated at 1500°C for 5 h in air. The heat-treated discs were crushed and ground into powder in the same mortar. The process of heat treatment and grinding was conducted three times for homogenization of the final samples. The resulting powder was pressed uniaxially into disc-type specimens and pressed isostatically at ca. 138 MPa. The specimens were then finally sintered at 1600°C for 10 h in air and cooled down to room temperature at a rate of 10 Kmin⁻¹. The phase analysis of the sintered specimen was carried out by a powder X-ray diffraction method using a Rigaku Denki D/MAX RINT 2000 diffractometer with Cu K α radiation. To avoid the effect of water vapor incorporation into the specimen from the surrounding air, the powder X-ray diffraction analysis was also carried out for the same as-sintered specimen at room temperature in N₂ atmosphere immediately after cooling the speci-

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men which had been heated at 600°C for 2h in the high temperature attachment of an X-ray diffractometer. The electrical conductivity of the specimens was measured in a tube-type furnace by a conventional a.c. two-probe method with the disc-type specimen coated with platinum(Pt) and with gold(Au) paste as the electrodes. The impedance data obtained by a Hewlett Packard 4284A LCR (inductance-capacitance-resistance) meter were analyzed to estimate the contributions of the bulk, the grain-boundary and the electrode to the total conductivity. The water vapor pressure of the carrier gas was controlled to observe the effect of water vapor on the conductivity; wet N_2 refers to N_2 carrier gas passed through a water bath of $p_{\text{H}_2\text{O}}=6.1$ hPa.

Results and Discussion

Typical X-ray diffraction patterns for the LaScO_3 compositions doped with 10~40 at% Ba^{2+} on La sites are shown in Fig. 1. As shown in this figure, the secondary phases were not detected in all compositions. $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{3-\delta}$ was considered to be a single cubic phase because no peaks for secondary or other structural phases were detected. $\text{La}_{0.9}\text{Ba}_{0.1}\text{ScO}_{3-\delta}$, $\text{La}_{0.8}\text{Ba}_{0.2}\text{ScO}_{3-\delta}$ and $\text{La}_{0.7}\text{Ba}_{0.3}\text{ScO}_{3-\delta}$ were considered to consist of two cubic and orthorhombic phases because all the detected peaks were in good agreement with cubic and orthorhombic peaks.

These results could be explained in terms of a tolerance factor:

$$\text{tolerance factor} = \frac{(r_A + r_O)}{\sqrt{2}(r_A + r_O)}$$

where r_A , r_B and r_O are the ionic radii of the A-site

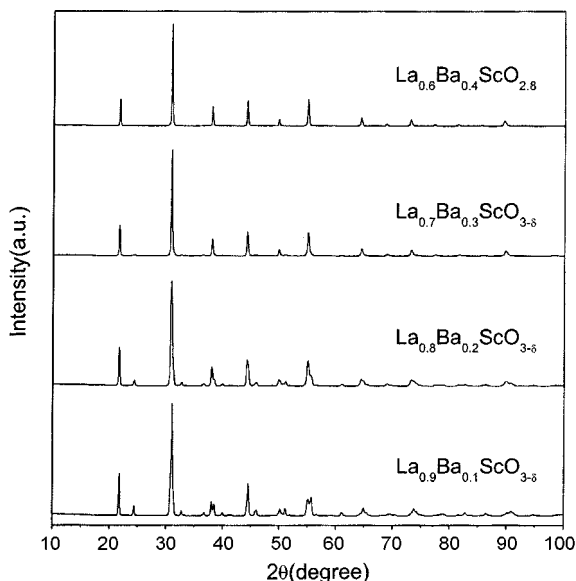
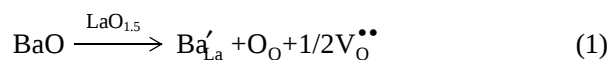


Fig. 1. Powder X-ray diffraction patterns of $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ sintered at 1600°C for 10h.

cation, B-site cation and oxygen ion, respectively. When this factor is close to 1, the perovskite structure becomes more symmetric. As the proportion of the large Ba^{2+} ion ($r_{\text{Ba}}=1.61\text{\AA}$, coordination number(C.N.)=12) doped on the La site ($r_{\text{La}}=1.36\text{\AA}$) in the LaScO_3 structure increases, the tolerance factor becomes closer to 1. Thus a single cubic structure was found in the compositions $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{3-\delta}$ which had a relatively large BaO content. For the composition forms a single cubic phase, $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{3-\delta}$, oxygen vacancies are considered to be formed by the doping Ba^{2+} ions on the La sites according to Eq. (1),



where is a Ba^{2+} ion on a La site. This suggestion is supported by the X-ray diffraction results that only single phase without any secondary phase was detected as shown in Fig. 1. It is, therefore, thought that doped Ba^{2+} ions were completely substituted on La sites to produce oxygen vacancies so that the oxygen vacancies produced could be incorporated by water vapor from surrounding air during the cooling process after sintering. The number of oxygen vacancies could be determined for these compositions. Thus the composition of $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{3-\delta}$ could be represented as $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$. On the other hand, $\text{La}_{0.9}\text{Ba}_{0.1}\text{ScO}_{3-\delta}$, $\text{La}_{0.8}\text{Ba}_{0.2}\text{ScO}_{3-\delta}$ and $\text{La}_{0.7}\text{Ba}_{0.3}\text{ScO}_{3-\delta}$ were in the two phases region in the phase diagram. In this region, the compositions and the proportion of cubic and orthorhombic phases might be determined by the lever rule.

Typical impedance data of $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ which were measured at 800°C and 750°C in a wet N_2 atmosphere ($p_{\text{H}_2\text{O}}=6.1$ hPa) using Pt electrodes are shown in Fig. 2. In general, the grain boundary resistance does not contribute to the total resistance at relatively high temperatures, and it is reasonable that the resistance of the grain is almost same as that of the electrolyte at these temperatures. Thus the circular arc in the high frequency region is considered to be the grain or electrolyte resistance. However the grain boundary resistance can not be ignored low temperatures. The impedance data of $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ which were measured at 200°C in a wet N_2 atmosphere ($p_{\text{H}_2\text{O}}=6.1$ hPa)

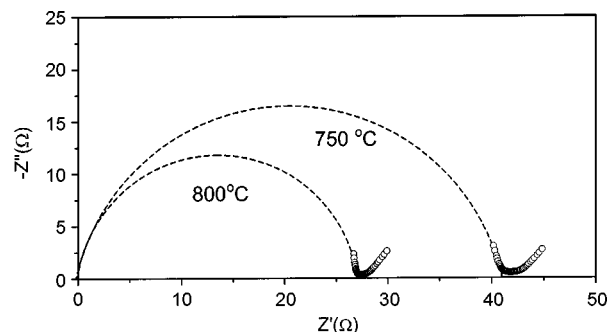


Fig. 2. Impedance data of $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ in wet N_2 atmosphere.

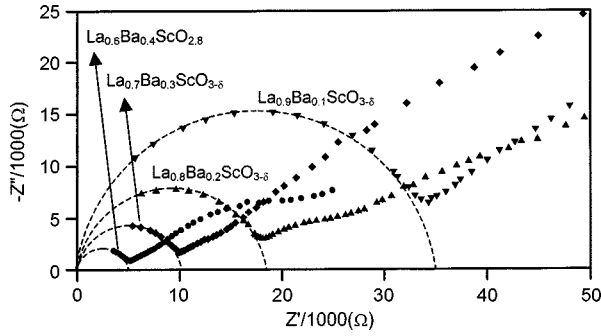


Fig. 3. Impedance data of $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ at 200°C in wet N_2 atmosphere.

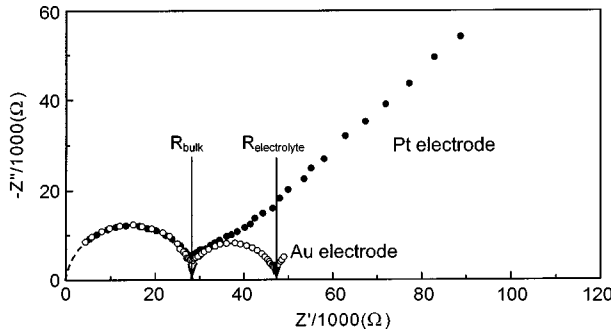


Fig. 4. Impedance data of $\text{La}_{0.7}\text{Ba}_{0.3}\text{ScO}_{3-\delta}$ at 170°C in wet N_2 atmosphere using Pt and Au electrodes.

using Pt electrodes are shown in Fig. 3. As shown in Fig. 3, it is possible to separate the bulk resistance which corresponds to the circular arc in the figure from the total resistance and this is also possible below 300°C for all compositions. However grain boundary resistance still can not be separated out in this temperature range. In the proton conduction dominant temperature range, the Pt electrodes were changed to Au electrode to separate grain and grain boundary resistances. Figure 4 shows the impedance data of $\text{La}_{0.7}\text{Ba}_{0.3}\text{ScO}_{3-\delta}$ which were measured at 170°C in a wet N_2 atmosphere using Pt and Au electrodes. The bulk resistances for Pt and Au electrodes were almost the same. The separation of the grain and grain boundary resistances from the total resistance data was possible when Au electrodes were used. The circular arc in the high frequency region may correspond to the bulk (grain) resistance and the arc in the intermediate frequency region may correspond to the grain boundary resistance. The capacitance values obtained using Eq. (2) at the minimum points in the imaginary part of the impedance data were pFcm^{-1} order for the bulk and nFcm^{-1} order for the grain boundary, respectively,

$$C = \frac{1}{2\pi fR} \quad (2)$$

where C , f , and R are the capacitance, the frequency and the resistance, respectively. The impedance data in the low frequency region with a very large capacitance

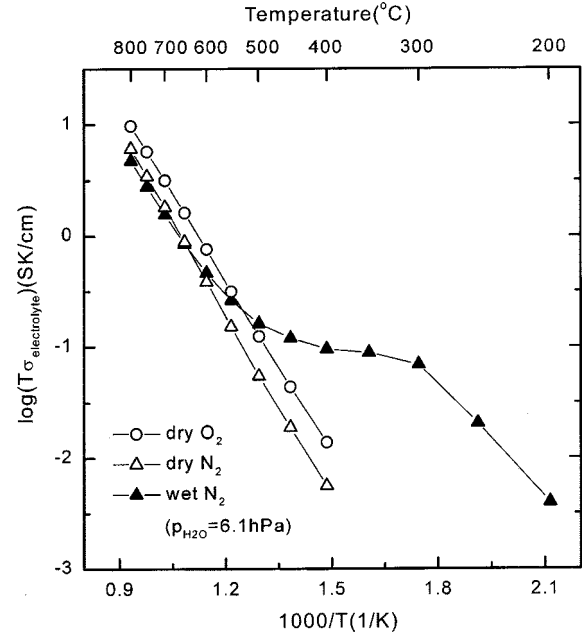


Fig. 5. Temperature dependence of electrical conductivity for $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ in dry and wet atmospheres.

value of μFcm^{-1} order might be attributed to the contribution of the electrode.

Figure 5 shows the temperature dependence of the electrical conductivity for $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ in dry and wet atmospheres. $\log(T\sigma_{\text{electrolyte}})$ was plotted against the reciprocal temperature ($1/T$). The measurements were made upon cooling from 1000°C. The conductivity data in a dry O_2 atmosphere were higher than those in a dry N_2 one over the measured temperature range, implying that p-type conduction occurred in the high oxygen partial pressure region. The conductivity data measured in a wet N_2 atmosphere decreased linearly with decreasing temperature over the temperature range from 800~650°C as did those in a dry N_2 atmosphere. However, the conductivity in a wet N_2 atmosphere showed a downward concave between 600 and 500°C. In the temperature region between 450 and 300°C, a plateau in the conductivity in a wet N_2 atmosphere was observed as shown in Fig. 5. It is clearly seen in Fig. 5 that the conductivity at 450°C in a wet N_2 atmosphere was much higher, about one order of magnitude, than that in a dry N_2 atmosphere, implying that proton conduction was dominant below this temperature. $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ might be considered as a pure proton conductor below 300°C.

It has been reported that absorbed water vapor filled the oxygen vacancies below certain temperatures, according to Eq. (3),



where $\text{V}_{\text{O}}^{\bullet\bullet}$, O_{O} and $\text{OH}_{\text{O}}^{\bullet}$ are the oxygen vacancy, oxygen ion on oxygen site and hydroxyl ion on oxygen

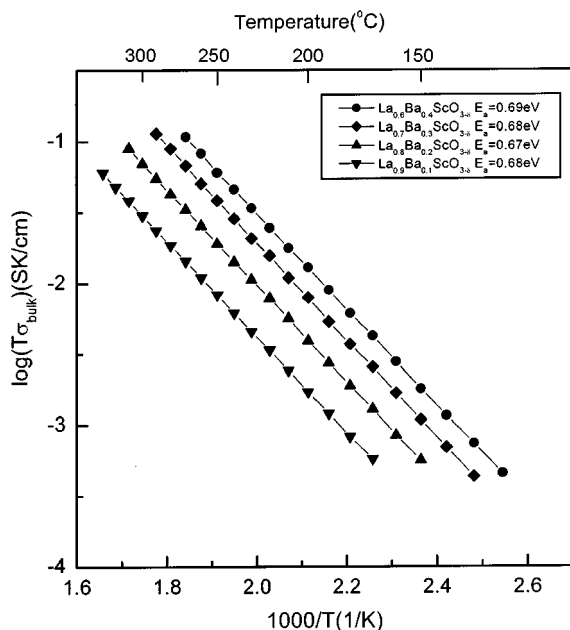


Fig. 6. Temperature dependence of bulk conductivity for $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ in wet N_2 atmosphere.

site, respectively. Proton conduction is governed by Eq. (3) and the principal features of the proton transport mechanism are rotational diffusion of the protonic defect and proton transfer towards a neighboring oxide ion [13]. In perovskite-type oxides, this proton conduction mechanism has been generally agreed.

Figure 6 shows the temperature dependence of the bulk conductivity for $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ compositions at proton-dominant temperatures in wet N_2 atmospheres. The measurements were made during a cooling process at a rate of 10 K h^{-1} . In Fig. 6, the slopes of conductivity data represent activation energies for the proton conduction for their compositions, respectively. The activation energies which were calculated from the slopes were from 0.67 to 0.69 eV for all compositions. The bulk conductivity of $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ was higher than that of any other composition.

Conclusions

The phase formation and proton conduction in BaO doped LaScO_3 with perovskite structures were studied. In the present study, the following conclusions could be

drawn.

(1) $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ was analyzed to be a single cubic phase, while $\text{La}_{0.9}\text{Ba}_{0.1}\text{ScO}_{3-\delta}$, $\text{La}_{0.8}\text{Ba}_{0.2}\text{ScO}_{3-\delta}$ and $\text{La}_{0.7}\text{Ba}_{0.3}\text{ScO}_{3-\delta}$ were analyzed to consist of two cubic and orthorhombic phases.

(2) The p-type conduction occurred in the high oxygen partial pressure region for all compositions.

(3) The dominant conduction species were oxygen ions above 600°C and protons below 450°C , respectively.

(4) Below 300°C $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-\delta}$ might be considered as a pure proton conductor.

(5) The bulk conductivity of $\text{La}_{0.6}\text{Ba}_{0.4}\text{ScO}_{2.8}$ was higher than that of any other composition.

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