# OXIDE-ION CONDUCTIVITY OF THE OXYGEN DEFICIENT PEROVSKITE SOLID-SOLUTION SYSTEM, $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ (*M*=Y OR Ga)

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## Abstract

In order to elucidate the mechanism of oxide-ion conductivity for $(Ba_{0.5-x}Sr_xLa_{0.5})(In_{1-y}M_y)_2O_{5.5}$ (*M*=Y or Ga, $0 \leq x \leq 0.2$, $0 \leq y \leq 0.2$) solid-solution system, the electrical conductivity was measured as a function of oxygen partial pressure and temperature, and the results were investigated in terms of a dopant content and unit cell free volume. The system was confirmed to be an oxide-ion conductor from the oxygen partial pressure dependence on electrical conductivity. The oxide-ion conductivity increased with increasing the unit cell free volume at first. However, it showed a maximum at a value of free volume, and then decreased. The decreasing conductivity *vs.* the volume would be related to the crystal symmetry change.

**Keywords:** crystal symmetry, oxide-ion conductivity, perovskite structure, unit cell free volume

## Introduction

Oxide-ion conductors have been studied for applications as oxygen sensors, oxygen-permeable membrane reactors, and electrolytes of solid oxide fuel cells. The operation of these devices with high efficiency requires high oxide-ion conductivity. A lot of research [1–3] has been conducted in order to discover a high oxide-ion conducting material or to elucidate the conductive mechanism.

The $Ba_2In_2O_5$ with the brownmillerite-type structure is one of the oxide-ion conductors and has an order-disorder transition associated with arrangement of oxygen vacancy around 1203 K. Above the transition, it has very high oxide-ion conductivity due to the disordering of oxide-ions, the conductivity is higher than that of yttria-stabilized zirconia [4]. Therefore, this compound has attached considerable attention. Yamamura *et al*. [5] and Yao *et al*. [6] reported that a cubic phase was obtained in the $Ba_2(In_{1-x}Ga_x)_2O_5$ system, but the electrical conductivity could not exceed that of yttria-stabilized zirconia. Kuramochi *et al*. [7] investigated the crystal

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structure and electrical conductivity of the $Ba_2In_2O_5$ system, partially substituting $Pb^{2+}$ for $Ba^{2+}$. The temperature dependence on the electrical conductivity of this system did not show a discontinuous jump and the value of the electrical conductivity was higher than that of $Ba_2In_2O_5$ in the low temperature range. Fisher *et al*. [8] investigated the electrical conductivity of the $Ba_2(In,M)_2O_5$ ($M$=Y, Yb, Sc, Ga) system and clarified the relationship between the order-disorder transition temperature and the unit cell free volume.

We have been studying the properties of the La doped $Ba_2In_2O_5$ system, and found that it is of cubic structure, where the oxygen vacancy is in disorder in wide range of temperature. The oxide-ion conductivity of this system increases with increasing temperature and reaches to 0.07 S cm$^{-1}$ at 1073 K in the case of $(Ba_{0.4}La_{0.6})_2In_2O_{5.6}$ [10]. Moreover, the Sr doped $(Ba_{1-x}La_x)_2In_2O_{5+x}$ system has higher oxide-ion conductivity with a maximum value of 0.12 S cm$^{-1}$ at 1073 K, which is higher than that of yttria stabilized zirconia [17].

In the present paper, in order to investigate the key factors for oxide-ion conductivity in this system, the electrical conductivity for $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga: $0{\leq}x{\leq}0.2$, $0{\leq}y{\leq}0.2$) solid-solution system was measured as function of oxygen partial pressure and temperature, and the results are discussed from the viewpoint of the dopant content and unit cell free volume.

## Experimental

Powder samples of the $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) system were prepared by a solid-state reaction. The starting materials, $BaCO_3$ (99.9%, Wako Chemical Co.), $SrCO_3$ (99.9%, Wako Chemical Co.), $La_2O_3$ (99.99%, Wako Chemical Co.), $Y_2O_3$ (99.99%, Kojundo Chemical Co.), $Ga_2O_3$ (99.99%, Kojundo Chemical Co.) and $In_2O_3$ (99.95%, Kojundo Chemical Co.), were mixed for 16 h using a ball mill. The mixture was dried at 373 K for several hours, and then calcined at 1273 K for 10 h. The powder, which was sieved to under 54 μm, was pressed at 4.9 MPa into a rectangular shape (30×5×5 mm) and then isostatically pressed again at 196 MPa. The samples of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ were sintered at 1673 K for 10 h in air. The samples of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}Ga_y)_2O_{5.5}$ were sintered at 1573 K for 10 h in air. The relative density of all the sintered specimens was higher than 90%, which was estimated from their dimensions and mass. The single phase of the sample was confirmed by X-ray diffractometry using $CuK_{\alpha}$ radiation at room temperature. The chemical composition was determined by ICP method, which showed that all the samples were well synthesized. Platinum electrodes were connected to the samples by firing at 1173 K for 1 h in air. The electrical conductivity of the sintered samples was measured by DC four-probe method under various conditions in the temperature range from 873 to 1273 K and at the oxygen partial pressure from $1.013{\times}10^5$ to 32 Pa.

## Results and discussion

The XRD patterns of $(Ba_{0.5}La_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga: $0 \leq y \leq 0.2$) and $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ ($0 \leq y \leq 0.02$) were identified to be a single phase of perovskite-type structure with cubic symmetry. However, the pattern of $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ ($0.02 \leq y \leq 0.2$) showed slight splits in high diffraction angle, indicating as a tetragonal symmetry. The lattice constants calculated from the XRD patterns are shown in Fig. 1. A primitive lattice of the perovskite structure is selected as the unit cell, in order to understand the change of lattice constant consistently. Using the ion radii by Shannon [11], it is concluded that the substitution of $Ga^{3+}$ (0.62 Å) into In (0.80 Å) site shrinks the unit cell, while the substitution of $Y^{3+}$ (0.90 Å) enlarges it.
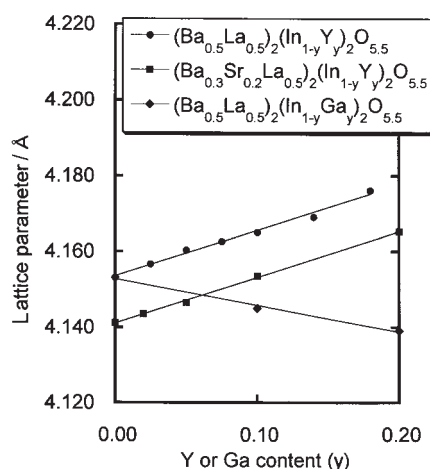


**Fig. 1** Lattice parameters of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) solid-solution system as a function of Y or Ga content

In order to confirm the conducting carrier of the system, the oxygen partial pressure and the electrical conductivity were measured. The typical results are shown in Fig. 2. The electrical conductivity of $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{0.98}Y_{0.02})_2O_{5.5}$ system is independent of oxygen partial pressure in the range from $\log[P_{O_2}$ (Pa)]=5.0 to 1.5. However, the electrical conductivity of $(Ba_{0.5}La_{0.5})_2(In_{0.925}Y_{0.075})_2O_{5.5}$ and of $(Ba_{0.5}La_{0.5})_2(In_{0.9}Ga_{0.1})_2O_{5.5}$ system is independent of the pressure under $\log[P_{O_2}$ (Pa)]=4.3. In the previous study, it was reported that $Ba_2In_2O_5$ [4] was the hole-oxide mixed conductor, and that the La and Sr doped $Ba_2In_2O_5$ [$(Ba_{1-x-y}Sr_xLa_y)_2In_2O_{5+y}$] [17] changed to oxide-ion conductor with increasing La content. The results of electrical conductivity for $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) system as a function of oxygen partial pressure agree with the previous reports [4, 10]. As the oxide-ion conductivity was of interest, the electrical conductivity was measured in argon gas ($\log[P_{O_2}$ (Pa)]=1.5).

Arrhenius plots of the oxide-ion conductivity for $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) system under argon gas are shown in Figs 3–5. The oxide-ion conductivity of $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ and $(Ba_{0.5}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ system is
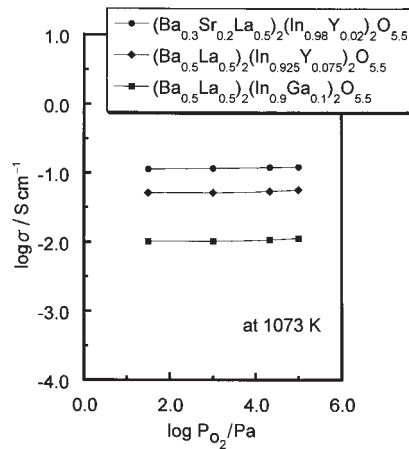
**Fig. 2** Electrical conductivity of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) solid-solution system at 1073 K as a function of oxygen partial pressure

higher than that of 8 mol%$Y_2O_3$ doped $ZrO_2$, while that of $(Ba_{0.5}La_{0.5})_2(In_{1-y}Ga_y)_2O_{5.5}$ system is lower. All lines of the Arrhenius plots are straight *vs*. the reciprocal of temperature, which give the activation energy of 80~90 kJ mol$^{-1}$. The value of the activation energy is very close to that of yttria-stabilized zirconia [12] and aliovalent cation doped ceria systems [13]. The results suggest that the oxygen vacancy of the system is in disordered state.

In general, the oxide-ion conductivity is dependent on the content of oxygen vacancy. But the magnitude of oxide-ion conductivity of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) system changes with the dopant content without changing oxygen vacancy concentration. The results suggest that the ion conductivity of the
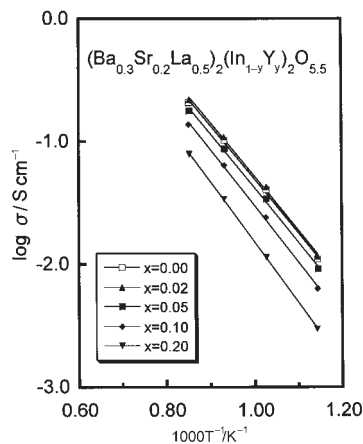


**Fig. 3** Arrhenius plots of $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ solid-solution system under argon gas

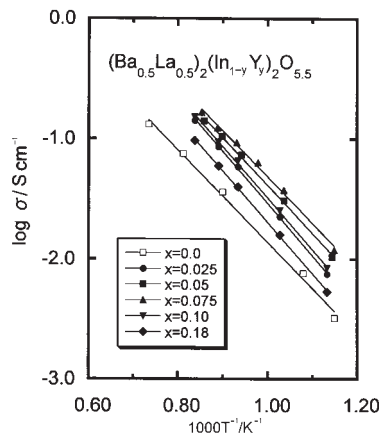**Fig. 4** Arrhenius plots of $(Ba_{0.5}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ solid-solution system under argon gas



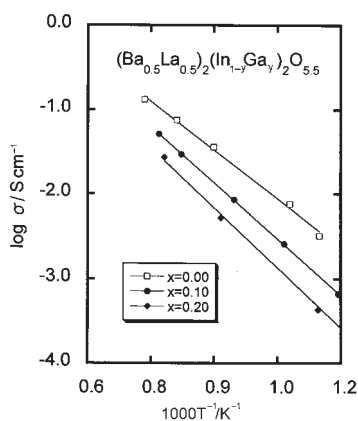**Fig. 5** Arrhenius plots of $(Ba_{0.5}La_{0.5})_2(In_{1-y}Ga_y)_2O_{5.5}$ solid-solution system under argon gas

$(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ (*M*=Y or Ga) system should be dominated not only by the oxygen vacancy but also by the other parameters. In order to discuss about the dominant parameter for the oxide-ion conductivity of the system, the ion conductivity at 1073 K is plotted as a function of Y or Ga content (Fig. 6). The oxide-ion conductivity of $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ system increases with the dopant content at first. However, it shows a maximum value at a free volume, and then decreases. The maximum conductivity of the system is about 0.12 S cm$^{-1}$ in $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{0.98}Y_{0.02})_2O_{5.5}$. In contrast, the conductivity of $(Ba_{0.5}La_{0.5})_2(In_{1-y}Ga_y)_2O_{5.5}$ decreased with Ga content. The results suggest that the oxide-ion conductivity is also dependent on the dopant cation. In general, the unit cell free volume [15, 16], unit cell volume [14] and saddle point [16], which change with dopant cation, influence the oxide-ion conductivity. Especially, the ox-
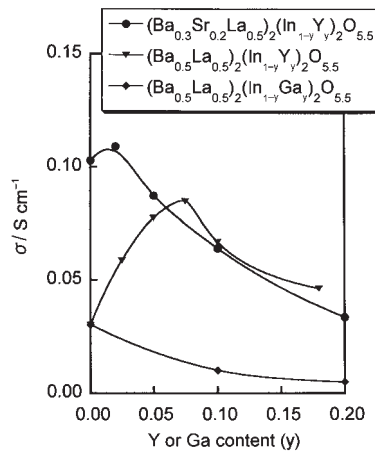
**Fig. 6** Oxide-ion conductivity of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) solid-solution system at 1073 K as a function of dopant content



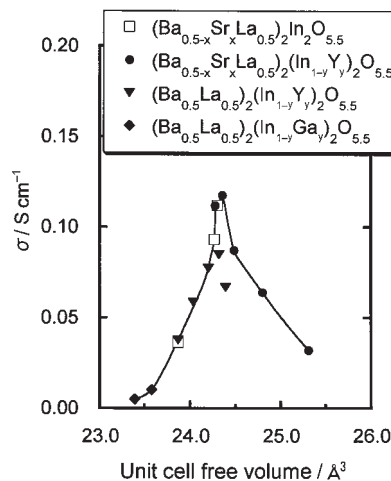**Fig. 7** Oxide-ion conductivity of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) solid-solution system at 1073 K as a function of unit cell free volume

ide-ion conductivity of perovskite-type oxide has been reported to be strongly dependent on the unit cell free volume [15,16]. The unit cell free volume is defined as the difference between the total unit cell volume and the sum of volumes occupied by individual ions in the unit cell. In the cubic structure, the volume was calculated as follows [15],

$$\text{Unit cell free volume} = a^3 - \sum m_i(4/3)\pi r_i^3 \tag{1}$$

where $a$ is the lattice parameter shown in Fig. 1, $m_i$ is the chemical composition ratio of the ion, and $r_i$ is the ionic radii. In the previous paper, the oxide-ion conductivity of $(Ba_{1-x-y}Sr_xLa_y)_2In_2O_{5+y}$ system was strongly dependent on the unit cell free volume [17]. The oxide-ion conductivity of the $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) system is shown as a function of the unit cell free volume in Fig. 7, where the plots of the conductivity of the $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) system are a single curve. The oxide-ion conductivity increases with the unit cell free volume at first.



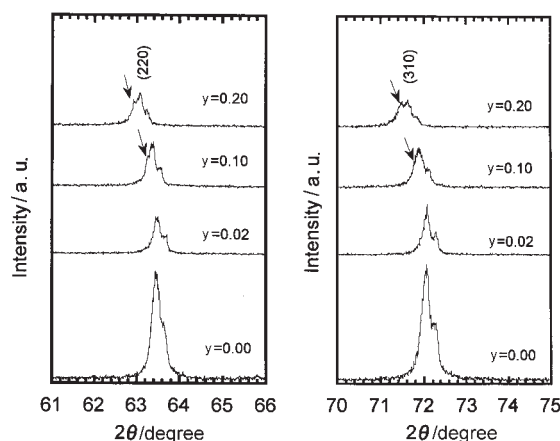**Fig. 8** XRD peaks of (220) and (310) for $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ solid-solution system

However, it shows a maximum value at 24.3 $\text{Å}^3$, and then it decreases. The results suggest that the oxide-ion conductivity is dependent on unit cell free volume under the unit cell free volume of 24.3 $\text{Å}^3$. But, above the free volume, the oxide-ion conductivity would be dominated by the other parameter. In general, the crystal symmetry is one of the dominant parameters for the oxide-ion conductivity. The XRD peaks of (310) and (220) of $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}Y_y)_2O_{5.5}$ system are shown in Fig. 8, where the peak originated from $CuK\alpha_2$ is not eliminated. The conductivity decreases with increasing the dopant content above $y$=0.02, where the unit cell free volume is larger than 24.3 $\text{Å}^3$. In the region, the peaks of (310) and (220) are splitted slightly in low diffraction angle. The results suggest that the crystal structure should change to low symmetry above the volume of 24.3 $\text{Å}^3$. In the viewpoint of tolerance factor for the perovskite structure, a doping of large radius ion in B site causes the factor to decrease. The low crystal symmetry would bring about the decrease of oxide-ion conductivity in this system.

## Conclusions

The oxide-ion conductivity and crystal structure of the $(Ba_{0.5-x}Sr_xLa_{0.5})_2(In_{1-y}M_y)_2O_{5.5}$ ($M$=Y or Ga) solid-solution system was investigated as a function of temperature and oxygen partial pressure. The conductivity was independent of oxygen partial pressure, and

thus the system was confirmed to be an oxide-ion conductor. The ion conductivity of $(Ba_{0.3}Sr_{0.2}La_{0.5})_2(In_{0.98}Y_{0.02})_2O_{5.5}$ has a maximum value of 0.12 S cm$^{-1}$, which is higher than that of the yttria stabilized zirconia. The oxide-ion conductivity increases with increasing the dopant content at first. However, it shows a maximum value at a free volume, and then decreases. In the increasing region, the unit cell free volume would be one of the key parameter of oxide-ion conductivity. In the decreasing region, the doping a large aliovalent cation in In site would occur the crystal symmetry to be low and would decrease conductivity against the free volume.

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