Oxide-Ion Conductivity of $\text{BaLaInMO}_{5.5}$ ($M = \text{Sc, Ga and In}$) and $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ ($x = 0.1, 0.2$ and 0.3)

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$\text{BaLaInMO}_{5.5}$ ($M = \text{Sc, Ga と In}$) と $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ ($x = 0.1, 0.2$ と 0.3) の酸化物イオン導電性について

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Solid solutions of $\text{BaLaIn}_2\text{O}_{5.5}$ and $\text{BaLaInMO}_{5.5}$ that formed by partial replacement of In by Sc and Ga have a cubic perovskite structure. The Sc^{3+} - and Ga^{3+} -doped compounds, which had almost the same electrical conductivities, exhibited lower conductivities than the parent compound $\text{BaLaIn}_2\text{O}_{5.5}$ in the temperature range from 573 to 1273 K. The Ga compound showed a transference number, t_i , of unity at both high and low oxygen partial pressures in the temperature range from 973 to 1273 K. As for the Sc compound kept at 973–1273 K, a t_i of nearly unity was observed at low oxygen partial pressure, while the t_i was slightly lower than unity at high oxygen partial pressures at higher temperatures. The In compound had a t_i of almost unity at high oxygen partial pressure, whereas the number decreased to a value less than 0.9 at low partial pressures of oxygen. The stepwise increase in the Sc content from 0.1 to 1.0 in $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ caused a monotonic decrease in conductivity. The decrease in conductivity and the increase in activation energy caused by Sc^{3+} and Ga^{3+} doping were ascribed to the partial ordering of originally disordered oxygen vacancies and a decrease in the size of the triangle formed by two A-site cations and one B-site cation, through which the oxide ion proceeds, respectively.

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1. Introduction

The compound $\text{Ba}_2\text{In}_2\text{O}_5$ with the brownmillerite structure has received considerable attention, because it exhibits a high conductivity at 1273 K comparable to that of yttria-stabilized zirconia (YSZ).¹⁾ However, the total conductivity decreased by an order of magnitude below ca. 1203 K, and electronic contributions to the total conductivity became significant.¹⁾ Thus far, Ba^{2+} and/or In^{3+} ions in $\text{Ba}_2\text{In}_2\text{O}_5$ have been partially replaced by cations such as Sr^{2+} , Pb^{2+} , Al^{3+} , Ga^{3+} , Zr^{4+} , Hf^{4+} , and rare-earth ions,^{1)–5)} and some improvements in oxide-ion conduction have been attained. Goodenough et al.¹⁾ doped Ce^{4+} at the In^{3+} site to prepare $\text{Ba}_2\text{In}_{1.75}\text{Ce}_{0.25}\text{O}_{5.125}$, which exhibited an oxide-ion conductivity comparable to that of YSZ in the temperature range of ca. 833–1103 K. Kuramochi et al.²⁾ found that $(\text{Ba}_{0.80}\text{Pb}_{0.09})_2\text{In}_2\text{O}_5$ showed a higher conductivity than $\text{Ba}_2\text{In}_2\text{O}_5$ in the temperature range of 673 to 1103 K. Kakinuma et al.³⁾ reported that $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ shows a high oxide-ion conductivity, which exceeds that of YSZ at $x = 0.6$ at 1073 K. According to the latest investigation of the $(\text{Ba}_{1-x-y}\text{Sr}_x\text{La}_y)_2\text{In}_2\text{O}_{5+y}$ system by Kakinuma et al.,⁴⁾ oxide-ion conductivity increases with La or Sr content. The oxide-ion conductivity for $x = 0.2$ and $y = 0.5$ at 1073 K exhibits a maximum value of $0.12 (\text{S/cm})$, which exceeded that of YSZ. In our previous work⁶⁾ we prepared $\text{Ba}_2\text{In}_{2-x}\text{Ce}_x\text{O}_{5+x/2}$ compounds ($x = 0, 0.1, 0.2, 0.3$ and 1.0) and measured their conductivities as a function of temperature. It was found that the disordered phase of $\text{Ba}_2\text{In}_2\text{O}_5$ was stabilized at temperatures as low as 773 K by doping Ce^{4+} ions at contents higher than $x = 0.2$, and the conductivities of the Ce^{4+} -doped compounds below the transition temperature were higher than that of the parent compound.

In this work, we prepared $\text{BaLaInM}_{0.5}\text{O}_{5.5}$ ($M = \text{Sc, Ga,}$

and In) and $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ ($x = 0.1, 0.2$, and 0.3) and measured their conductivities and transference numbers as functions of temperature.

2. Experimental

The samples of $\text{Ba}_2\text{In}_{2-x}\text{M}_x\text{O}_{5.5}$ ($x = 0.1, 0.2, 0.3$, and 1.0 for Sc and $x = 1.0$ for Ga) were prepared by solid-state reactions using barium carbonate, lanthanum oxide, indium oxide, and either scandium oxide or gallium oxide of reagent grade as starting materials. The reagents were mixed in stoichiometric proportion for 6 h using an electric mortar with methanol as a dispersing agent. The dried samples were calcined twice at 1373 K for 6 h in air. The powders prepared by crushing were passed through a 75-mesh sieve and pressed into disks 13 mm in diameter and ca. 1 mm thick. After a isostatically pressing at 308 MPa, the disks were sintered at 1623–1923 K for 6 h in air.

The powdered samples were analyzed by an X-ray diffraction (XRD) technique using a Rigaku RINT 2000 with $\text{Cu K}\alpha$ to determine their phases and lattice constants. The total electrical conductivities of the sintered disks of $\text{Ba}_2\text{In}_{2-x}\text{M}_x\text{O}_{5.5}$ ($x = 0.1, 0.2, 0.3$, and 1.0 for Sc and $x = 1.0$ for Ga) with platinum electrodes were measured using a frequency response analyzer (Solartron FRA 1255) over a frequency range from 0.2 Hz to 2 MHz in the temperature range of approximately 573–1273 K in air, N_2 , and O_2 . The flow rates of N_2 and O_2 were kept at 80 ml/min. The bulk resistivities were estimated from the complex-impedance plane diagrams. Measurement temperatures were determined by an R-type thermocouple placed near the sample. The oxide ionic transference number, t_i , at a high oxygen partial pressure of $1.013 \times 10^5 \text{ Pa}$ was estimated from the electromotive force (EMF) of the oxygen concentration cell of oxygen//air and that at low

oxygen partial pressures from the EMF value of the cell of a mixed gas of 96% nitrogen and 4% hydrogen saturated with water vapor at 307 K//air. In the estimation, the EMF value of 8YSZ measured under the same conditions as above was considered to correspond to a transference number of unity.

3. Results and discussion

3.1 Structure, conductivity, and ionic transference number of BaLaInMO_{5.5} (M=In, Sc, and Ga)

Figure 1 shows the XRD patterns of BaLaInMO_{5.5} (M=Al, In, Sc and Ga) measured at room temperature. The compounds in which Sc³⁺ and Ga³⁺ were substituted for In³⁺ exhibited almost the same patterns of peaks as BaLaIn₂O_{5.5} with a cubic perovskite structure. This indicates that the Sc³⁺- and Ga³⁺-doped compounds, which probably formed solid solutions, also have a cubic perovskite structure. As for the Al³⁺-doped compound, the peaks indexed to LaAlO₃ were observed in addition to those occurring in the compounds such as BaLaIn₂O_{5.5} and BaLaInAlO_{5.5}. This suggests that the Al³⁺-doped compound is composed of mixed phases. The calculated lattice parameters are given in Table 1 using the ionic radii of the sixfold coordination for M³⁺.⁷⁾ The lattice parameters decreased with decreasing ionic radius of M³⁺. The Arrhenius plots of BaLaInMO_{5.5} measured under nitrogen are depicted in Fig. 2. The Sc³⁺- and Ga³⁺-doped compounds, which have almost the same conductivities, exhibited much lower values than those of the parent (In) compound in the entire temperature range. It is evident from Fig. 2 that the In compound has the lowest activation

energy (65.7 kJ/mol), followed by the Sc compound (76.4 kJ/mol). Figures 3 and 4 show t_i values of BaLaInMO_{5.5}

Fig. 2. Total electrical conductivities of BaLaInMO_{5.5} (M=In³⁺: ■, Ga³⁺: ○, and Sc³⁺: ▲ measured in N₂).

Fig. 1. XRD patterns of BaLaInMO_{5.5} (M=Al³⁺, Ga³⁺, In³⁺ and Sc³⁺) at room temperature. ○ LaAlO₃

Table 1. Crystal Structural Data for BaLaInMO_{5.5} (M=Ga³⁺, In³⁺ and Sc³⁺)

Compound	Crystal system	Lattice parameter (nm)	Ionic radius (nm) of 6-coordinate ion
		a	
BaLaInGaO _{5.5}	Cubic	0.407	0.062
BaLaIn ₂ O _{5.5}	Cubic	0.416	0.080
BaLaInScO _{5.5}	Cubic	0.413	0.0745

Fig. 3. Ionic transference numbers of $\text{BaLaInMO}_{5.5}$ ($M=\text{In}^{3+}$: ■, Ga^{3+} : ○, and Sc^{3+} : ▲) at oxygen partial pressure of 1.013×10^5 Pa. Measurement conditions: O_2 -Air concentration cell, Gas flow rate 100 ml/min.

Fig. 4. Ionic transference numbers of $\text{BaLaInMO}_{5.5}$ ($M=\text{In}^{3+}$: ■, Ga^{3+} : ○, and Sc^{3+} : ▲) under low oxygen partial pressure. Measurement conditions: Air- H_2 concentration cell (H_2 : 4% H_2 - N_2 saturated with H_2O at 307 K), Gas flow rate 100 ml/min.

($M=\text{Sc}$, Ga and In) measured at a high oxygen partial pressure of 1.013×10^5 Pa and a low partial pressure of oxygen, respectively. As for the Sc compound, a t_i close to unity was observed at a low partial pressure in the temperature range from 973 to 1273 K, whereas the value decreased to lower than 0.9 at the high partial pressure at higher temperatures. It is appropriate to consider that the low value originated, not from the hole conductivity caused by the oxidation of In from $3+$ to $4+$, but from the hole conductivity caused by the equilibrium between vacancies and oxygen because the existence of the oxidation state of $4+$ for indium has not been reported.⁸⁾ The In compound had a t_i of approximately unity at the high partial pressure of oxygen, while it was lower than unity at the low partial pressure. In contrast to our results, Kakinuma et al.³⁾ reported that the In compound with the same composition as ours had a t_i of unity at both high and low partial pressures of oxygen. The Ga compound also showed a t_i of nearly

Fig. 5. Total electrical conductivities of $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ ($x=0.1, 0.2, 0.3$, and 1.0) measured in N_2 . ■ $\text{BaLaIn}_2\text{O}_{5.5}$, ○ $\text{BaLaIn}_{1.9}\text{Sc}_{0.1}\text{O}_{5.5}$, △ $\text{BaLaIn}_{1.8}\text{Sc}_{0.2}\text{O}_{5.5}$, □ $\text{BaLaIn}_{1.7}\text{Sc}_{0.3}\text{O}_{5.5}$, ● $\text{BaLaInScO}_{5.5}$.

unity at both high and low partial pressures of oxygen. The high t_i suggests that the charge carrier in $\text{BaLaInMO}_{5.5}$ ($M=\text{Sc}$, Ga and In) is chiefly the oxide ion.

EXAFS investigation of the Ga -doped $\text{Ba}_2\text{In}_2\text{O}_5$ by Yao et al.⁹⁾ revealed that the coordination number of Ga^{3+} is 4. Fourfold coordination by the smaller cation Ga^{3+} probably ordered part of the originally disordered vacancies, which resulted in a decrease in the number of mobile oxygen vacancies. This is probably a reason for the decrease in the conductivity of the Ga compound. This may also hold for the Sc system. The activation energy in $\text{BaLaInMO}_{5.5}$ ($M=\text{Sc}$, Ga and In) increased with decreasing ionic radius of the doped cation in the order of In , Sc and Ga . Cook and Sammells¹⁰⁾ have reported that, because the oxide ion migrates through a triangle formed by two A-site cations and one B-site cation in the perovskite structure, the so-called saddle point, the activation energy should be correlated to the size of the saddle point. The sizes of the saddle points in $\text{BaLaInMO}_{5.5}$ ($M=\text{Sc}$, Ga and In) were calculated to be 0.0924, 0.0918, and 0.0910 nm, respectively. It is appropriate to consider that the decrease in the size of the saddle point due to doping led to the increase in activation energy.

3.2 Conductivity and transference number of $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ ($x=0.1, 0.2$ and 0.3)

Because the substitution of Sc^{3+} and Ga^{3+} for one-half the In^{3+} content did not improve conductivity, the In^{3+} ion was replaced to a small extent with the Sc^{3+} ion to examine how the conductivity varied. The Arrhenius plots are illustrated in Fig. 5. The conductivity decreased and the activation energy increased with increasing Sc^{3+} content. The doping with Sc^{3+} did not improve the conductivity or the activation energy. The transference number is plotted in Figs. 6 and 7. The ionic transference numbers were high at both partial pressures of oxygen, but had a tendency to decrease with increasing x values at the high partial pressure.

Fig. 6. Ionic transference numbers of $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ ($x=0.1, 0.2, 0.3$, and 1.0) at oxygen partial pressure of 1.013×10^5 Pa.

■ $\text{BaLaIn}_2\text{O}_{5.5}$, ○ $\text{BaLaIn}_{1.9}\text{Sc}_{0.1}\text{O}_{5.5}$, △ $\text{BaLaIn}_{1.8}\text{Sc}_{0.2}\text{O}_{5.5}$, □ $\text{BaLaIn}_{1.7}\text{Sc}_{0.3}\text{O}_{5.5}$, ● $\text{BaLaInScO}_{5.5}$.
Measurement conditions: O_2 -Air concentration cell, Gas flow rate 100 ml/min.

Fig. 7. Ionic transference numbers of $\text{BaLaIn}_{2-x}\text{Sc}_x\text{O}_{5.5}$ ($x=0.1, 0.2, 0.3$, and 1.0) under low oxygen partial pressure.

■ $\text{BaLaIn}_2\text{O}_{5.5}$, ○ $\text{BaLaIn}_{1.9}\text{Sc}_{0.1}\text{O}_{5.5}$, △ $\text{BaLaIn}_{1.8}\text{Sc}_{0.2}\text{O}_{5.5}$, □ $\text{BaLaIn}_{1.7}\text{Sc}_{0.3}\text{O}_{5.5}$, ● $\text{BaLaInScO}_{5.5}$.
Measurement conditions: Air- H_2 concentration cell (H_2 : 4% H_2 - N_2 saturated with H_2O at 307 K), Gas flow rate 100 ml/min.

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