— Note —

Crystal Structure of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ and Its Oxide Ion Conductivity

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Crystal structures of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.00, 0.20, 0.30, 0.40, 0.50$) were analyzed and electrical conductivity were measured. The Rietveld results for $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.20, 0.40$) revealed that these oxides belonging to cubic $Pm\bar{3}m$ space group. This result indicated that the oxide ion vacancies distribute randomly in the cubic perovskite type structure. The electrical conductivities of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.20, 0.40, 0.50$) did not show a sharp discontinuity because the disorder phase of defective perovskite type structure was stabilized at low temperature by doping La^{3+} cations. The oxide ion transference number of the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ determined by blocking method is 1.00.

Key Words : Brownmillerite, Perovskite, Oxide Ion, Crystal Structure

1 Introduction

Recently, a significant amount of work has been devoted to solid oxide fuel cells (SOFCs) and steam electrolyzers utilizing oxide ion conductors as electrolyte.^{1, 2)} When the operating temperature is reduced to intermediate-temperature range (700–800°C), SOFCs could be constructed by less costly materials for interconnectors, for example alloys, and technical advantages such as increase of reliability and lifetime will be attained. Since oxide ion conductivity of stabilized zirconia decreases at such temperatures, some of the major problems found in the SOFCs can be attributed to difficulties in lowering the resistance of the oxide ion conductors. This can be achieved by increasing the specific ionic conductivity of the oxide ion conductor.

Oxides with perovskite and perovskite-related structures have been widely investigated for the electrolyte material for the SOFCs at intermediate-temperature range.^{3–7)} The defect perovskite-related oxide $\text{Ba}_2\text{In}_2\text{O}_5$ has been reported to have high oxide ion conductivity, which is higher than that of calcia- and yttria-stabilized zirconia, at high temperature.^{5–7)} $\text{Ba}_2\text{In}_2\text{O}_5$ has a characteristic order-disorder transition temperature (T_d) at 930°C. In order to utilize as the electrolyte for SOFCs, it is important to stabilize the high temperature phase. In this work, we have attempted to stabilize the high temperature phases by doping La cation at A-site. The crystal structure of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ was analyzed by powder X-ray Rietveld method and the oxide ion conductivity was discussed.

2 Experimental

Pure and La doped $\text{Ba}_2\text{In}_2\text{O}_5$ powder was prepared by conventional solid state reaction starting with barium carbonate (Wako Chemical Co. Inc., 99.9%), indium oxide

(Wako Chemical Co. Inc., 99.9%), and lanthanum oxide (Wako Chemical Co. Inc., 99.9%). The crystal structure of the product was determined by XRD using Mo-K α radiation. For the Rietveld analysis, a powder XRD pattern was collected using a Model RINT-TTR powder X-ray diffractometer (Rigaku Co.). The Rietveld calculation was performed on the vector processor (Cray Y-MP2E/264) at the Institute for Chemical Research, Kyoto University, by using “Rievtec” computer program.^{8–10)} The total electrical conductivity of the oxides is measured using impedance spectroscopy using impedance analyzer (Solatron 1260) connected with potentiostat (Solatron 1287) under air atmosphere. The ion-blocking technique is used to determine the oxide ion transference numbers. Non-porous platinum electrode was used as an oxide ion-blocking electrode and porous platinum electrode was used as a reversible electrode. The electronic or hole conductivity was obtained from a plot of steady-state current versus applied voltage between the blocking electrode and the reversible electrode under air atmosphere.

3 Results and Discussion

Figure 1 shows XRD patterns of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.00, 0.20, 0.30, 0.40, 0.50$) at room temperature. XRD pattern of $\text{Ba}_2\text{In}_2\text{O}_5$ was indexed to an orthorhombic lattice. On the other hand, XRD pattern of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.20, 0.30, 0.40, 0.50$) was indexed to a cubic lattice. The lattice parameters and other structural parameters were refined by the Rietveld method and it was confirmed that the $\text{Ba}_2\text{In}_2\text{O}_5$ belonging to orthorhombic $Ibm2$ space group.¹¹⁾ $\text{Ba}_2\text{In}_2\text{O}_5$ has Brownmillerite structure, which consists of the stacking of alternating two-dimensional layers of corner-shared InO_6 octahedra and corner-shared InO_4 distorted tetrahedra.

Figure 2 shows the results of the Rietveld analysis of

Fig. 1 XRD patterns of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.00, 0.20, 0.30, 0.40, 0.50$) at room temperature.

Fig. 2 Rietveld result of $(\text{Ba}_{0.8}\text{La}_{0.2})_2\text{In}_2\text{O}_{5.2}$ at room temperature. The calculated and observed patterns are shown in the top by the solid line and the dots, respectively. The difference between observed and calculated is plotted below.

$(\text{Ba}_{0.8}\text{La}_{0.2})_2\text{In}_2\text{O}_{5.2}$ at room temperature. The observed pattern agreed well with the calculated pattern. The obtained lattice parameters are given in Table 1. R_{wp} , R_f , and R_b are small enough to guarantee the reliability, and it was confirmed that $(\text{Ba}_{0.8}\text{La}_{0.2})_2\text{In}_2\text{O}_{5.2}$ belonging to cubic $Pm\bar{3}m$ space group. This result indicates that the oxide ion vacancies distribute randomly in the cubic perovskite type structure. La^{3+} cations were randomly distribute at A-site and oxygen vacancy is introduced at oxygen site by keeping an electroneutrality. As a result of the oxygen distribution, the oxide ion vacancies distribute randomly. The lattice constant decreased with increasing La content, because ionic radius of La^{3+} cation is smaller than that of Ba^{2+} cation.

Figure 3 shows electrical conductivities of

Table 1 Refined atomic parameters for $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.20, 0.40$) at room temperature.

$(\text{Ba}_{0.8}\text{La}_{0.2})_2\text{In}_2\text{O}_{5.2}$					
Cubic perovskite-type					
Space Group : $Pm\bar{3}m$					
Atom	site	x	y	z	N
Ba,La	1a	0	0	0	1.0
In	1b	0.5	0.5	0.5	1.0
O	3c	0	0.5	0.5	0.866
$a = 4.20391(3) \text{ \AA}$					
$R_{wp}, R_f, R_b = 0.0878, 0.1138, 0.0633$					

$(\text{Ba}_{0.6}\text{La}_{0.4})_2\text{In}_2\text{O}_{5.4}$					
Cubic perovskite-type					
Space Group : $Pm\bar{3}m$					
Atom	site	x	y	z	N
Ba,La	1a	0	0	0	1.0
In	1b	0.5	0.5	0.5	1.0
O	3c	0	0.5	0.5	0.9
$a = 4.17214(2) \text{ \AA}$					
$R_{wp}, R_f, R_b = 0.0944, 0.0878, 0.0459$

Fig. 3 Electrical conductivities of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.00, 0.20, 0.40, 0.50$) samples.

$(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.00, 0.20, 0.40, 0.50$) samples. For pure $\text{Ba}_2\text{In}_2\text{O}_5$, electrical conductivity rapidly increased at about 930°C due to the order-disorder transition of oxygen vacancy. The electrical conductivities of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.20, 0.40, 0.50$) did not show a sharp discontinuity in the conductivity because the disorder phase of defective perovskite type structure was stabilized by doping La^{3+} cations at A-site even at low temperature. The oxide ion transference number of the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.20, 0.40, 0.50$) determined by blocking method is 1.00 (Table 2).

The oxide ion conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ in

Table 2 Oxide ion transference number determined by ion-blocking electrode.

Temperature(°C)	900	800	700	600
t_i^a	1.00	1.00	1.00	1.00

^a)Oxide ion transference number

creased with increasing La content even with the decrease of the oxygen vacancy concentration with increasing La content. Sammells and co-workers suggested that the oxide ion conductivity in perovskite oxides have a strong relationship with the width of saddle point in the perovskite lattice.^{12,13)} The saddle point for oxide ion migration occurs via a triangle formed by two A-site cations and B-site cation. The radius of saddle point was calculated by using following equation from the lattice parameter determined by the powder X-ray Rietveld method and the Shanon's ionic radius.¹⁴⁾

$$r_{\text{critical}} = \frac{-r_A^2 + \frac{3}{4}a^2 - \sqrt{2}ar_B + r_B^2}{2r_A + \sqrt{2}a - 2r_B} \quad [1]$$

where r_A is the ionic radius of A-site cation, r_B is the ionic radius of B-site cation, and a is the lattice parameter. The radius of saddle point of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x = 0.20, 0.40$) are 0.912 and 0.933 Å respectively, which is smaller than that of oxide ion, 1.4 Å. Therefore, the radius of saddle point is expected to influence the oxide ion migration. The radius of saddle point of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ increased with increasing La content, the fact may be one reason for high oxide ion conductivity of the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ having high La content.

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