

Cation Distribution and Electrical Conductivity in $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ System with Excess Alkaline Earth Oxide

Katsuyoshi KAKINUMA, Tooru ARISAKA, Hiroshi YAMAMURA and Tooru ATAKE*

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama-shi 221-8686

*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama-shi 226-8503

過剰のアルカリ土類酸化物を含む $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ 系の陽イオン分布と導電率

柿沼克良・有坂 通・山村 博・阿竹 徹*

神奈川県横浜市神奈川区六角橋 3-27-1

*東京工業大学応用セラミックス研究所, 226-8503 横浜市緑区長津田町 4259

We have investigated the influence of the excess doping of alkaline earth oxides on the structure and electrical conductivity of the $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ ($x+y \geq 0.5$) system. It was found that over 0.10 mol of BaO or SrO could be doped in 1 mol of the cation stoichiometric system ($x+y=0.50$). We propose that some of the Sr cation move from A-sites to B-sites in this system to maintain the cation stoichiometry [$(x+y+0.50) : \text{In} = 1 : 1$]. The dependence of the electrical conductivity on the oxygen partial pressure varied with the magnitude of the oxide ion conductivity. The oxide ion conductivity of the excess-doped system was dependent on the unit cell free volume. The relationship corresponded to that of stoichiometric $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25}$ ($x+y=0.50$) and $\text{Ba}_{1-y}\text{La}_y\text{InO}_{2.50+y}$ systems. [Received June 18, 2005; Accepted March 16, 2006]

Key-words : Perovskite structure, Cation defect, Rietveld analysis, Unit cell free volume, Oxide ion conductivity

1. Introduction

Oxide-ion conductors have received much attention for their possible uses in oxide fuel cells, oxygen sensors, and oxygen-permeable membrane reactors.^{1)–4)} An interesting example of these oxide-ion conductors is the perovskite system. The chemical formula of such an oxide is ABO_3 ; the A-site cation is 12-coordinate and the B-site is 8-coordinate. An appropriate aliovalent substitution of the A or B-site cation can result in the generation of oxide-ion vacancies in the system. That improves the oxide-ion conductivity. Thus, the perovskite LaGaO_3 oxide showed a high oxide-ion conductivity when co-doped with divalent Sr or Mg ions.^{5),6)} In addition, other authors have reported that oxide ion conductivity is influenced by particular crystallographic properties, such as the order–disorder arrangement of oxide ion vacancies,^{7),8)} the unit cell free volume,⁹⁾ and the dopant ion radii.¹⁰⁾ For example, in the $\text{Ba}_2\text{In}_2\text{O}_5$ system, the oxide ion conductivity improved with La doping, because the number of disordered oxygen vacancies increased. Moreover, since the unit cell free volume of the system also expanded with Sr doping, particularly high oxide ion conductivity appeared in this system.^{11),12)}

On the other hand, the perovskite oxide of ABO_3 is single phase not only in the cation stoichiometric condition ($A : B = 1 : 1$) but also in the cation nonstoichiometric one ($A : B \neq 1 : 1$).^{13),14)} For example, the BaCeO_3 and LaGaO_3 systems became single phase, when an A-site cation was in deficient condition.^{13),14)} The ion conductivity of these systems was also dependent on the amount of A-site cation nonstoichiometry. In addition, the electrical conductivity of the LaMnO_3 and LaCrO_3 systems improved with an increasing degree of A-site cation deficient.¹⁵⁾ From these reports, it is predicted that the $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system would be synthesized for the compositions not only of the cation stoichiometry, $(x+y+0.50) : \text{In} = 1 : 1$, but also of the cation nonstoichiometry, $(x+y+0.50) : \text{In} \neq 1 : 1$, and that the cation deficiency would

affect the conducting behavior. For this paper, we have explained the alkaline earth oxide, of which the content was more than $x+y=0.50$, as an excess alkaline earth oxide.

We have expected the distribution of the excess alkaline earth cation in $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ ($x+y \geq 0.50$) system by Rietveld analysis of XRD patterns. Further, we have measured the electrical conductivity of the chosen system as functions of temperature, oxygen partial pressure and content of excess alkaline earth oxide. Finally, we discuss the effect of excess alkaline earth doping on the oxide-ion and electronic conductivity.

2. Experimental

The sintered samples for conductivity measurement and the powder samples for Rietveld analysis 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%, Kojundo Chemical Co.) and In_2O_3 (99.95%, Kojundo Chemical Co.), were mixed by a ball mill for 24 h with ethanol as a medium. 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 $54 \mu\text{m}$, was pressed at 4.9 MPa into a rectangular shape ($30 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$) and then isostatically pressed again at 196 MPa. The samples were sintered at 1673 K for 10 h in air.

The relative density, estimated from their dimensions and weight, of all the sintered specimens was higher than 90%. The single phase nature of the samples was confirmed by X-ray diffractometry with $\text{Cu K}\alpha$ radiation at room temperature. The sintered sample was crushed into powder by an agate mortar. Rietveld analysis of the X-ray profile was performed using the 'RIETAN-2000' computer program.

Platinum electrodes were connected to the samples by firing at 1223 K for 1 h in air. The electrical conductivity of the sintered samples was measured by the DC four-robe method

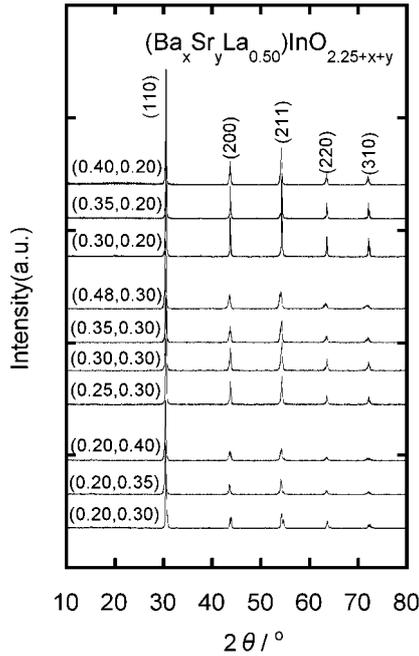


Fig. 1. XRD patterns of $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system.

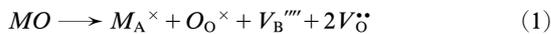
under various conditions over a range of temperatures between 873 K to 1273 K and oxygen partial pressures ranging from 1.0×10^5 Pa to 1.0×10^{-15} Pa, levels which were controlled by an oxygen pump or by varying the composition of a gas mixture (Ar-O_2 or $\text{H}_2\text{-H}_2\text{O}$).

3. Results and discussion

In these experiments we have further doped the alkaline earth oxide component in the stoichiometric $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ ($x+y=0.50$) system. The XRD patterns of the samples obtained are shown in Fig. 1. We were able to assign each peak to the perovskite phase, and did not observe the peaks by impurity phase. We allowed the doping level of SrO in the $\text{Ba}_{0.20}\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.45+y}$ system to be $0.40 \geq y \geq 0.30$. In addition, we also confirmed the doping level of BaO in the $\text{Ba}_x\text{Sr}_{0.30}\text{La}_{0.50}\text{InO}_{2.55+x}$ system to be $0.38 \geq x \geq 0.20$ and in the $\text{Ba}_x\text{Sr}_{0.20}\text{La}_{0.50}\text{InO}_{2.45+x}$ to be $0.40 \geq x \geq 0.30$. We were also able to confirm that the each distinct peak became broadened on doping; in our opinion, the synthesized samples were cubic or pseudo-cubic.

In Fig. 2, we show the lattice parameter of the $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system as a function of $x+y$. In general, the lattice parameter of a single phase tends to change linearly with increasing dopant content; however, the lattice parameter of this system increased nonlinearly when doped with excess alkaline earth oxide. From this result, we believe that excess alkaline earth oxide does not simply occupy the A and O-site of the perovskite oxide.

If the excess alkaline earth element was occupied just in the A-site of the perovskite oxide, a cation vacancy would be generated in the B-site, as in the following equation:



where MO denotes the alkaline earth oxide. In the perovskite structure, the B-site cation consists of an octahedral polyhedron framework coordinated with 6 oxide ions, suggesting that a B-site vacancy would have difficulty existing in this system. Moreover, the A-site cation and oxide ion in the perov-

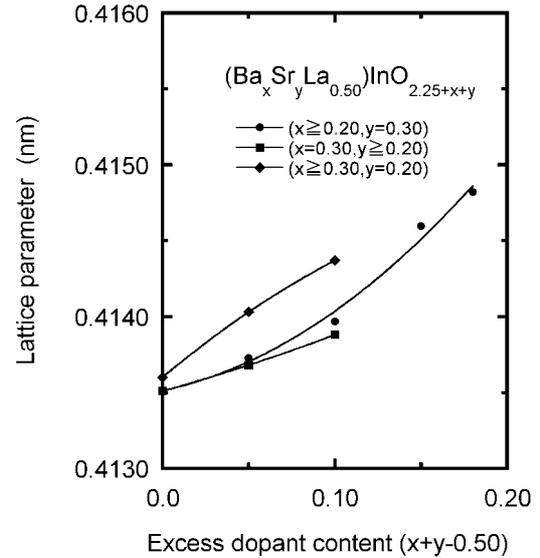
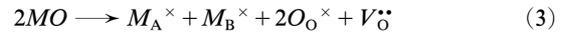


Fig. 2. Lattice parameter of $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system as a function of the excess alkaline earth oxide content ($x+y-0.50$).

skite structure are in a closed-packed arrangement. Nor could the excess alkaline earth oxide exist in an interstitial site in the perovskite oxide, as formula (2) demonstrates:



The case remains in which the alkaline earth element might occupy not only the A-site of the perovskite, but also the B-site.



When the defect reaction of formula (3) occurs in this system, a part of the alkaline earth element would displace to the B-site to keep the cation stoichiometry [$(x+y+0.50) : \text{In} = 1 : 1$] fixed. The same displacement was also proposed to occur in the perovskite oxides of the BaCeO_3 and $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ system, doped with excess BaO.¹⁶⁻¹⁸ In addition, the solution energy of Sr in both the A and B-site of LaInO_3 was reported to be lower than that of Ba.¹⁹ The alkaline earth elements Mg, Sr and Ca could be doped into the B-site of the $(\text{Ba}_{0.50}\text{La}_{0.50})\text{InO}_{2.75}$ system series, though Ba could not.²⁰ It is predicted that a part of the Sr would replace the B-site with a doping of excess BaO or SrO in the cation stoichiometric $(\text{Ba}_x\text{Sr}_y\text{La}_{0.50})\text{InO}_{2.75}$ ($x+y=0.50$) system; in the following manner:

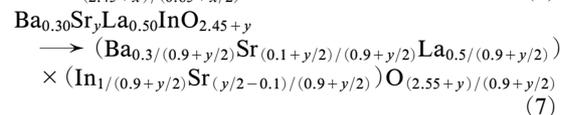
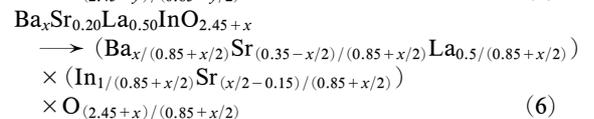
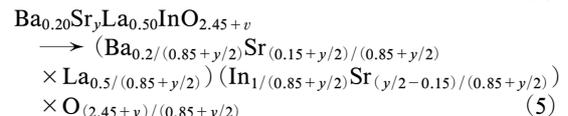
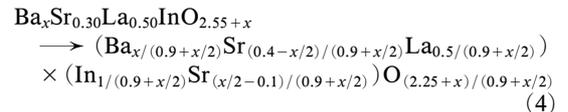


Table 1. Refined Crystal Parameter of $\text{Ba}_{0.30}\text{Sr}_{0.30}\text{La}_{0.50}\text{InO}_{2.85}$.
(a) Crystal Parameter of $\text{Ba}_{0.30}\text{Sr}_{0.30}\text{La}_{0.50}\text{InO}_{2.85}$ which was Originated from Formula (3),

a)		Space group: $Pm\bar{3}m$		a=0.41005 (1) nm		S=1.36(%)	
Atom	site	x	y	z	Occupancy	$B_j(\text{\AA}^2)$	
Ba	1a	0	0	0	0.286	2.54(4)	
Sr	1a	0	0	0	0.238	2.54(4)	
La	1a	0	0	0	0.476	2.54(4)	
In	1b	1/2	1/2	1/2	0.952	1.36(6)	
Sr	1b	1/2	1/2	1/2	0.048	1.36(6)	
O	3c	0	1/2	0	0.905	10.6(1)	

$$R_{wp}=11.72\%, R_c=8.32\%, R_p=8.57\%, R_B=5.08\%, R_F=5.71\%$$

(b) Crystal Parameter of $\text{Ba}_{0.30}\text{Sr}_{0.30}\text{La}_{0.50}\text{InO}_{2.85}$ which was Originated from Formula (1)

b)		Space group: $Pm\bar{3}m$		a=0.41005 (1) nm		S=1.40(%)	
Atom	site	x	y	z	Occupancy	$B_j(\text{\AA}^2)$	
Ba	1a	0	0	0	0.274	2.83(6)	
Sr	1a	0	0	0	0.274	2.83(6)	
La	1a	0	0	0	0.452	2.83(6)	
In	1b	1/2	1/2	1/2	0.909	1.10(3)	
O	3c	0	1/2	0	0.863	11.8(8)	

$$R_{wp}=13.84\%, R_c=8.34\%, R_p=9.49\%, R_B=6.73\%, R_F=9.08\%$$

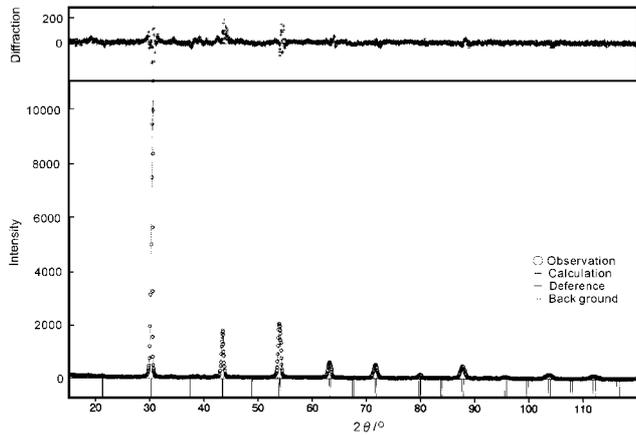


Fig. 3. Rietveld analysis of $\text{Ba}_{0.30}\text{Sr}_{0.30}\text{La}_{0.50}\text{InO}_{2.85}$. The open circle denotes the observed value, and the dotted line the estimated value.

The Rietveld analysis of the X-ray diffraction pattern would be one of the appropriate tools in order to confirm the cation arrangement. The $\text{Ba}_{0.30}\text{Sr}_{0.30}\text{La}_{0.50}\text{InO}_{2.85}$ system was selected as a representative system. The crystal structure was estimated from the formulas (3) and (1). The corresponded crystal parameters are summarized in Tables 1(a) and (b). The space group of $Pm\bar{3}m$ was chosen for this representative system, because the mother substrate of $\text{Ba}_2\text{In}_2\text{O}_5$ has $Pm\bar{3}m$ symmetry in the disordered cubic state.²¹⁾ The observed and calculated X-ray diffraction patterns of the system are presented in Fig. 3. The difference factor “S” for the model of formulas (3) and (1) reached 1.36 and 1.40. The magnitude of factor from the formula (3) is close to that of the magnitude of factor from the formula (1), but it would be prefer to model the defect by the formula (3). Moreover the simulation result and experimental report was also support for the formula (3).^{19),20)} We believe that the Sr cation might occupy both the A and the B-site of the $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system when doped with excess alkaline earth element, and that, as shown in the formulas (4)–(7), the cation stoichiometry $[(x+y+0.50) : \text{In} = 1 : 1]$ would be maintained.

The defect equilibrium reactions affect the generation of

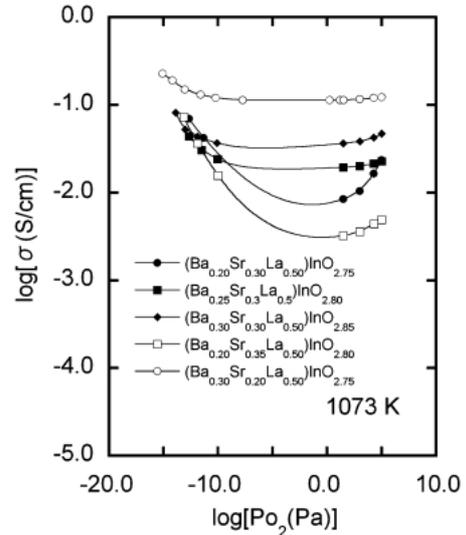
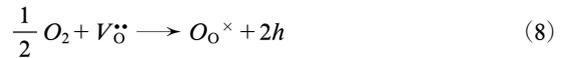
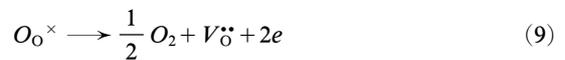


Fig. 4. Electrical conductivity of $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system with excess BaO or SrO as a function of oxygen partial pressure.

the conducting carrier. In the $(\text{Ba}_{1-y}\text{La}_y)\text{InO}_{2.50+y/2}$ system, hole conductivity was reported to appear in the high oxygen partial pressure region by the following defect equilibrium reactions:⁴⁾



In the low oxygen partial pressure region, electron conductivity was also reported to appear:



Because the oxide ion conductivity is sensitive to crystallographic properties, the total electrical conductivity of the $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.75}$ system should change with the degree of excess BaO or SrO content. We measured the electrical conductivity of the excess-doped system at 1073 K as a function of the oxygen partial pressure; the results appear in Fig. 4.

In the high oxygen partial pressure region, the slope for the $(\text{Ba}_{0.20}\text{Sr}_{0.30}\text{La}_{0.50})\text{InO}_{2.75}$ system approached the value of 1/4, suggesting that the defect reaction of formula (8) does apply in this system. In the low oxygen partial pressure region, the slope was most consistent with that of formula (9). It was also confirmed that the hole and electron was dominant conducting carrier in $(\text{Ba}_{0.20}\text{Sr}_{0.30}\text{La}_{0.50})\text{InO}_{2.75}$ system. But, with doping BaO, the plateau region of electrical conductivity against oxygen partial pressure appeared in $(\text{Ba}_{0.20}\text{Sr}_{0.30}\text{La}_{0.50})\text{InO}_{2.75}$ system. In the case of the other $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system with excess BaO or SrO, the oxide-ion conductivity decreased and the pure oxide-ion conducting region narrowed with excess dopant content.

The Arrhenius plots of the conductivity for these systems under an Ar atmosphere ($\log [P_{\text{O}_2}(\text{Pa})] = 1.5$), where Fig. 5 shows that the main conducting carrier of this system was the oxide ion, are shown in Figs. 6(a)–(c). The plots are straight against the reciprocal temperature. Each activation energy was 80–90 kJ/mol, values which were very close to that of other oxide ion conductors.²²⁾ Presumably, the oxygen vacancy is in a disordered state, which differs from the situation in the $\text{Ba}_2\text{In}_2\text{O}_5$ mother substrate.

The compositional dependence of the oxide ion conductivity

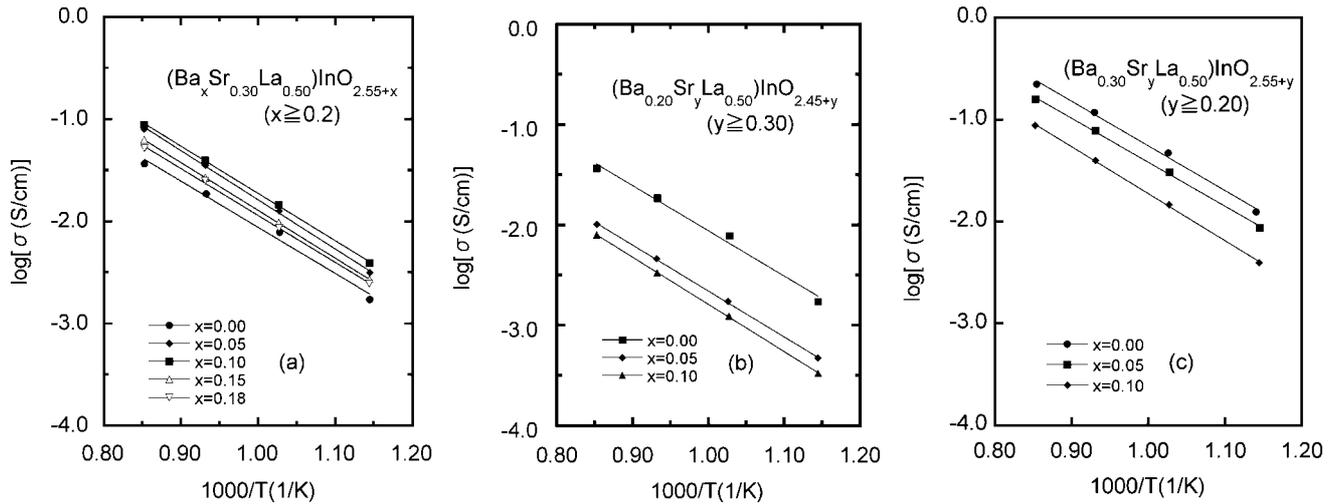


Fig. 5. Arrhenius plots of oxide-ion conductivity of $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system with excess BaO or SrO. (a) $\text{Ba}_x\text{Sr}_{0.30}\text{La}_{0.50}\text{InO}_{2.55+x}$, (b) $\text{Ba}_{0.20}\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.45+y}$, (c) $\text{Ba}_{0.30}\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.55+y}$

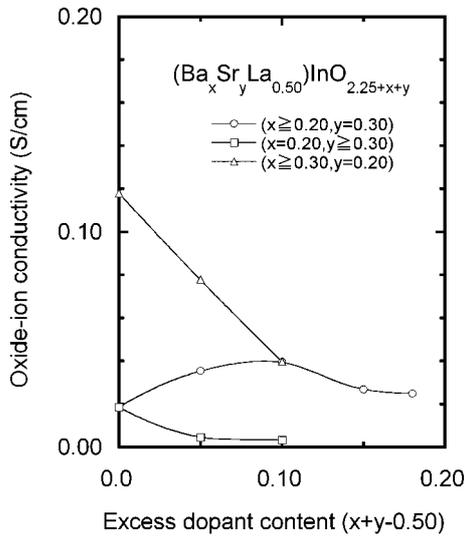


Fig. 6. Oxide ion conductivity at 1073 K as a function of excess dopant content.

at 1073 K is plotted in Fig. 6. The oxide ion conductivity of the $(\text{Ba}_{0.20}\text{Sr}_{0.30}\text{La}_{0.50})\text{InO}_{2.75}$ system increased with excess BaO doping up to $x=0.1$ and then decreased. The oxide ion conductivity of the other two systems decreased with excess dopant content. Although the oxygen content of the $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system increased monotonically with excess alkaline earth oxide dopant agreement with formulas (4)–(7), the compositional dependency of oxide ion conductivity was different in each case.

The oxide ion conductivity of an excess doped system might be influenced not only by the oxygen content, but also by other factors. Several authors have discussed important parameters of the oxide ion conductivity in perovskites. Nomura and Tanase reported that the activation energy of oxide ion conductivity was strongly dependent on both the unit cell free volume and the tolerance factor in the $(\text{La}_{0.9}\text{Sr}_{0.1})\text{M}^{\text{III}}\text{O}_{3-\delta}$ ($\text{M}^{\text{III}} = \text{Al}, \text{Ga}, \text{Sc}, \text{In}$ and Lu) system.²³ A similar result for oxide ion conductivity of the $\text{A}^{\text{III}}\text{B}^{\text{III}}\text{O}_3$ system was also reported by Hayashi et al.²⁴ Yao et al. investi-

gated the perovskite-related oxide $\text{Ba}(\text{In}_{1-x}\text{Ga}_x)\text{O}_{2.5}$, and highlighted the relationship between the oxide-ion conductivity and the saddle point of the perovskite oxide.⁸

We have also reported that the oxide-ion conductivity of $(\text{Ba}_{0.50-y}\text{Sr}_y\text{La}_{0.50})\text{InO}_{2.75}$ was strongly dependent on the crystal symmetry, oxygen content and unit cell free volume.^{12),20),25} In the cubic symmetry material, the oxide ion conductivity of the system initially increased with the unit cell free volume. But, it showed a maximum value at a free volume of 0.0243 nm^3 and then decreased, because of a reduction in the crystal symmetry.

In the excess-doped system, the unit cell free volume was calculated based on the crystal model as shown in the formulas (4)–(7) by formula (10).

$$\text{Unit cell free volume} = a^3 - \sum_i m_i \frac{4}{3} \pi r_i^3, \quad (10)$$

where a is the lattice parameters shown in Fig. 4, m_i is the chemical composition ratio of an ion, and r_i is the ionic radii reported by Shannon.²⁶ The calculated unit cell free volume was shown in Fig. 7 as a function of the content of excess doped alkaline earth oxide. The unit cell free volume increased with content of alkaline earth element ($x+y$). In case of the reaction of formulas (4)–(8), the oxygen vacancy increases with alkaline earth element. The lattice parameter also increased with the element as shown in Fig. 4. The result would suggest that the unit cell free volume strongly affected with the lattice parameter and oxygen vacancy.

The oxide ion conductivity of the excessively doped system as a function of unit cell free volume is shown in Fig. 8. In the same figure, the unit cell free volume dependence of the oxide ion conductivity in the $(\text{Ba}_{0.50-y}\text{Sr}_y\text{La}_{0.50})\text{InO}_{2.75}$ and $(\text{Ba}_{0.50}\text{La}_{0.50})\text{InO}_{2.75}$ systems are shown by dotted lines. We found that the behavior of the oxide ion conductivity for the $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system with excess BaO or SrO were similar to that of the stoichiometric $(\text{Ba}_{0.50-y}\text{Sr}_y\text{La}_{0.50})\text{InO}_{2.75}$ and $(\text{Ba}_{0.50}\text{La}_{0.50})\text{InO}_{2.75}$ systems. Where the oxide ion conductivity of the excess doped system decreased with an increasing unit cell free volume, the XRD peaks broadened, as shown in Fig. 1. We conclude that the crystal symmetry changed from cubic to pseudo-cubic with increasing excess alkaline earth oxide, and this lower crystal symmetry decreased the oxide ion

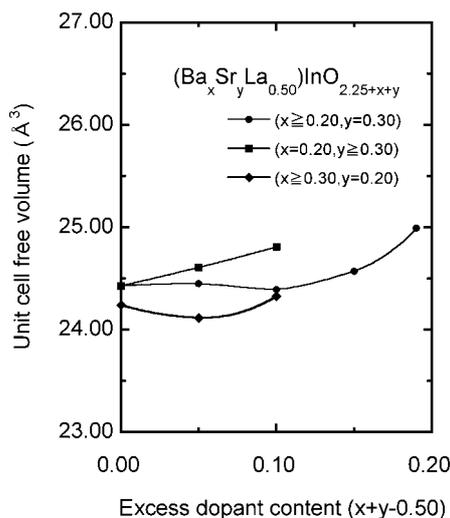


Fig. 7. Unit cell free volume as a function of excess dopant content.

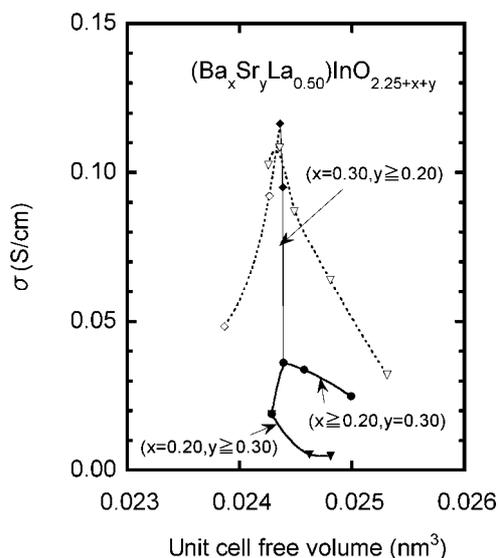


Fig. 8. Oxide ion conductivity at 1073 K as a function of unit cell free volume. The oxide ion conductivity of $(\text{Ba}_{0.50-y}\text{Sr}_y\text{La}_{0.50})\text{InO}_{2.75}$ (\diamond) and $(\text{Ba}_{0.30}\text{Sr}_{0.20}\text{La}_{0.50})(\text{In}_{1-z}\text{Y}_z)\text{O}_{2.75}$ (∇) are shown as a reference.²⁵⁾

conductivity.

4. Conclusion

We have investigated the crystal phase and electrical conductivity of $\text{Ba}_x\text{Sr}_y\text{La}_{0.50}\text{InO}_{2.25+x+y}$ system with excess BaO or SrO. From the Rietveld analysis of the XRD pattern, the cation stoichiometry $[(x+y+0.50) : \text{In} = 1 : 1]$ is maintained by the movement of a Sr ion from the A-site to the B-site, even when there is excess alkaline earth oxide doped into the system. The oxide ion conductivity was strongly dependent on the excess content of the alkaline earth element. The unit cell free volume dependence of the oxide ion conductivity was found to be similar to that of the stoichiometric $(\text{Ba}_{0.50-y}\text{Sr}_y\text{La}_{0.50})\text{InO}_{2.75}$ and $(\text{Ba}_{1-y}\text{La}_y)\text{InO}_{2.50+y/2}$ systems.

Acknowledgement This study was supported by the High Technology Research Project at Kanagawa University from the Ministry of Education, Science, Sports and Culture and by a Grant-in-Aid for Scientific Research from the same Ministry.

References

- 1) Zacate, M. O., Minervini, L., Bradfield, D. J., Grimes, R. W. and Sickafus, K. E., *Solid State Ionics*, Vol. 128, pp. 243–254 (2000).
- 2) Akikusa, J., Adachi, K., Hoshino, K., Ishihara, T. and Takita, Y., *J. Electrochem. Soc.*, Vol. 148, pp. A1275–A1278 (2001).
- 3) Aizumi, Y., Takamura, H., Kamegawa, A. and Okada, M., *J. Ceram. Soc. Japan*, Suppl., Vol. 112, pp. S724–S728 (2004).
- 4) Kakinuma, K., Arisaka, T., Yamamura, H. and Atake, T., *Solid State Ionics*, Vol. 175, pp. 139–143 (2004).
- 5) Ishihara, T., Matsuda, H. and Takita, Y., *J. Am. Chem. Soc.*, Vol. 116, pp. 3801–3803 (1994).
- 6) Ishihara, T., Furutani, H., Arikawa, H., Honda, M., Akbay, T. and Takita, Y., *J. Electrochem. Soc.*, Vol. 146, pp. 1643–1649 (1999).
- 7) Kakinuma, K., Yamamura, H., Haneda, H. and Atake, T., *J. Thermal. Anal. Calorimetry*, Vol. 57, pp. 737–743 (1999).
- 8) Yao, T., Uchimoto, Y., Kinuhata, M., Inagaki, T. and Yoshida, H., *Solid State Ionics*, Vol. 132, pp. 189–198 (2000).
- 9) Yamamura, H., Nishino, H., Kakinuma, K. and Nomura, K., *J. Ceram. Soc. Japan*, Vol. 111, pp. 902–906 (2003).
- 10) Nishino, H., Yamamura, H., Arai, T., Kakinuma, K. and Nomura, K., *J. Ceram. Soc. Japan*, Vol. 112, pp. 541–546 (2004).
- 11) Kakinuma, K., Yamamura, H., Haneda, H. and Atake, T., *Solid State Ionics*, Vol. 140, pp. 301–306 (2001).
- 12) Kakinuma, K., Yamamura, H., Haneda, H. and Atake, T., *Solid State Ionics*, Vol. 154–155, pp. 571–576 (2002).
- 13) Stevenson, J. W., Armstrong, T. R., Pederson, L. R., Li, J., Lewinsohn, C. A. and Baskaran, S., *Solid State Ionics*, Vol. 113–115, pp. 571–583 (1998).
- 14) Ma, G., Matsumoto, H. and Iwahara, H., *Solid State Ionics*, Vol. 122, pp. 237–247 (1999).
- 15) Stevenson, J. W., Hallmann, P. F., Armstrong, T. R. and Chick, L. A., *J. Am. Ceram. Soc.*, Vol. 78, pp. 507–512 (1995).
- 16) Guan, J., Dorris, S. E., Balachandran, U. and Liu, M., *J. Electrochem. Soc.*, Vol. 145, pp. 1780–1786 (1998).
- 17) Shima, D. and Haile, S. M., *Solid State Ionics*, Vol. 97, pp. 443–455 (1997).
- 18) Kakinuma, K. and Fueki, K., *Solid State Commun.*, Vol. 105, pp. 173–177 (1998).
- 19) Levy, M. R., Steel, B. C. H. and Grimes, R. W., *Solid State Ionics*, Vol. 175, pp. 349–352 (2004).
- 20) Kakinuma, K., Takahashi, N., Yamamura, H., Nomura, K. and Atake, T., *Solid State Ionics*, Vol. 168, pp. 69–74 (2004).
- 21) Speakman, S. A., Richardson, J. W., Mitchell, B. J. and Misture, S. T., *Solid State Ionics*, Vol. 149, pp. 247–259 (2002).
- 22) Tianshu, Z., Hing, P., Huang, H. and Kilner, J., *Solid State Ionics*, Vol. 148, pp. 567–573 (2002).
- 23) Nomura, K. and Tanase, S., *Solid State Ionics*, Vol. 98, pp. 229–236 (1997).
- 24) Hayashi, H., Inaba, H., Matsushita, M., Lan, N. G., Dokiya, M. and Tagawa, H., *Solid State Ionics*, Vol. 122, pp. 1–15 (1999).
- 25) Kakinuma, K., Yamamura, H. and Atake, T., *J. Thermal Anal. and Calorimetry*, Vol. 69, pp. 897–904 (2002).
- 26) Shannon, R. D., *Acta Cryst.*, Vol. A32, pp. 751–753 (1976).