Analysis of crystal structure and phase relationship of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ by high temperature synchrotron X-ray diffraction and thermal analyses — Control of electrical conductivity and crystal structure by concentration of oxide ion vacancy

Takuya HASHIMOTO,[†] Takayuki SUGIMOTO, Kazuki OMOTO, Masashi YOSHINAGA, Masahiko TANAKA* and Masatomo YASHIMA**

Department of Integrated Sciences in Physics and Biology, College of Humanities and Sciences, Nihon University, Sakurajousui, Setagaya-ku, Tokyo 156–8550

*NIMS Beamline Station at Spring-8, National Institute for Materials Science, Sayo, Hyogo 679–5198

**Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuda, Yokohama 226–8502

Phase relationship of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ has been investigated by using dilatometry, differential scanning calorimetry and synchrotron X-ray diffraction at high temperatures. Decrease of the temperature of the first order phase transition, from brownmillerite orthorhombic to tetragonal, was observed with an increase of La content in $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ for $x = 0.0–0.2$, whereas little variation was detected on temperature of the second order phase transition, from tetragonal to distorted cubic, in the specimens with $x = 0.0–0.3$. $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with x larger than 0.4 showed no phase transition by temperature. Crystal structure of the specimens with $0.4 \leq x \leq 1.0$, $1.2 \leq x \leq 1.7$ and $x = 2.0$ were ideal cubic, tetragonal and orthorhombic distorted perovskite, respectively. $\text{Ba}_{1.3}\text{La}_{0.7}\text{In}_2\text{O}_{5+\delta}$ with ideal cubic perovskite structure showed higher oxide ion conductivity below 800°C than that of $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ with distorted cubic structure, supporting that removal of the structural distortion should be effective to improve mobility of oxide ion, resulting in as high oxide ion conductivity as that of yttria stabilized zirconia.

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Key-words : $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$, Synchrotron X-ray diffraction, Thermal expansion, Differential scanning calorimetry, Phase relationship, Oxide ion conductor

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1. Introduction

$\text{Ba}_2\text{In}_2\text{O}_5$ exhibits higher oxide ion conductivity than that of yttria stabilized zirconia (YSZ) above 910°C.⁽¹⁾ It has been recognized that the high oxide ion conductivity in $\text{Ba}_2\text{In}_2\text{O}_5$ above 910°C is due to random distribution of oxide ion vacancy in the perovskite structure.⁽²⁾ If the random distribution of oxide ion vacancy could be maintained to low temperatures, $\text{Ba}_2\text{In}_2\text{O}_5$ might be an alternative material for YSZ, which is widely employed as an electrolyte of solid oxide fuel cells, gas sensors and so on. However, brownmillerite phase with ordered oxide ion vacancy and low oxide ion conductivity is stable for $\text{Ba}_2\text{In}_2\text{O}_5$ below 910°C. In order to stabilize the high temperature perovskite phase, partial cation substitution has been investigated. It was reported that the phase transition temperature decreased with Ga^{3+} substitution for In^{3+} site,^(3–5) probably because the tolerance factor for ideal perovskite structure approached 1 with Ga substitution; however, a slight distortion from ideal cubic perovskite exists in crystal structure of $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ at high temperatures⁽⁶⁾ and the phase transition temperature could not be reduced below 780°C.⁽⁵⁾ One of the possible reasons of distortion from the ideal cubic perovskite and phase transition temperature above 780°C

for $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ system should be an amount of oxide ion vacancy as high as 1/6, which is excess as an ideal cubic perovskite structure, as also proposed by Kakinuma et al.⁽⁷⁾ It can be regarded that an increase of oxygen content should be required to remove the distortion and stabilize the perovskite structure, which might result in a higher oxide ion conductivity at low temperatures. One possible method to decrease oxide ion vacancy is the substitution of the trivalent ion, such as La^{3+} , for Ba^{2+} site.

The crystal structure, electrical conductivity and property as an electrolyte of SOFC of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ have been examined by several groups. Uchimoto et al.⁽⁸⁾ and Kakinuma et al.⁽⁷⁾ reported cubic perovskite structure of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with x more than 0.4 and 1.0, respectively, at room temperature and improvement of oxide ion conductivity below 900°C by La^{3+} substitution. Mitome et al.⁽⁹⁾ concluded that crystal structure of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ at room temperature varied from orthorhombic through tetragonal to cubic with an increase of x from electron diffraction analysis. However, there has been no report which analyzes the variation of crystal structure on not only La^{3+} content but also temperature, which should be important information of the application of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ system. In addition, distortion from cubic structure in cation substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system is so small that so far employed diffraction measurements using $\text{Cu K}\alpha$ radiation or electron might fail to observe minor signals, which indicate the distortion, due to deficient sensitivity and

[†] Corresponding author: T. Hashimoto; E-mail: takuya@chs.nihon-u.ac.jp

resolution.⁶⁾

In this study, the structural phase relationship of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ system has been analyzed by using thermal analyses, such as differential scanning calorimetry (DSC) and dilatometry, and high temperature X-ray diffraction. In order to detect small deviations from ideal cubic perovskite structures, X-ray from a synchrotron light source has also been employed for diffraction measurements.⁶⁾

2. Experimental

$\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ specimens were prepared with the solid state reaction method. The nominal amount of BaCO_3 (99.9%, Furuuchi Chem. Corp.), In_2O_3 (99.9%, Furuuchi Chem. Corp.) and La_2O_3 (99.9%, Furuuchi Chem. Corp.) powder were mixed in ethanol with alumina mortar. Prior to mixing, BaCO_3 and In_2O_3 were dried at 100°C for more than 12 h in air and La_2O_3 was heated at 1000°C for more than 12 h in air to decompose impurities such as $\text{La}(\text{OH})_3$ and $\text{La}_2(\text{CO}_3)_3$. The mixed powder was calcined at 800°C for 24 h in air, followed by being uniaxially pressed into a cylindrical shape with $5\text{ mm}\phi \times 13\text{--}18\text{ mm}$ height. The prepared pellets were sintered at 1400°C for 17 h in air. To obtain single phase, the sintered pellets were pulverized, pressed into cylindrical shapes with the same size and heated at 1400°C for 17 h in air, again.

In order to investigate crystal structure of obtained $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ at room temperature, X-ray diffraction measurements were carried out using Cu $K\alpha$ radiation (50 kV, 250 mA, Rigaku Co., Ltd.: RINT-2500). For some specimens, synchrotron X-ray diffraction measurements were performed at high temperatures in air using originally designed furnace equipped at BL-3A, Photon Factory, KEK.¹⁰⁾ The wavelength of the synchrotron X-ray was 90.06 pm calibrated by diffraction peaks of CeO_2 .

Fig. 1. Cu $K\alpha$ X-ray diffraction patterns of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ($x = 0.0\text{--}1.0$) at room temperature. Diffraction pattern of $\text{Ba}_2\text{In}_2\text{O}_5$ can be indexed as orthorhombic brownmillerite structure. Diffraction pattern of $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$ can be indexed as tetragonal symmetry with $a = c = \sqrt{2}b/4 \approx 5.9\text{ \AA}$, showing agreement with the results of electron diffraction measurements.⁹⁾ Diffraction patterns of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with $x = 0.5\text{--}1.0$ can be indexed as ideal cubic perovskite. The peaks represented by a closed circle indicate slight distortion from ideal cubic.

For analyses of phase transition at high temperatures, thermal expansion behaviors of sintered specimens between room temperature and 1300°C in air were measured with dilatometry using TMA8310 (Rigaku Co., Ltd.). Al_2O_3 was used for reference, sample stage and push rod. The heating rate was $10^\circ\text{C}/\text{min}$. Also measured were the DSC of powder $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ specimens by using DSC8270 (Rigaku Co., Ltd.) between room temperature and 1200°C in air. Pt and Al_2O_3 powder were employed as pan and reference, respectively. The heating rate was $10^\circ\text{C}/\text{min}$.

Temperature dependence of electrical conductivity of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ sintered specimens was measured with dc four probe method in air. Pt was used as a material for electrode and lead wire. By comparison with phase relationships obtained by thermal analysis and high temperature X-ray diffraction, the effect of structural phase transition on oxide ion conductivity was analyzed.

3. Results and discussion

3.1 Crystal structure of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ at room temperature

Figure 1 shows Cu $K\alpha$ X-ray diffraction patterns of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ($x = 0.0\text{--}1.0$) at room temperature. Diffraction pattern of $\text{Ba}_2\text{In}_2\text{O}_5$ can be indexed as orthorhombic brownmillerite structure, which agreed with the preceding studies.^{2),5),6)} With substitution of La^{3+} for Ba^{2+} site, a decrease of the number of diffraction peaks were observed for the specimens with x below 1.0, indicating a higher crystal symmetry. Diffraction pattern of $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$ can be indexed as tetragonal symmetry with $a = c = \sqrt{2}b/4 \approx 5.9\text{ \AA}$, showing agreement with the results of electron diffraction measurements.⁹⁾ Diffraction patterns of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with $x = 0.5\text{--}1.0$ can be indexed as ideal cubic perovskite, suggesting random distribution of oxide ion vacancy. However, the reduction of crystal symmetry was observed for La^{3+} substitution more than 1.0 as shown in Fig. 2.

Fig. 2. Cu $K\alpha$ X-ray diffraction patterns of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ($x = 1.0\text{--}2.0$) at room temperature. The pattern of the specimen with $x = 2.0$ can be indexed as orthorhombic distorted perovskite.¹¹⁾ The patterns of $x = 1.2\text{--}1.7$ can be indexed as tetragonally distorted perovskite.

Fig. 3. Thermal expansion and expansion behavior of sintered $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ($x = 0.0$ – 1.0). The solid and dashed arrows represent the first order phase transition and the second order one, respectively.

In diffraction patterns of $x = 1.2$ – 1.7 , the peak which could not be indexed as cubic was observed and its intensity increased with an increase of x . It was suggested that cubic symmetry varied to tetragonal with an increase of x to 1.2 – 1.7 . The symmetry of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ reduced to orthorhombic with a further increase of x . The diffraction pattern of $\text{La}_2\text{In}_2\text{O}_6$ could be indexed as GdFeO_3 type orthorhombic, as reported in the literature.¹¹⁾

Apparent cubic structure of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with $x = 0.5$ – 1.0 at room temperature suggested that these specimens were promising as an oxide ion conductor due to random distribution of oxide ion vacancy if the crystal structure was maintained at higher temperatures. For assessment of crystal structure and potential as an oxide ion conductor, analysis of structural phase transition behavior of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ using thermal analyses and diffraction measurements at high temperatures using synchrotron X-ray have been carried out.

3.2 Analysis of phase transition behavior of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with dilatometry and DSC

Figure 3 shows thermal expansion behaviors and expansion coefficients of sintered $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with $x = 0.0$ – 1.0 . As was already reported,¹²⁾ abrupt shrinkage corresponding to the first order structural phase transition was observed at about 900°C as depicted by arrows in thermal expansion of $\text{Ba}_2\text{In}_2\text{O}_5$. In the thermal expansion coefficient, which is temperature differential of thermal expansion, another second order phase transition was observed as a base line shift at 1070°C besides the peak around 900°C corresponding to the first order phase transition. With La^{3+} substitution, temperature and the shrinkage of the first order structural phase decreased and disappeared for $\text{Ba}_{1.7}\text{La}_{0.3}\text{In}_2\text{O}_{5+\delta}$, whereas almost a constant second order phase transition temperature was observed for $x = 0.0$ – 0.3 . For the specimens with x larger than 0.4 , no phase transition was observed as shown in Fig. 3. In the specimens with x larger than 1.0 where tetragonal or orthorhombic perovskite structure is stable, no phase transi-

Fig. 4. Thermal expansion and expansion behavior of sintered $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ($x = 1.0$ – 2.0). No phase transition was observed.

tion was observed in thermal expansion behavior as shown in Fig. 4.

DSC curves depicted in Figs. 5 and 6 showed agreement with the results obtained with dilatometry. In $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with $x = 0.0$ – 0.2 , endothermic peaks were observed corresponding to the first order phase transition. The temperature and variation of enthalpy, ΔH , calculated from the peak area reduced with an increase of x . The second order phase transition, observed as a base line shift, was observed for the specimens with $x = 0.0$ – 0.3 . The temperature of the second order phase transition showed little dependence of La content. No phase transition was observed for the specimens with x larger than 0.4 .

3.3 Analysis of structure and phase relationship of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with synchrotron X-ray diffraction

In the preceding paper, we have concluded that the distortion

from ideal cubic perovskite is so slight in the high temperature phase of $\text{Ba}_2\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ that misidentification of their crystal structure as ideal cubic has been reported by using

Fig. 5. DSC curves of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ($x = 0.0$ – 1.0). The solid and dashed arrows represent the first order phase transition and the second order one, respectively.

$\text{Cu K}\alpha$ X-ray diffraction. Since it has been also concluded that X-ray diffraction with higher sensitivity and resolution is necessary to distinguish crystal structure of cation substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system,⁶⁾ synchrotron X-ray diffraction measurements were performed on $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ at various temperatures.

Figure 7 shows synchrotron X-ray diffraction patterns of (a) $\text{Ba}_2\text{In}_2\text{O}_5$, (b) $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$ and (c) $\text{Ba}_{1.3}\text{La}_{0.7}\text{In}_2\text{O}_{5+\delta}$ at various temperatures. X-ray diffraction pattern of $\text{Ba}_2\text{In}_2\text{O}_5$ at 700°C could be indexed as brownmillerite orthorhombic symmetry. The diffraction pattern of $\text{Ba}_2\text{In}_2\text{O}_5$ at 1000°C was different from that of 700°C , corresponding to the first order structural phase transition. The almost diffraction peaks at 1000°C could be indexed as tetragonal structure with $a = c = \sqrt{2}b/4 \approx 5.9 \text{ \AA}$, suggesting the same phase as $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_5$ at room temperature. For the diffraction pattern of $\text{Ba}_2\text{In}_2\text{O}_5$ at 1200°C , which was above the sec-

Fig. 6. DSC curves of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ($x = 1.0$ – 2.0). No phase transition was observed.

Fig. 7. Synchrotron X-ray diffraction patterns of (a) $\text{Ba}_2\text{In}_2\text{O}_5$, (b) $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$ and (c) $\text{Ba}_{1.3}\text{La}_{0.7}\text{In}_2\text{O}_{5+\delta}$ at various temperatures. Miller indices were assigned as orthorhombic brownmillerite for (a) at 700°C , tetragonal for (a) at 1000°C and (b) at 550°C and 900°C . Ideal cubic perovskite structure was assumed for indexing Miller indices for the other diffraction patterns. Closed circles represent peaks which cannot be assigned by above described crystal symmetry.

ond order phase transition, minor peaks were observed besides the peaks indexed as ideal cubic, indicating that crystal structure of $\text{Ba}_2\text{In}_2\text{O}_5$ above the second order phase transition was distorted cubic perovskite.

For diffraction pattern of $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$, almost all peaks could be indexed as the tetragonal symmetry at 550°C, however, peaks which could not be indexed as tetragonal was also observed. These peaks could not be observed with Cu K α X-ray diffraction measurements due to deficient sensitivity and resolution. Since the Bragg angles of the extra peaks were similar to those of brownmillerite, we suspect that $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$ below 550°C might be a mixture of tetragonal and orthorhombic phase. Also it was suspected that Cu K α X-ray diffraction pattern of $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$ at room temperature (Fig. 1) could be apparently indexed to tetragonal single phase although it contained orthorhombic brownmillerite phase. The diffraction pattern at 930°C, which was higher than that of the first order phase transition, could be indexed as tetragonal symmetry, indicating that remained brownmillerite phase changed to tetragonal phase at the first order phase transition. Almost all the diffraction peaks of $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$ at 1200°C could be indexed as ideal cubic perovskite; however, minor peaks, indicating distortion from ideal cubic structure, were observed although its number and intensity decreased compared with diffraction pattern of $\text{Ba}_2\text{In}_2\text{O}_5$ at 1200°C.

All the diffraction patterns of $\text{Ba}_{1.3}\text{La}_{0.7}\text{In}_2\text{O}_5$ from 550°C to 1200°C could be indexed assuming ideal cubic perovskite structure, showing agreement with no phase transition in this composition. No minor peaks, indicating distortion from ideal cubic structure, supported expectation that a decrease of concentration of oxide ion vacancy by La^{3+} substitution should be effective to stabilize cubic structure with random distribution of oxide ion vacancy.

3.4 Phase relationship of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ and electrical conductivity

Figure 8 shows phase relationship of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ proposed in this study. For the specimens with low La content, brownmillerite type orthorhombic phase, depicted as “I” in Fig. 8, is stable below the first order phase transition. Above the first order phase transition, tetragonal phase depicted as “II” is stable, whereas crystal structure changes distorted cubic, denoted as phase III, above the second order phase transition. With an increase of La content up to 0.2, temperature of the first order phase transition decreases to about 600°C. In the region of x around 0.2 below 600°C, mixture of phase I and II is stable. For the specimen with x around 0.3, phase II is stable between room temperature and 1050°C resulting in the absence of the first order phase transition. On the contrary, the temperature of the second order phase transition is scarcely affected by La content. A further increase of La content, x between 0.4 and 1.0 changes crystal structure to ideal cubic, denoted as phase IV in Fig. 8. Phase IV, which is stable between room temperature and 1200°C, is different from phase III since it is free from distortion from ideal cubic perovskite. Figure 8 also depicts the results of synchrotron X-ray diffraction shown in Fig. 7, showing agreement with the proposed phase relationship.

Assuming that valences of Ba, La and In in $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ are maintained at 2+, 3+ and 3+, respectively, δ can be estimated. Especially in phase III and IV with perovskite structure, the concentration of oxide ion vacancy can be evaluated. Since number and intensity of extra diffraction peaks, indicating distortion from ideal cubic perovskite, decreased with an increase of La content as shown in diffraction patterns of $\text{Ba}_2\text{In}_2\text{O}_5$ and

$\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5.1}$ at 1200°C (Fig. 7), it was concluded that distortion from ideal cubic perovskite in phase III reduced with an increase of La content from 0.0 to 0.2, *i. e.*, reduction of concentration of oxide ion vacancy from 16.7% to 15%. A further increase of La content up to $x = 0.7$, *i. e.*, reduction of concentration of oxide ion vacancy to 10.8%, stabilized phase IV with ideal cubic perovskite structure from room temperature to 1200°C, indicating that reduction of concentration of oxide ion vacancy was effective to remove structural distortion from ideal cubic perovskite structure as prospected by Kakinuma and coworkers.⁷⁾ Further increase of x induces a reduction of crystal symmetry, resulting in tetragonal and orthorhombic distorted perovskite, denoted as phase V and VI, respectively with less oxide ion vacancy.

Since phase IV is stable from room temperature to 1200°C and its crystal symmetry is cubic with random distribution of oxide ion vacancy whose concentration is relatively high, it was prospected that $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with $x = 0.7$ –1.0 is promising as an oxide ion conducting material. Figure 9 shows temperature dependence of electrical conductivity, σ , of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$. Almost Arrhenius type temperature dependence of electrical conductivity was observed for every specimen, showing agreement with the preceding studies.^{7,8)} For $\text{Ba}_2\text{In}_2\text{O}_5$, an abrupt increase of σ at 910°C and variation of activation energy at 1070°C due to first order and second order phase transition, respectively, were observed as already reported in other literature.^{1),5)} For $\text{Ba}_{1.8}\text{La}_{0.2}\text{In}_2\text{O}_{5+\delta}$, a smaller increase of σ due to the first order phase transition was observed at 600°C. With a further increase of La content to 0.4 and 0.7, an abrupt increase of σ and variation of activation energy disappeared, showing agreement with the phase relationship depicted in Fig. 8. $\text{Ba}_{1.3}\text{La}_{0.7}\text{In}_2\text{O}_{5+\delta}$ with ideal cubic perovskite structure showed the compatible electrical conductivity with that of yttria stabilized zirconia below 800°C, as was also reported by Kakinuma et al.,⁷⁾ and Uchimoto et al.⁸⁾ In addition, the electrical conductivity was more than one

Fig. 8. Phase relationship of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ proposed in this study.

- I: brownmillerite orthorhombic (represented by open square),
- II: tetragonal phase (represented by open triangle),
- III: distorted cubic (represented by open circle),
- IV: ideal cubic perovskite (represented by closed circle),
- V: tetragonal distorted perovskite,
- VI: orthorhombic distorted perovskite.

The symbols represent the temperature and composition, the crystal structures of which were confirmed by synchrotron X-ray diffraction in this study.

Fig. 9. Temperature dependence of electrical conductivity of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ ceramics. $\text{Ba}_{1.3}\text{La}_{0.7}\text{In}_2\text{O}_{5+\delta}$ with ideal cubic structure showed the highest conductivity below 800°C , which is compatible with that of yttria stabilized zirconia.

order higher than that of $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ ⁶⁾ with distorted perovskite structure, supporting that removal of the structural distortion should be effective to improve mobility of oxide ion.

4. Conclusions

The phase relationship on La content and temperature of $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ has been proposed with thermal analyses and synchrotron X-ray diffraction. Decrease of the temperature of the first order phase transition, from brownmillerite orthorhombic to tetragonal, was observed with an increase of La content in $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ for $x = 0.0\text{--}0.2$, whereas little variation was detected on temperature of the second order phase transition, from tetragonal to distorted cubic, in the specimens with $x = 0.0\text{--}0.3$. $\text{Ba}_{2-x}\text{La}_x\text{In}_2\text{O}_{5+\delta}$ with x larger than 0.4 showed no phase tran-

sition by temperature. Crystal structure of the specimens with $0.4 \leq x \leq 1.0$, $1.2 \leq x \leq 1.7$ and $x = 2.0$ were ideal cubic, tetragonal and orthorhombic distorted perovskite, respectively.

$\text{Ba}_{1.3}\text{La}_{0.7}\text{In}_2\text{O}_{5+\delta}$ with ideal cubic perovskite structure showed higher oxide ion conductivity below 800°C than that of $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ with distorted cubic structure. It can be regarded that the removal of the structural distortion should be effective to improve mobility of oxide ion, resulting in compatible conductivity with that of yttria stabilized zirconia.

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