Structural analysis of oxide ion conductor, $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ — Significance of synchrotron X-ray diffraction at high temperatures

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High temperature synchrotron X-ray diffraction measurements have been performed on $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$, which exhibits two kinds of structural phase transition and high oxide ion conductivity at the high temperature phase. It has been revealed that the synchrotron X-ray diffraction with high sensitivity and resolution is necessary to detect any slight distortion from ideal cubic perovskite in cation substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system. By using synchrotron X-ray diffraction, the slight distortion from ideal cubic perovskite in $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$, which could not be observed by using Cu K α X-ray diffraction, has been clarified. The larger and smaller distortions have been observed with an increase of Sr and Ga content, respectively, which can be explained from the viewpoint of variation of the tolerance factor.

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1. Introduction

Oxide ion conductor, which can be operated at temperatures below 600°C, has been desired for application to solid oxide fuel cells, gas sensors and so on. One of the candidate materials is structure-controlled $\text{Ba}_2\text{In}_2\text{O}_5$ system. $\text{Ba}_2\text{In}_2\text{O}_5$ shows low oxide ion conductivity below 910°C, however, an abrupt increase of oxide ion conductivity, which is higher than that of yttria stabilized zirconia (YSZ) is observed at 910°C.¹⁾ It was reported that the increase of oxide ion conductivity could be ascribed to the first order structural phase transition; ordered distribution of oxide ion vacancies in $\text{Ba}_2\text{In}_2\text{O}_5$ with brownmillerite structure varied to disordered one in $\text{Ba}_2\text{In}_2\text{O}_5$ with ideal cubic perovskite structure at 910°C.²⁾ It was proposed that if the high oxide ion conductivity originating from the random distribution of oxide ion vacancies in “ideal” perovskite structure above 910°C could be maintained to lower temperatures, $\text{Ba}_2\text{In}_2\text{O}_5$ system might be an alternative material for YSZ. However, the so far proposed ideal cubic structure of $\text{Ba}_2\text{In}_2\text{O}_5$ at a high temperature is wrong. Some of the authors have established another second order structural phase transition at 1070°C, which was proposed with ¹⁷O-NMR measurements,³⁾ by thermal analyses and high temperature Cu K α X-ray diffraction⁴⁾ and reported that crystal structure of $\text{Ba}_2\text{In}_2\text{O}_5$ between 910–1070°C was not ideal cubic but distorted perovskite. Also reported was that the distortion from ideal cubic perovskite was diminished but maintained even above 1070°C by using Cu K α X-ray diffraction with high intensity.⁴⁾

In order to improve oxide ion mobility in $\text{Ba}_2\text{In}_2\text{O}_5$ system, we prospect that cubic structure with a perfect random oxide ion distribution should be desired.

As a probable method to remove the structural distortion from cubic structure without varying concentration of oxide ion vacancies, preparation and characterization of partially substituted specimens by isovalent cation, such as $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$,^{5),6)} $\text{Ba}_2\text{In}_{2-x}\text{Re}_x\text{O}_5$ (Re = Ga,⁶⁾⁻⁸⁾ Sc, Lu, Yb, Y, Dy, Gd, Sm⁹⁾), have been examined. **Figure 1** summarizes our proposed phase relationship of $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ system obtained with thermal analysis.^{5),7)} Horizontal axis is the tolerance factor, t , calculated with $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where r_A , r_B and r_O indicate mean ionic radius of Ba^{2+} and Sr^{2+} , that of In^{3+} and Ga^{3+} and that of O^{2-} , respectively, evaluated by using ionic radii proposed by Shannon.¹⁰⁾ Three phases denoted as phase I (brownmillerite), II (distorted perovskite) and III (slightly distorted perovskite) were also observed in partially cation substituted specimens and the phase transition temperature decreased with an increase of t , i.e., an increase of Ga substitution. However, Cu K α X-ray diffraction patterns of phase III^{5),7)} presented in **Fig. 2** apparently showed a contradiction with the phase relationship depicted in **Fig. 1**. X-ray diffraction patterns of $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_3$ at phase III depicted in **Fig. 2(a)** were apparently indexed as ideal cubic, whereas some peaks which could not be indexed as ideal cubic perovskite were observed in those of $\text{Ba}_2\text{In}_2\text{O}_5$ and $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{In}_2\text{O}_5$ in **Fig. 2(b)** and (c), suggesting that phase III of region “A” and “B” in **Fig. 1** might be different. However, there is a possibility that the distortion from ideal cubic structure is so small that Cu K α X-ray diffraction pattern of $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_3$ could apparently be indexed as cubic due to insufficient sensitivity and resolution. Therefore, X-ray diffraction measurements with higher sensitivity and resolution at high temperatures are required for the establishment of phase relationship of cation substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system.

In this study, synchrotron X-ray diffraction patterns of cation substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system were measured at high temperatures using

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Fig. 1. Phase relationship of $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ as a function of tolerance factor and temperature.^{5),7)} Closed and open circles represent first order and second order structural phase transition, respectively, of $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ measured by dilatometry. Closed and open triangles represent first order and second order structural phase transition, respectively, of $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ measured by dilatometry. Region “A” and “B” represent phase III of $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$.

an originally designed furnace.¹¹⁾ Using diffraction measurements with high sensitivity and resolution,^{12),13)} phase relationship depicted in Fig. 1 was assessed.

2. Experimental

$\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ ($x = 0.0-0.2$) and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ ($x = 0.0-0.45$) ceramic specimens were prepared by solid state reaction of nominal composition of powder mixture of BaCO_3 , SrCO_3 , In_2O_3 and Ga_2O_3 . The minute preparation conditions are the same as the previously reported ones.^{5),7)} The X-ray diffraction using $\text{Cu K}\alpha$ radiation at room temperature revealed that all the prepared specimens were single phase brownmillerite. Thermal analysis such as dilatometry and differential scanning calorimetry indicated two kinds of phase transition in $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$, temperatures of which showed correspondence with those depicted in Fig. 1.

In order to obtain structural information of the specimens at high temperatures, X-ray diffraction patterns were measured by using either $\text{Cu K}\alpha$ radiation (50 kV, 250 mA, Rigaku Co., Ltd., RINT-2000) with heating apparatus or monochromated synchrotron X-ray

Fig. 2. X-ray diffraction patterns of (a) $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ at 1000°C, (b) $\text{Ba}_2\text{In}_2\text{O}_5$ at 1200°C and (c) $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{In}_2\text{O}_5$ at 1200°C using $\text{Cu K}\alpha$ radiation. The pattern of (a) is apparently indexed assuming ideal cubic perovskite. The peaks indicated by the closed circle cannot be indexed as cubic symmetry.

at BL-3A, Photon Factory, KEK. The wavelength of the synchrotron X-ray was 90.06 pm calibrated by diffraction peaks of CeO_2 . For the synchrotron X-ray diffraction measurements at high temperatures, the originally designed furnace was used.¹¹⁾ All the diffraction measurements were carried out between room temperature and 1300°C in air, where concentration of oxide ion vacancy was confirmed to be maintained with thermogravimetry.⁴⁾

3. Results and discussion

3.1 Significance of synchrotron X-ray diffraction for analysis of $\text{Ba}_2\text{In}_2\text{O}_5$ system

Figure 3 shows the X-ray diffraction patterns of $\text{Ba}_2\text{In}_2\text{O}_5$ at (a) 700°C, (b) 1000°C and (c) 1200°C. Upper parts are diffraction patterns obtained by using synchrotron radiation, whereas ones observed by using $\text{Cu K}\alpha$ radiation are displayed in lower parts for comparison. For comparison of both patterns, the horizontal axes were converted to d -spacing using the Bragg formula. Full width at half maximum (FWHM) of synchrotron X-ray diffraction signals was smaller than those of $\text{Cu K}\alpha$, showing a higher resolution.

Fig. 3. X-ray diffraction patterns of $\text{Ba}_2\text{In}_2\text{O}_5$ obtained using synchrotron X-ray and $\text{Cu K}\alpha$ radiation at (a) 700°C, (b) 1000°C and (c) 1200°C. The peaks are indexed as (a) orthorhombic brownmillerite, (b) tetragonal and (c) cubic symmetry. Closed circles represent unidentified peaks.

The diffraction pattern at 700°C obtained by using Cu K α source can be indexed as orthorhombic brownmillerite structure. The synchrotron X-ray diffraction pattern with higher sensitivity and resolution at 700°C could also be indexed as the same brownmillerite structure, indicating that diffraction using Cu K α was sufficient for structural analysis of phase I. For the diffraction pattern at 1000°C, where phase II was thermodynamically stable, both patterns could be indexed as the same tetragonal symmetry although extra minor peaks represented by closed circles were observed. The origin of the extra peaks was not certainly identified; however, Bragg angle of the peaks suggested that phase I might remain even at 1000°C due to slow kinetics of the phase transition.⁴⁾ Smaller intensity of the extra peaks in synchrotron X-ray diffraction pattern might be ascribed to the longer period for measurement exposed at 1000°C. The difference of diffraction patterns by X-ray source was observed for phase III at 1200°C as Fig. 3(c) shows. The Cu K α diffraction pattern at 1200°C could be apparently indexed as the ideal cubic perovskite structure. However, minor peaks, which could not be indexed as cubic symmetry and indicates slight distortion from cubic symmetry, were successfully observed for synchrotron X-ray diffraction due to higher sensitivity and resolution. If the minor peaks are overlooked, the diffraction patterns of Fig. 3(c) can be indexed as ideal cubic symmetry. Therefore, it is concluded that the synchrotron X-ray diffraction with high sensitivity and resolution is necessary for analysis of crystal structure and structural phase transition of $\text{Ba}_2\text{In}_2\text{O}_5$ system, especially those of phase III.

3.2 X-ray diffraction of phase III of $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$

In order to estimate the variation of crystal structure of cation substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system, especially phase III with the smallest distortion from ideal perovskite among three phases, X-ray diffraction patterns of $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{In}_2\text{O}_5$ and $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ at high temperature were measured by using monochromated synchrotron X-ray radiation. Lower parts of Fig. 4 show synchrotron X-ray diffraction patterns of (a) $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{In}_2\text{O}_5$ at 1200°C and (b) $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ at 1000°C. For comparison, Cu K α X-ray diffraction patterns of the corresponding temperature and samples are depicted in upper parts of Fig. 4. Horizontal axes were converted to d -spacing by using Bragg's formula. According to Fig. 1^{5,7)} phase III should be stable

for both specimens under the temperature. In the diffraction pattern of the upper part of Fig. 4(a), the minor peaks, which could not be indexed as ideal cubic, were observed besides one, which could be indexed assuming cubic symmetry. The minor peaks were also observed in synchrotron X-ray diffraction pattern shown in the lower part of Fig. 4(a), suggesting that distortion from cubic perovskite structure existed in phase III of $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{In}_2\text{O}_5$.

All the peaks of Cu K α X-ray diffraction pattern of phase III of $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ shown in upper part of Fig. 4(b) could be apparently indexed as ideal cubic structure. If the crystal system of phase III of $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ is ideal cubic, it can be concluded that phase III of Sr substituted and Ga substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system, depicted as region "A" and "B", respectively in Fig. 1, are different phases. However, it can be clarified from synchrotron X-ray diffraction measurements that very slight distortion exists in phase III of $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$. As the lower part of Fig. 4(b) shows, minor peaks with low intensity, represented by a closed circle were observed, besides the peaks which could be indexed as ideal cubic perovskite. It could be regarded that the distortion from ideal cubic perovskite was so slight in phase III of $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ that the X-ray diffraction pattern, which could apparently be interpreted as ideal cubic structure, was observed by using Cu K α radiation. Also regarded was the evidence of the slight distortion shown in the Cu K α X-ray diffraction pattern in Fig. 4(b) could be the tail observed around the 110 peak represented by the dotted circle. From comparison between X-ray diffraction patterns depicted in the upper and lower part of Fig. 4(b), it could be concluded that the tail around the 110 peak of Cu K α diffraction pattern originated from minor peaks in the dotted circle in the lower part of Fig. 4(b).

It can be concluded from Fig. 4 that phase III of Sr substituted $\text{Ba}_2\text{In}_2\text{O}_5$ (region "A" in Fig. 1) and Ga substituted one (region "B" in Fig. 1) is the same distorted perovskite. From the Bragg angle and intensity of minor peaks shown in Fig. 4, it can be proposed that distortion from ideal perovskite structure of phase III increases with Sr substitution, whereas it decreases with Ga substitution. This tendency can be explained qualitatively from the viewpoint of variation of the tolerance factor, which decreases with Sr substitution and approaches 1 with Ga substitution as shown in Fig. 1. In order to evaluate the distortion quantitatively, accurate structural analysis including space group, atomic position and lattice constants is nec-

Fig. 4. X-ray diffraction patterns of (a) $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{In}_2\text{O}_5$ at 1200°C and (b) $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ at 1000°C using Cu K α and synchrotron radiation. The patterns are indexed assuming ideal cubic perovskite structure. The • peaks, which cannot be indexed as cubic, are regarded to originate from distortion from cubic structure. Apparently, Cu K α X-ray diffraction pattern of $\text{Ba}_2\text{In}_{1.55}\text{Ga}_{0.45}\text{O}_5$ at 1000°C can be indexed as cubic symmetry, however, • peaks are observed in synchrotron X-ray diffraction pattern especially in the d -spacing region represented by a dotted circle.

essary and now in progress.

It was also concluded that the distortion decreased but was maintained with substitution of Ga. We regard that the removal of distortion is desired for the improvement of oxide ion conductivity in $\text{Ba}_2\text{In}_2\text{O}_5$ system. One probable method should be the reduction of oxide ion vacancy as a perovskite structure by substitution of cation with different valence and its trial will be reported in a separate paper.¹⁴⁾

4. Conclusion

It was revealed that X-ray diffraction with high sensitivity and resolution using synchrotron radiation was necessary for precise analysis of crystal structure and phase relationship of cation substituted $\text{Ba}_2\text{In}_2\text{O}_5$ system. Although distortion from ideal cubic perovskite is not observed in phase III of $\text{BaIn}_{1.55}\text{Ga}_{0.45}\text{O}_5$ by Cu $K\alpha$ X-ray diffraction measurement, its existence in phase III in $\text{Ba}_{2-x}\text{Sr}_x\text{In}_2\text{O}_5$ and even in $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_5$ was indicated by synchrotron X-ray diffraction. The distortion reduced with a decrease of Sr content and an increase of Ga content, showing correspondence with variation of the tolerance factor.

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