CRYSTAL STRUCTURE OF METAL CATION-DOPED Ba$_2$In$_2$O$_5$
AND ITS OXIDE ION CONDUCTIVITY

Y. Uchimoto, M. Kinuhata, H. Takagi, and T. Yao
Department of Fundamental Energy Science
Graduate School of Energy Science, Kyoto University
Yoshida, Sakyo-ku, Kyoto 606-8501, JAPAN

and

T. Inagaki and H. Yoshida
Technical Research Center
The Kansai Electric Power Company, Inc.
11-20 Nakoji 3-Chome Amagasaki, Hyogo-ken 661-0974, JAPAN

ABSTRACT

Crystal structures of Ba$_2$In$_2$O$_5$, Ba$_2$(Ini$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.20, 0.25, 0.30, 0.35, 0.40, 0.45), and (Bai$_{1-x}$La$_x$)In$_2$O$_5$ (X=0.20, 0.30, 0.40, 0.50) were analyzed and electrical conductivity were measured. Rietveld analysis indicated that Ba$_2$In$_2$O$_5$ belongs to orthorhombic space group at room temperature and cubic space group at 1100°C.

The Rietveld results for Ba$_2$(Ini$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.20, 0.25, 0.30, 0.35, 0.40, 0.45) revealed that these oxides belong to cubic space group. This result indicated that the oxide ion vacancies distribute randomly in the cubic perovskite type structure. Fourier transform of In K-edge EXAFS of Ba$_2$(Ini$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.00, 0.10, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45) showed a peak between 1.2 and 2.0 Å attributed to the nearest oxide ions around In$^{3+}$ cation. The peak was back-Fourier transformed, and the structural parameters were refined by the least square fitting. The coordination number of In$^{3+}$ cation increased with increasing Ga$^{3+}$ cation content. This result indicates that coordination number of Ga$^{3+}$ cation is 4. Electrical conductivities of pure Ba$_2$In$_2$O$_5$ and Ba$_2$(Ini$_{1-x}$Ga$_x$)$_2$O$_5$ samples indicated that for pure Ba$_2$In$_2$O$_5$ electrical conductivity rapidly increased at about 930°C due to the order-disorder transition of oxygen vacancy. The electrical conductivities of Ba$_2$(Ini$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.25, 0.30, 0.35, 0.40, 0.45) did not show a sharp discontinuity in the conductivity because the disorder phase of defective perovskite type structure was stabilized by doping Ga$^{3+}$ cations at low temperature. Ba$_2$(Ini$_{0.75}$Ga$_{0.25}$)$_2$O$_5$ sample exhibits the maximum electrical conductivity at relatively low temperature. Crystal structure of (Bai$_{1-x}$La$_x$)In$_2$O$_5$ and its oxide ion conductivity are also discussed. The oxide ion transference number of Ga- and La-doped Ba$_2$In$_2$O$_5$ determined by blocking method is 1.00.

INTRODUCTION

Recently, a significant amount of work has been devoted to solid oxide fuel cells (SOFCs) 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 increased reliability and lifetime will be attained. Since oxide ion conductivity of...
stabilized zirconia decreases at such temperatures, some of the problems found in the SOFCs can be attributed to difficulties in lowering the resistance of the oxide ion conductors. This can be circumvented 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 the intermediate-temperature range (3-7). The defect perovskite-related oxide Ba$_2$In$_2$O$_5$ has been reported to have a high oxide ion conductivity, which is higher than that of calcia- and yttria-stabilized zirconia, at high temperature (5-7). The Ba$_2$In$_2$O$_5$ has a characteristic order-disorder transition temperature (Td) 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 cation doping. The crystal structures of Ba$_2$In$_2$O$_5$ and metal cation-doped Ba$_2$In$_2$O$_5$ were analyzed by EXAFS and the powder X-ray Rietveld method.

EXPERIMENTAL

Pure and doped Ba$_2$In$_2$O$_5$ powders were prepared by usual solid state reaction starting with BaCO$_3$, In$_2$O$_3$ and dopant metal oxides. The crystal structure of the product was determined by XRD using Mo-Kα radiation for Ba$_2$In$_2$O$_5$ and doped Ba$_2$In$_2$O$_5$ samples. For the Rietveld analysis, a powder XRD pattern was collected using a Model RINT-TTR powder X-ray diffractometer. The Rietveld calculation was performed on the vector processor (Cray Y-MP2E/264) at the Institute for Chemical Research, Kyoto University, by using ‘Rievec’ computer program (8-10). Well-ground fine powder of the sample was sandwiched between Scotch tapes (3M Consumer Products Group, St.Paul, MN, USA), the EXAFS in the vicinity of In K-edge were measured at the beam line BL01B1 station at SPring-8 in Japan Synchrotron Radiation Research Institute. EXAFS analysis was conducted by using ‘MELMS’ computer program (11, 12). The total electrical conductivity of the oxides was measured using impedance spectroscopy using impedance analyzer (Solartron 1260) connected with potentiostat (Solartron 1287). The ion-blocking technique was used to determine the oxide ion transference numbers.

RESULTS AND DISCUSSION

Crystal Structures of Ba$_2$In$_2$O$_5$ at Different Temperatures

The Rietveld method was used to refine the structural change before and after the order-disorder transition. XRD pattern of Ba$_2$In$_2$O$_5$ at room temperature was indexed to an orthorhombic lattice. The lattice parameters and other structural parameters were refined by the Rietveld method. Fig. 1 shows the results of the Rietveld analysis of room temperature sample. The observed pattern agreed well with the calculated pattern. The obtained lattice parameters are given in Table 1. $R_p$, $R_w$, and $R_B$ are small enough to guarantee the reliability, and it was confirmed that Ba$_2$In$_2$O$_5$ belonged to orthorhombic $Ibmm$ space group. On the other hand, at high temperature of 1100 °C, the pattern was indexed to cubic lattice. The refined crystal parameters for Ba$_2$In$_2$O$_5$ at 1100 °C (after the phase transition) revealed that Ba$_2$In$_2$O$_5$ transformed to a cubic structure with $Pm3m$ space group. Below the transition temperature, Ba$_2$In$_2$O$_5$ has brownmillerite structure, which consists of alternating two-dimensional layers of corner-shared InO$_6$ octahedra and corner-shared InO$_4$ distorted tetrahedra and the average coordination number of In$^{3+}$ cation is 5. Above the transition temperature, the oxygen vacancies distribute randomly in the cubic perovskite type structure. These results indicate that disordering of oxygen vacancy is important to construct a novel defective-perovskite-type ion conductor having high oxide ion conductivity.
Crystal Structures of Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$

We attempted to stabilize the disorder phase by doping trivalent cation of Ga$^{3+}$ at B-site or by doping trivalent cation of In$^{3+}$ at A-site. Fig. 2 shows the Rietveld results of Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ at room temperature. The refined lattice parameters for Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.25, 0.30, 0.35, 0.40, 0.45) are given in Table 2. R$_{wp}$, R$_p$, and R$_B$ are small enough to guarantee the reliability of refinements. The Rietveld results for Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.25, 0.30, 0.35, 0.40, 0.45) revealed that these oxides belong 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 lattice constant decreased with increasing Ga content, because ionic radius of Ga$^{3+}$ cation is smaller than that of In$^{3+}$ cation. The local structures of In$^{3+}$ cations were analyzed by EXAFS measurement.

Fig. 3 shows Fourier transform data of In K-edge EXAFS of Ba$_2$In$_2$O$_5$ and Ba$_2$(In$_{0.65}$Ga$_{0.35}$)$_2$O$_5$. This figure shows that a peak between 1.2 and 2.0 Å. The peaks are attributed to the nearest oxide ion around the In$^{3+}$ cation. As described before, there are two kinds of cation sites, that is corner-shared InO$_6$ octahedra and corner-shared InO$_4$ distorted tetrahedra, respectively. The contribution of the oxide ion from the octahedral and tetrahedral sites overlapped into these peaks, because the differences in the In-O interionic distance is small. In order to analyze the coordination number of In$^{3+}$ cation, the peak between 1.2 and 2.0 Å was back-Fourier transformed.

The back-Fourier transformed EXAFS function $\chi(k)$ can be expressed as

$$\chi(k) = \frac{N}{kR^2} \left| f_0(k) \right| \exp(-2\sigma^2 k^2) \times \exp(-2R/\lambda) \sin(2kR + \delta(k))$$  

where $\chi(k)$ is the EXAFS function attributed to the In$^{3+}$ ions, $k$ is the wave vector of the photoelectron, $f_0(k)$ is the backscattering amplitude of the oxide ion, $R$ is the distance from In$^{3+}$ cation to the oxide ion, $\sigma^2$ is the variance in the distance $R$, $\lambda$ is the mean free path of photoelectron, and $\delta$ is the phase shift. The average coordination number of oxide ion around In$^{3+}$ cations is represented by parameter $N$.

In the fitting procedure, the ab initio calculated value was used for the backscattering amplitude (13). The values of phase shift $\delta$ were corrected by using Ba$_2$In$_2$O$_5$ as the standard assuming the coordination number $N$ is 5.0. The average coordination number of oxide ion around In$^{3+}$ cations and the other parameters in Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.10, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45) were calculated to give the least-squares fit between the experimental and calculated values of $\chi(k)$. Figure 4 shows the experimental (solid line) and the calculated (dashed line) EXAFS function of undoped Ba$_2$In$_2$O$_5$ and Ba$_2$(In$_{0.65}$Ga$_{0.35}$)$_2$O$_5$ oxide. Table 3 shows the results of the parameter fitting of the EXAFS function for Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.10, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45). R$_{wp}$ is small enough to guarantee the reliability. These results indicate that the coordination number of In$^{3+}$ cation increases with increasing Ga$^{3+}$ cation content. This result indicates that coordination number of Ga$^{3+}$ cation is 4.

From EXAFS results of Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.10, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45), we can conclude that Ga$^{3+}$ cations were randomly distributed and the coordination of Ga$^{3+}$ cation may be nearly 4. As a result of the Ga$^{3+}$ cation distribution, the oxide ion vacancies distribute randomly.

Oxide Ion Conductivity in Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$

Figure 5 shows electrical conductivities of pure Ba$_2$In$_2$O$_5$ and Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$.
samples. For pure Ba$_2$In$_2$O$_5$, electrical conductivity rapidly increased at about 930°C due to the order-disorder transition of oxygen vacancy. The electrical conductivities of Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X= 0.25, 0.30, 0.35, 0.40, 0.45) did not show a sharp discontinuity in the conductivity because the disorder phase of defective perovskite type structure was stabilized by doping Ga$^{3+}$ cations at low temperature. Ba$_2$(In$_{0.75}$Ga$_{0.25}$)$_2$O$_5$ sample exhibits the maximum electrical conductivity at relatively low temperature. Activation energy of the electrical conduction was calculated by using Arrhenius plot of Fig. 5. As indicated in Fig. 6, a clear relationship between the activation energy of the electrical conduction and Ga content is not observed. The oxide ion transference number of Ba$_2$(In$_{0.75}$Ga$_{0.25}$)$_2$O$_5$ determined by blocking method is 1.00.

Sammels and co-workers suggested that the activation energies of oxide ion in perovskite oxides have strong relationship to saddle point in the perovskite lattice (14, 15). 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 Shannon's ionic radius (16).

$$r_{\text{critical}} = \frac{-r_A^2 + \frac{3}{4}a^2 - \sqrt{2}a_r + r_B^2}{2r_A + \sqrt{2}a - 2r_B}$$

[2]

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. Figure 8 shows that the relationship between the saddle point and Ga content in the Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$. This figure shows that the radius of saddle point does not have strong influence on Ga content. The radius of saddle point of Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X= 0.25, 0.30, 0.35, 0.40, 0.45) is between 0.887 and 0.882 Å, 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. In the case of Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$, lattice parameter decreases with increasing Ga content, however, the radius of saddle point does not change clearly. Therefore, clear relationship between the activation energy of the electrical conduction and Ga content is not observed.

Crystal Structure of (Ba$_{1-x}$La$_x$)$_2$In$_2$O$_5$ and Their Oxide Ion Conductivity

We have attempted to stabilize the disorder phase by doping trivalent cation of La$^{3+}$ at A-site. XRD pattern of (Ba$_{1-x}$La$_x$)$_2$In$_2$O$_5$ (X=0.20, 0.30, 0.40, 0.50) was indexed to a cubic lattice. The Rietveld results for (Ba$_{q-1}$La$_q$)$_2$In$_2$O$_5$ revealed that the oxide belonged to cubic Pm3m space group. This result indicate that the oxide ion vacancies distribute randomly in the cubic perovskite type structure.

Figure 8 shows electrical conductivities of (Ba$_{1-x}$La$_x$)$_2$In$_2$O$_5$ (X=0.00, 0.20, 0.30, 0.40, 0.50) samples. For pure Ba$_2$In$_2$O$_5$, electrical conductivity rapidly increased at about 930°C due to the order-disorder transition of oxygen vacancy. The electrical conductivities of (Ba$_{1-x}$La$_x$)$_2$In$_2$O$_5$ (X=0.20, 0.30, 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 (Ba$_{0.6}$La$_{0.4}$)$_2$In$_2$O$_5$ determined by blocking method is 1.00.

ACKNOWLEDGMENT

We are grateful to Dr. T. Uruga at Japan Synchrotron Radiation Research Institute and Dr. M. Takahashi at Osaka University for useful suggestion for the EXAFS experiment at SPring-8. This research has been partially supported by the Japan Society for the Promotion of Science, "Research for the Future" Program, Production- and Utilization-Technol-
ogy of Hydrogen Aiming at the Hydrogen Energy Society. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

REFERENCES

1) A. J. Appleby and F. R. Foulkes, Fuel Cell Handbook, p. 579, Van Nostrand Reinhold, New York (1989).
2) N. Q. Minh and T. Takahashi, Science and Technology of Ceramic Fuel Cells, Elsevier, Amsterdam (1995).
3) T. Ishihara, M. Matsuda, Y. Takita, J. Am. Chem. Soc., 116, 3801 (1994).
4) M. Feng, J.B. Goodenough, Mat. Res. Symp. Proc., 369, 333 (1995).
5) J. B. Goodenough, J. E. Ruiz-Diaz, and Y. S. Zhen, Solid State Ionics, 44, 21 (1990).
6) S. B. Adler, J. A. Reimer, J. Baltisberger, and U. Werner, J. Am. Chem. Soc., 116, 675 (1994).
7) G. B. Zhang and D. M. Smyth, Solid State Ionics, 82, 161 (1995).
8) T. Yao, Y. Oka, and N. Yamamoto, Mater. Res. Bull., 27, 669 (1992).
9) T. Yao, Y. Oka, and N. Yamamoto, J. Mater. Chem., 32, 331 (1992).
10) T. Yao, T. Ito, and T. Kokubo, J. Materials Research, 10, 1079 (1995).
11) T. Yao, O. Imafuji, and H. Jinno, J. Am. Ceram. Soc., 74, 314 (1991).
12) T. Yao, Jpn. J. Appl. Phys., 32, 755 (1993).
13) A.G. Makale, B.W. Veal, A.P. Paulikas, S.K. Chan, and G.S. Knapp, J. Am. Chem. Soc., 110, 3763 (1988).
14) R.L. Cook and A.F. Sammells, Solid State Ionics, 45, 311 (1991).
15) A.F. Sammels, R.L. Cook, J.H. White, J.J. Osborne, and R.C. MacDuff, Solid State Ionics, 52, 111 (1992).
16) R.D. Shanon, Acta Cryst., A32, 751 (1976).

Figure 1 Rietveld result of Ba2In2O5 at room temperature. The calculated and observed patterns are shown in the top by the solid line and the dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The trace in the bottom is a plot of the difference: observed minus calculated.

Electrochemical Society Proceedings Volume 99-19
Table 1 Refined atomic parameters for Ba₂In₂O₅ at room temperature.

| Atom | site | X     | Y     | Z     | N  |
|------|------|-------|-------|-------|----|
| Ba   | 8c   | 0.0120(03) | 0.1091(01) | 0.5026(14) | 1.0 |
| In(1) | 4a   | 0     | 0     | 0     | 1.0 |
| In(2) | 4b       | 0.9252(05) | 0.25 | 0.0333(13) | 1.0 |
| O(1) | 8c       | 0.2988(36) | 0.0061(15) | 0.3005(43) | 1.0 |
| O(2) | 8c       | 0.0017(51) | 0.0629(16) | 0.8941(46) | 1.0 |
| O(3) | 4b       | 0.5749(33) | 0.25 | 0.0221(83) | 1.0 |

a, b, c = 6.10476(11), 16.7541(02), 5.97253(10) Å

Figure 2 Rietveld result of Ba₂(In₀.₆₅Ga₀.₃₅)₂O₅ at room temperature. The calculated and observed patterns are shown in the top by the solid line and the dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The trace in the bottom is a plot of the difference: observed minus calculated.
Table 2  Refined atomic parameters for Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ at room temperature.

| Atom | site | x    | y    | z    | N  |
|------|------|------|------|------|----|
| Ba   | 1a   | 0    | 0    | 0    | 1.0|
| In&Ga| 1b   | 0.5  | 0.5  | 0.5  | 1.0|
| O    | 3c   | 0    | 0.5  | 0.5  | 0.833|

| Ga contents : X | a / Å | R$_{wp}$ | R$_{b}$ | R$_{b}$ |
|-----------------|-------|----------|---------|---------|
| 0.25            | 4.19725(23) | 0.0998   | 0.0992  | 0.0535  |
| 0.30            | 4.18641(28) | 0.1027   | 0.1423  | 0.0761  |
| 0.35            | 4.17804(31) | 0.1285   | 0.1573  | 0.0870  |
| 0.40            | 4.17362(28) | 0.1120   | 0.1293  | 0.0860  |
| 0.45            | 4.16697(20) | 0.0999   | 0.1203  | 0.0844  |

Figure 3  Fourier transform of In K-edge EXAFS of Ba$_2$In$_2$O$_5$ and Ba$_2$(In$_{0.65}$Ga$_{0.35}$)$_2$O$_5$.
Figure 4 Parameter fitting of inverse Fourier transform of the peak in Figure 3. Solid and broken lines represent experimental data and parameter-fit results, respectively.

Table 3 Results of the parameter fitting of the EXAFS for Ba$_2$(In$_{1-x}$Ga$_x$)$_2$O$_5$ (X=0.10, 0.25, 0.30, 0.35, 0.40, 0.45).

| Ga contents: X | 0.10  | 0.25  | 0.30  | 0.35  | 0.40  | 0.45  |
|----------------|-------|-------|-------|-------|-------|-------|
| R$_{wp}$       | 0.1017| 0.1456| 0.1454| 0.1187| 0.1222| 0.1108|
| In-O distance: R | 2.08  | 2.11  | 2.11  | 2.10  | 2.10  | 2.10  |
| Coordination number: N | 4.55  | 4.52  | 4.67  | 5.09  | 5.13  | 5.16  |
Figure 5 Temperature dependence of electrical conductivity of $\text{Ba}_2(\text{In}_1-x\text{Ga}_x)_2\text{O}_5$ ($X=0.00, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45$).

Figure 6 Activation Energy ($E_a$) versus Ga content.
**Figure 7** Radius of saddle point versus Ga content.

**Figure 8** Temperature dependence of electrical conductivity of \((\text{Ba}_{1-x}\text{La}_x)\text{In}_2\text{O}_5\) \((X=0.00, 0.20, 0.30, 0.40, 0.50)\).