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Electric property of mixed conductor $BaIn_{1-x}Co_xO_{3-\delta}$

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Abstract

We synthesized $BaIn_{1-x}Co_xO_{3-\delta}$ (x=0–0.8) with a defective perovskite structure by partly replacing In with Co in $Ba_2In_2O_5$. Based on XRD measurements, the synthesized compound was found to have cubic perovskite and orthorhombic brownmillerite structures depending on the amount of Co. $BaIn_{1-x}Co_xO_{3-\delta}$ (x=0.2 and 0.3) showed high total electrical conductivities without undergoing the structural transformation that the original $Ba_2In_2O_5$ undergoes. Some of the samples showed both electronic and oxide ionic conductivities. At the same time, the oxide ionic conductivity was comparable with that of $Ba_2In_2O_5$. For example, the sample with x=0.1 had a total electrical conductivity of 4.7×10^{-1} S cm^{-1} and an oxide ion transport number of 0.52 at 850 °C.

Keywords: Mixed conductor; Perovskite structure; Brownmillerite structure; Structural transition; Superlattice structure

1. Introduction

Barium indium oxide ($Ba_2In_2O_5$) has a cubic perovskite structure at high temperature and shows a high electric conductivity due to disordered oxygen vacancies; such oxygen vacancies are preferable for oxide ion transfer. $Ba_2In_2O_5$, however, has a characteristic structural transition at approximately 930 °C [1]; it has an orthorhombic brownmillerite structure below the transition temperature and shows a much reduced oxide ionic conductivity as compared to that above the transition temperature. Various attempts to stabilize the high-temperature phase have been made to date, and it has been clarified that high electric conductivity is retained even at lower temperatures by doping with Ga, Gd, or La [2–4]. A disordered distribution of ions of different sizes is expected to result in a disordered distribution of oxygen vacancies. On the other hand, the defective perovskite structure, such as that in the high-temperature phase of $Ba_2In_2O_5$, has many oxygen vacancies.

In this study, we attempted to synthesize mixed conductors by the substitution of transition metals for indium in $Ba_2In_2O_5$. If $Ba_2In_2O_5$ can be doped with a transition metal and restrain the structural transition [2–4], electronic conduction is also expected if the transition metal is in a mixed valence state. In our preliminary results, we found that Co can replace In in $Ba_2In_2O_5$. Doping $Ba_2In_2O_5$ with Co may be effective for the production of a mixed conductor. Istomin et al. have synthesized and structurally investigated $BaIn_{1-x}Co_xO_{3-\delta}$ (x=0.5–0.9) and concluded that a cubic phase was stabilized even in the low temperature for x=0.7–0.8 [5]. However, they have not described electric properties of these samples nor the samples of x<0.5. In the present study, $BaIn_{1-x}Co_xO_{3-\delta}$ is synthesized and its electrical property is investigated.

2. Experimental

Barium carbonate (Wako, 99.0%), indium oxide (Wako, 99.9%), and basic cobalt carbonate (Mitsuwa; Co, 47.6 wt.%) were mixed in various ratios for 5 h in an electric mortar. The mixtures were pressed into disks under a pressure of 110 MPa and heated at 1400 °C (x=0), 1300 °C (x=0.1–0.4), 1250 °C (x=0.5, 0.6), and 1200 °C (x=0.7, 0.8) for 8 h in air. The products were cooled in a furnace and ground with an almina mortar. The abovementioned heating procedures were repeated twice. The products thus obtained were analyzed by X-ray diffraction (XRD) using CuKα radiation at room temperature. After the XRD measurement, the product powder was shaped into a disk. This disk was pressed by a cold isostatic press at 392 MPa and sintered under the same conditions as those mentioned above. The sintered product was cut into a

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rectangular prism of dimensions 4×15×2 mm for the measurement of electrical conductivities.

To determine the phase transition temperatures, differential scanning calorimetry (DSC) was performed. The powders of $BaIn_{1-x}Co_xO_{3-\delta}$ ($0 \le x \le 0.8$) were heated to 1200 °C in air at the rate of 10 °C min^{-1}, maintained for 3 h at this temperature, and then cooled to room temperature at the rate of 10 °C min^{-1}.

The total electrical conductivities for $BaIn_{1-x}Co_xO_{3-\delta}$ ($0 \le x \le 0.8$) were measured by the DC four-probe method in the temperature range 600–1000 °C.

For the estimation of the oxygen ion transport number, concentration cells containing the samples as electrolytes were constructed and an atmosphere of air and a mixture of 99% N_2 and 1% O_2 was maintained. Their electromotive forces (EMFs) were measured for the temperature range 600–1000 °C.

3. Results and discussion

The XRD patterns of $BaIn_{1-x}Co_xO_{3-\delta}$ ($0 \le x \le 0.8$) are shown in Fig. 1. They were identified as orthorhombic brownmillerite structures for $x=0$ and 0.1 and cubic perovskite structures in the range $0.2 \le x \le 0.8$. The superlattice peaks were observed for $x=0.2$–0.4, as indicated in the figure. These peaks imply a double-period superlattice structure in the direction of the a axis or in the directions of both the a and b axes.

The lattice parameters of $BaIn_{1-x}Co_xO_{3-\delta}$ estimated from the XRD profiles are shown in Fig. 2. These decreased with

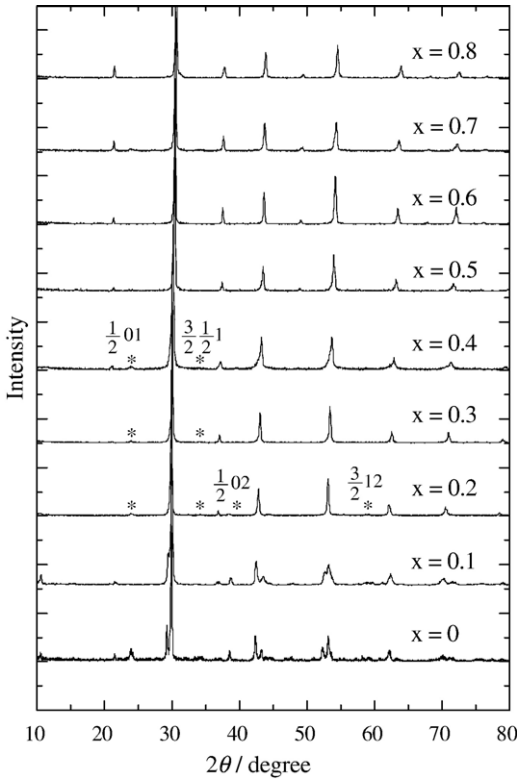

Fig. 1. XRD patterns for $BaIn_{1-x}Co_xO_{3-\delta}$ ($0 \le x \le 0.8$). The peaks indicated by asterisk marks express reflections due to a superlattice structure.

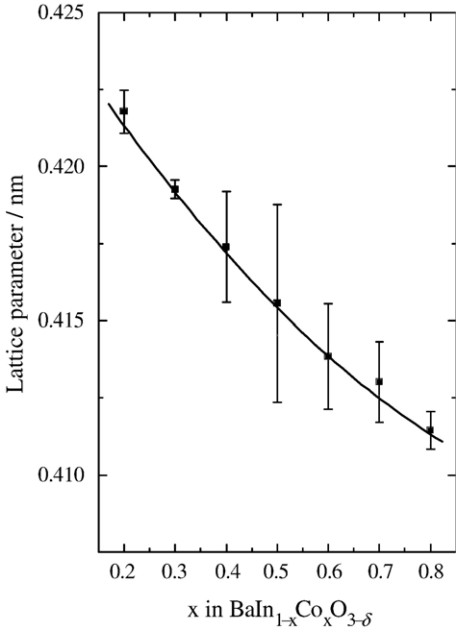

Fig. 2. Lattice parameter of $BaIn_{1-x}Co_xO_{3-\delta}$ against Co content.

increasing x. The slope decreased for large values of x. The deviation from a linear behavior implies a variation in the valence state of Co. Based on the fact that the Co valence state affects the concentration of electrons (or holes) and oxygen vacancies, which are the conduction carriers, an evaluation of the Co valence state is of significance for an investigation of the electrical property of these samples. Coexistence of different Co valence states may also be related to the double-period superlattice structure. The details of the Co valence state are currently under investigation and will be reported elsewhere.

Fig. 3 shows the DSC curves for $BaIn_{1-x}Co_xO_{3-\delta}$ ($0 \le x \le 0.3$). For $x=0$ and 0.1, sharp exothermal peaks were observed around 930 and 790 °C, respectively, in the heating processes. The relevant endothermal peaks appeared around 900 and 720 °C in the cooling processes. These peaks show the transition between the cubic perovskite and orthorhombic brownmillerite structures. This can also be expressed as an order–disorder transition of oxygen arrangement. For $x=0.2$ and 0.3, similar peaks were observed. The areas of these peaks were smaller than those for $x=0$ and 0.1, and were shifted to a higher temperature than that for $x=0$ and 0.1. A latent heat involved in disappearance of superlattice is expected to be smaller than that involved in structural transition between orthorhombic and cubic. Hence these results suggest that the superlattice structures disappear at high temperatures.

Arrhenius plots of total electrical conductivities (σ_t) for $BaIn_{1-x}Co_xO_{3-\delta}$ ($0 \le x \le 0.8$) are shown in Fig. 4. With increasing Co content, higher conductivities were obtained. For $x=0$ and 0.1, σ_t changed steeply around 930 and 750 °C, respectively. These temperatures agree with those of the DSC peaks. On the other hand, in the range $0.2 \le x \le 0.8$, no steep reduction in conductivity was observed. This is due to their