

NEW ION CONDUCTOR OF $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$

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Abstract

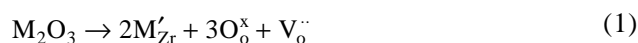
The structural characterization, thermogravimetric analysis and electrical properties for solid solution system, $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ with perovskite-type structure were investigated. X-ray diffraction showed that the orthorhombic phase was in the range of $0.0 \leq x \leq 0.3$, the tetragonal phase $0.3 < x \leq 0.5$, and the cubic phase $0.5 < x$. The sharp transition of electrical conductivity shifted to a lower temperature with increasing x and disappeared at the phase boundary between the orthorhombic and tetragonal phases. This perovskite-related oxide exhibited a pure oxide-ion conduction over the oxygen partial pressure range of 1 atm to $10^{-3.5}$ atm, and the electrical conductivity reached the value of $1.6 \cdot 10^{-1}$ (S cm^{-1}) at 1073 K, which was nearly equal to that of the yttria stabilized zirconia. These properties were successfully explained in terms of disordered oxygen ions.

Keywords: $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$, Brownmillerite structure, ion conductivity, order-disorder transition, perovskite-related structure, thermogravimetry

Introduction

The Brownmillerite structure ($\text{A}_2\text{B}_2\text{O}_5$) is a perovskite-related structure in which one sixth of the oxygens in the unit cell is removed. The B site ions are coordinated with the four and six oxygens, alternately. The ordered oxygen vacancy, which is arranged in the [101] direction [1] at low temperature, prevents the oxygen ion from contributing to ionic conduction. However, above 1203 K, the ion conductivity is abruptly raised due to the disorder of oxygen vacancy and exceeds that of yttria stabilized zirconia [2].

In order to improve the oxide-ion conductivity, a high crystal symmetry and a certain amount of oxygen vacancies are needed. For example, it is well known that the ionic conductivity of ZrO_2 and CeO_2 is improved with doping of rare earth ions. This behavior is related to the oxygen vacancy ($\text{V}_\text{o}^{\cdot\cdot}$) which is made as follows.



Many researchers have investigated the relationship between the electrical conductivity and dopant concentration in the Brownmillerite structure [3–6]. Yamamura *et al.* investigated the crystal structure of $\text{Ba}_2\text{In}_2\text{O}_5$, where In was substituted with Ga or Al [7]. They reported that the drastic jump of conductivity vanished between the orthorhombic structure and cubic one, though the conductivity at low temperature was not improved. These results can be explained by speculating that the oxygen vacancies were partially ordered or associated with cations. In order to improve the conductivity of this system, the present authors tried to substitute Ba with La in the $\text{Ba}_2\text{In}_2\text{O}_5$ system and examined the lattice parameter, electrical conductivity and thermogravimetric property.

Experimental

Powder samples of the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system were prepared by the solid state reaction. The starting materials were mixed in a ball mill for 16 h. The mixture was dried, calcined at 1273 K for 10 h, and then sintered at 1623 K for 16 h in air. The powder was passed through a sieve (35 μm), then isostatically pressed at 196 MPa into a rectangular shape (30 \times 5 \times 5 mm). The sample was sintered at 1623 K for 16 h in air. Relative densities of the sintered samples for $x=0.0, 0.1, 0.3, 0.5$ and 0.7 were 89.2, 91.6, 90.5, 92.0 and 93.0%, respectively. These samples were analyzed by X-ray diffraction using $\text{CuK}\alpha$ radiation at room temperature and the lattice parameters were also determined. The electrical conductivity of the sintered disks, which had four inserted platinum wires, was measured by the DC four-probe method under oxygen partial pressures from 1 atm to $10^{-3.5}$ atm. The thermogravimetric analysis was performed by a SEIKO TG/DTA-22 by using α -alumina powder as the reference. The heating rate was 10 K min^{-1} from room temperature to 1273 K in air.

Results and discussion

Crystal structure of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$

The X-ray diffraction profiles are shown in Fig. 1. The $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system was single phase and changed to a higher symmetric phase with increasing La content. The lattice parameter of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($x \leq 0.7$) is shown in Fig. 2 as a function of the La content. The lattice parameter of the sample with $x > 0.7$ is not shown in Fig. 2, because the single phase of these materials was not obtained. In the present study, unit cell was corresponded to ideal perovskite structure and therefore the lattice parameters of $\text{Ba}_2\text{In}_2\text{O}_5$ were equal to that of $2^{-0.5}a$, $2^{-0.5}b$, $1/4c$ which were reported by Goodenough [2]. It was found that a symmetry of the crystal structure was orthorhombic in the range of $0.0 \leq x \leq 0.3$, tetragonal for $0.3 < x \leq 0.5$, and cubic for $0.5 < x \leq 0.7$. Glazer reported that the crystal symmetry of the perovskite-related oxide changed under the influence of the oxygen octahedra tilting [9]. The reason why the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system changes from orthorhombic symmetry to a cubic one may be due to the relaxation by tilting of oxygen octahedra with La ion doping.

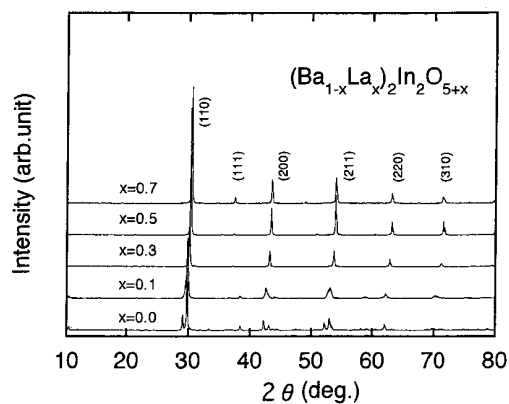


Fig. 1 X-ray diffraction pattern of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system

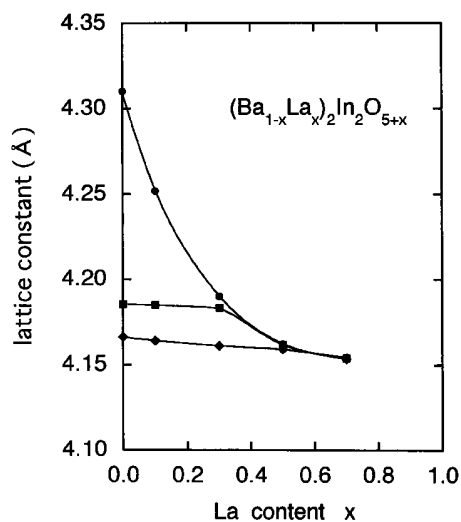


Fig. 2 Lattice parameter of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system as a function of La content \blacksquare , \bullet and \blacklozenge denote the lattice parameter of a-axis, b-axis and c-axis, respectively

Electrical conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$

Figure 3 shows the electrical conductivity of the $x=0.5$ sample as a function of oxygen partial pressure. It was found that the conductivity at all temperatures was independent of the oxygen partial pressure. This result and previous report [2] support that the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system is an oxygen ion conductor.

The Arrhenius plot of conductivity from 773 to 1273 K is shown in Fig. 4. The sharp transition in the conductivity shifted to low temperatures by substituting La in the site of Ba. The conductivity around 1073 K increased with increasing La content until $x=0.5$. Moreover, the conductivity of $x=0.5$ above 773 K was nearly equal to

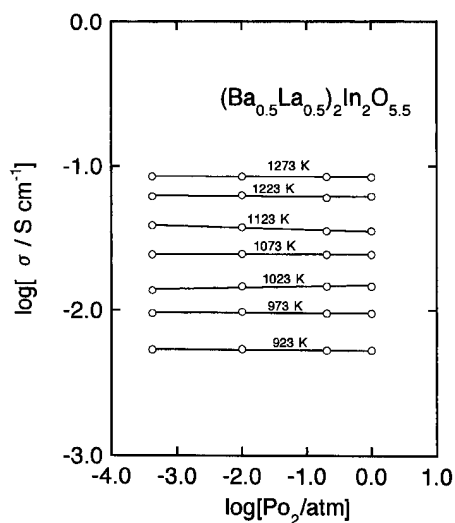


Fig. 3 Electrical conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system as a function of oxygen partial pressure

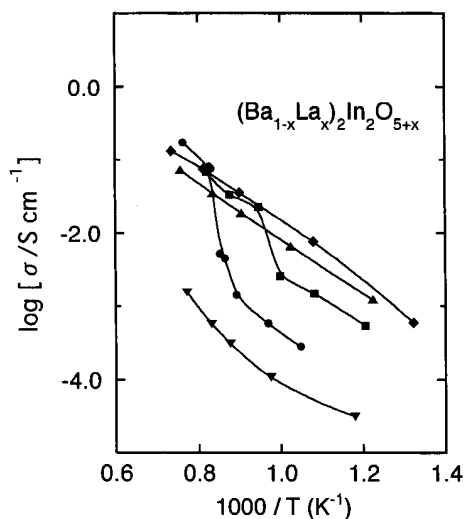


Fig. 4 Arrhenius plot for $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system \bullet , \blacksquare , \blacktriangle , \blacklozenge and \blacktriangledown denote the conductivity of $x=0.0, 0.1, 0.3, 0.5$ and 0.7

that of the yttria stabilized zirconia. The perovskite-related oxide with a large number of oxygen defects has a tendency for oxygen ion to order. It could be proposed that the increase in the La content will make the oxygen ion more disordered state and the conductivity will be improved.

The La content dependence on the conductivity and activation energy at 1073 K are shown in Figs 5(a) and (b). From $x=0$ to $x=0.5$, the ionic conductivity was found

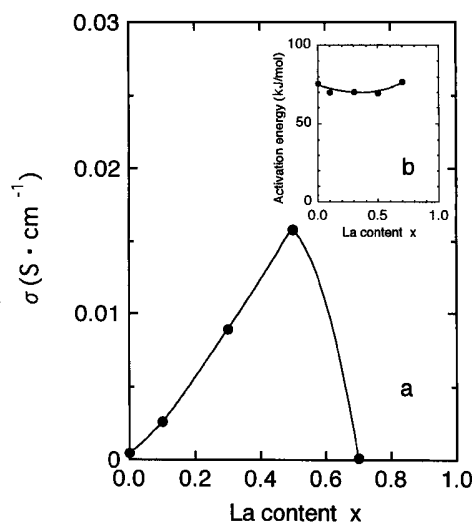


Fig. 5 The electrical conductivity (a) and activation energy (b) at 1073 K as a function of La content

to increase linearly with the La content, whereas the activation energy was almost independent. This result can be explained by the fact that the disordered oxygen ion, which acts as a carrier, linearly increases with La content. But, above $x=0.5$, ion conductivity drastically decreased with La content. This behavior is analogous to that of CeO_2 and ZrO_2 doped with rare earth ions [8], suggesting that ordered or associated oxygen ions ordered or associated with cation may affect the electrical conductivity.

Thermogravimetric analysis

Schober *et al.* reported that the $\text{Ba}_2\text{In}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ system exists as the α phase ($n < 1$), β phase ($n > 1$) and γ phase ($n = 0$) [11]. We carried out the thermogravimetric analysis and the results are shown in Fig. 6. From the total mass loss, water content at room temperature was estimated to $\text{Ba}_2\text{In}_2\text{O}_5 \cdot 0.50\text{H}_2\text{O}$ and $(\text{Ba}_{0.9}\text{La}_{0.1})_2\text{In}_2\text{O}_{5.1} \cdot 0.36\text{H}_2\text{O}$ for sample $x=0.0$ and $x=0.1$, respectively. The phase diagram of the system showed that $\text{Ba}_2\text{In}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($n=0.02\sim 1.0$) changed from the $\alpha + \beta$ phase to $\alpha + \gamma$ phase around 550 K, and changed from the $\alpha + \gamma$ phase to γ phase around 1200 K [11]. From this point of view, we assigned that the mass loss of $x=0.0$ and 0.1 around 590 and 1050 K corresponded to the phase change described above. On the other hand, a mass loss also appeared in the vicinity of 320 K. In order to ascertain reproducibility, Schober kept the sample in a dry atmosphere inside the apparatus of the thermogravimetry at 673 K for several hours and then slowly cooled [11]. In the present study, the thermogravimetric analysis was performed without such a pretreatment. Therefore, the thermogravimetric change around 320 K may be due to the desorption of adsorbed water.

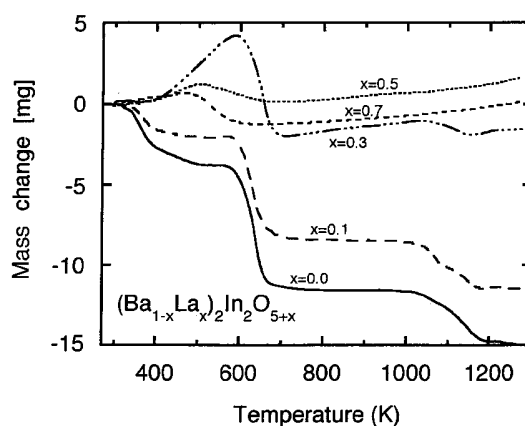


Fig. 6 Thermogravimetric change per one of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system

For $x=0.3$ and 0.5 , we found mass gain in the vicinity of 573 K. Feng reported that, in high humidity, $\text{Ba}_2\text{In}_2\text{O}_5$ absorbed water just below 573 K [10]. We speculated that the mass gain might be associated with absorbed water. Moreover, for $x=0.3$, a mass loss appeared around 1050 K. In connection with $x=0.0$ and 0.1 , this result may be related to the phase change from $\alpha+\gamma$ to γ .

Above $x=0.5$, the mass change was smaller than that for $x=0.0$, 0.1 and 0.3 . The lattice parameter of the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system decreased and the oxygen content increased with La doping. It is postulated that, above $x=0.5$, the γ phase may be difficult to absorb water due to the crystal stability because of a small amount of oxygen vacancy.

Conclusions

The structural characterization and electronic properties for the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ perovskite-related system were investigated. A single phase was found in the composition range from $x=0.0$ to $x=0.7$. By increasing the content of La, the sharp transition in the electrical conductivity shifted to a lower temperature and disappeared at the boundary between the orthorhombic and tetragonal phases. The electrical conductivity at 1073 K increased with La concentration and the conductivity of $x=0.5$ was nearly equal to that of the yttria stabilized zirconia. These results support that the disordering of oxygen ions will occur at low temperature and these mobile oxygen ions will increase with increasing La content

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