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The mechanism of multi-type carrier generation of polycrystal semiconductor $BaIn_xO_4$(x=1.58-1.88)

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$BaIn_xO_4$ (x = 1.58 - 1.88) ceramics were prepared by solid state reaction and the electrical conduction and the Seebeck coefficient were measured in varying temperature (700 - 850°C) and oxygen partial pressure (10^{-4} - 10^0 atm). These materials were *p*-type at low temperature and in high oxygen partial pressure, and changed its type to *n*-type as increasing temperature and decreasing oxygen partial pressure. The tendency to be *n*-type increased as increasing In/Ba ratio, *x*. This indicates that the *p*-type of these materials is due to the lattice defect of indium.

1. INTRODUCTION

Much attention has been paid to conducting oxides including indium as transparent electrodes[1] or thermoelectric materials[2]. However, complex oxides with indium and barium were not so major. Kalinina et al.[3] showed 5 stable compounds, $Ba_5In_2O_8$, $Ba_3In_2O_6$, $Ba_2In_2O_5$, $Ba_4In_6O_{13}$, and $BaIn_2O_4$, existed between the BaO and In_2O_3 quasi binary system below 1300°C. $Ba_2In_2O_5$ was known as an ionic conductor having brownmillerite structure and shows order-disorder transition of oxygen defects[4]. $BaIn_2O_4$ was reported to have $CaFe_2O_4$ related structure and to contain six-coordinated In^{3+} ions[5]. The electrical properties of $BaIn_2O_4$, specially the carrier of conduction, have merely been investigated. In this study, the electrical conduction and thermoelectricity of the ceramic bodies of indium-poor samples of $BaIn_2O_4$ were measured at high temperatures and the conduction type transition phenomena were investigated.

2. EXPERIMENTAL

As starting materials, barium carbonate ($BaCO_3$) of 99.9% purity and indium oxide (In_2O_3) of special grade purity were used. Those powders were mixed in a jar with hexane as a disperse medium for 1 h., then dried. The calcination of 1000°C for 4 h was performed twice in order to obtain single phase of $BaIn_2O_4$, which was confirmed by X-ray diffraction. These powders were uniaxially pressed into rectangular bars of about 4x4x20mm^3, and CIPed under 100MPa for 10min. These green bodies were sintered at 1330°C for 4h in a powder bed of the same composition as the samples'. The compositions of the obtained bodies were measured by ICP spectrometer. Electrical conductivity and Seebeck coefficient were measured as functions of oxygen partial pressure (PO_2) between 10^{-4} and 10^0 atm using mixed gas of oxygen and nitrogen, and temperature between 700 and 850°C.

3. RESULTS AND DISCUSSION

Fig. 1 shows the cation ratios (In/Ba) of nominal value of starting powders and measured value of sintered bodies. This shows that all samples of nominal composition from 1.8 to 2.2 had lost about 13% of their indium to barium, which indicated the vaporization of indium.

Fig. 2 shows the electrical conductivity of $BaIn_{1.74}O_4$ as a function of PO_2 at the temperature of 700, 750, 800 and 850°C. The electrical conductivity decreased monotonously as decreasing PO_2 at 700 and 750°C. At 800 and 850°C, it did not vary in the range of PO_2 below 10^{-1} atm and as PO_2 decreased it slightly increased. The slope which the electrical conductivity decreased as PO_2 decreased was 1/5.3, 1/6.3, 1/7.7, 1/9.1 for 700, 750, 800, 850°C, respectively. This indicated that at low

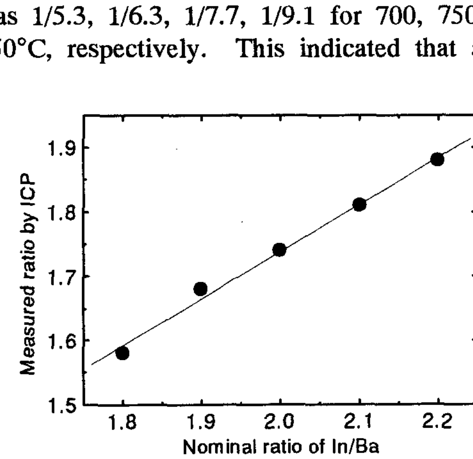

Fig. 1 Change of In/Ba ratio by sintering

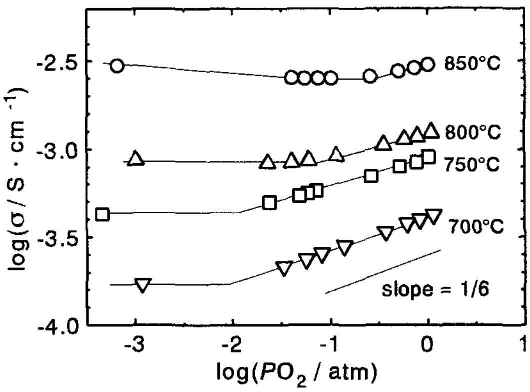

Fig. 2 Dependence of electrical conductivity(σ) of $BaIn_{1.74}O_4$ on oxygen partial pressure

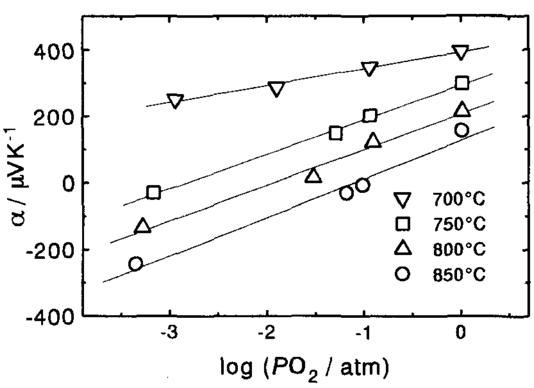

Fig. 3 Dependence of Seebeck coefficient (α) of $BaIn_{1.74}O_4$ on oxygen partial pressure

temperature and at high oxygen partial pressure, the material tended to be *p*-type conductor and vice versa. Fig. 3 shows dependence of Seebeck coefficient of $BaIn_{1.74}O_4$ on PO_2 at temperatures from 700 to 850°C. At any temperatures, Seebeck coefficient decreased as PO_2 decreased almost linearly. At the temperature more than 700 °C, the Seebeck coefficient changed its sign from positive to negative as decreasing PO_2. This indicated that the samples changed there conducting type from *p* to *n*, i.e., the conduction carrier changed from positive holes to electrons.

Fig. 4 shows the electrical conductivity of several samples differing In/Ba ratio, *x* ($BaIn_xO_4$) as a function of PO_2. As decreasing *x* from 1.88 to 1.58, PO_2 value where the slope of the conductivity changed decreased and conduction tended to be *p*-type. This tendency shows that the holes were generated by indium defects of the crystal. A reaction such as

$$2In_{In}^{\times} + O_O^{\times} \rightarrow In_2O \uparrow + 2V_{In}''' + V_O^{\bullet\bullet} + 4h^{\bullet}$$

seemed to occur during the sintering. This is thought to be the origin of *p*-type conduction. As PO_2 decreased during the measuring of conductivity, more oxygen were vaporized and a reaction such as

$$O_O^{\times} \rightarrow \frac{1}{2}O_2 \uparrow + V_O^{\bullet\bullet} + 2e'$$

occurred. From this reaction and the mass action law, the equation

$$K = PO_2^{1/2} \cdot [V_O^{\bullet\bullet}] \cdot n^2$$

is induced, where *K* is the equilibrium constant and *n* is the concentration of electron, [*e'*]. So,

$$n \propto PO_2^{-1/6}.$$

The electrons generated would combine with holes and eliminated. Since the product of concentration of carriers are constant, i.e., *pn* = const., where *p* is the hole concentration, so,

$$p \propto PO_2^{1/6}.$$

This seems to be the reason of slope of about 1/6 in fig.2 in the *p*-type conduction region.

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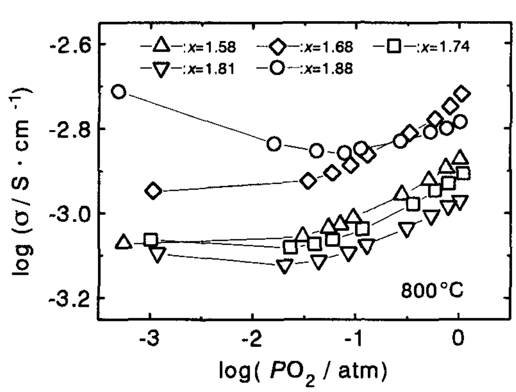

Fig. 4. Dependence of electrical conductivity(σ) of $BaIn_xO_4$ on oxygen partial pressure measure at 800°C