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Oxygen ion conduction in γ-Bi_2O_3 doped with Sb_2O_3

MASARU MIYAYAMA, HIROAKI YANAGIDA
Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Electrical conduction in bcc γ-Bi_2O_3 doped with Sb_2O_3 was investigated by measuring electrical conductivity, as a function of temperature and oxygen partial pressure (P_{O_2}), and ionic transference number. The γ-Bi_2O_3 doped with 1 to 3 mol % Sb_2O_3 was stable up to 550° C and showed an oxygen ionic conduction in the P_{O_2} region of 10^5 to 10^{-9} Pa. As the Sb_2O_3 content increased, ionic conductivity increased up to 2.5 mol % Sb_2O_3 ($1.8 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ at 500° C) and then decreased. However, the activation energy for ionic conduction remained almost unchanged. It was proposed that the γ-Bi_2O_3 contains a lot of oxygen vacancies and incorporated Sb^{5+} ions at tetrahedral sites which affect the concentration of oxygen vacancy effective for conduction.

1. Introduction

The body-centred cubic γ-form of pure Bi_2O_3 is a metastable form which appears during the cooling of the high-temperature stable fcc δ-form. The bcc γ-form can be stabilized by the addition of small amounts of dopant oxides to form the sillenite group of compounds $6Bi_2O_3 \cdot MO_x$ in the I23 space group [1–3]. The structure of the sillenite compounds has been determined: the M cations are tetrahedrally coordinated and occupy the body centred sites and the cube corners, linked by hepta-coordinated bismuth atoms. This lattice only achieves the perfect structure where the M cation is tetravalent giving the general formula $6Bi_2O_3 \cdot MO_2(Bi_{24}M_2O_{40}$ in the unit cell) [4–6].

The pure γ-Bi_2O_3 was first proposed by Sillen [1] to be isomorphous with the bcc $Bi_{24}Si_2O_{40}$ where bismuth atoms occupy the silicon positions in the cell. Other studies suggested that the γ-Bi_2O_3 contains $Bi_{26}O_{39}$ in the unit cell [7, 8]. Levin and Roth [2] indicated that the pure γ-Bi_2O_3 has the largest cell constant of the series of sillenite compounds reported. Craig and Stephenson [9] suggested that the γ-Bi_2O_3 is isomorphous with $Bi^{3+}_{24}Bi^{5+}Fe^{3+}O_{40}$ and has the composition $Bi^{3+}_{25}Bi^{5+}O_{40}$, where the two tetrahedral sites are occupied by one Bi^{3+} and one Bi^{5+} ion. Devalette *et al.* [10] reported that $Bi_{12}[A^{3+}_{1/2}B^{5+}_{1/2}]O_{20}$ and $Bi_{12}[Zn^{2+}_{1/3}B^{5+}_{2/3}]O_{20}$ (A = Fe, Ga and B = P, As, Bi) are derived from $Bi_{12}GeO_{20}$ by couple substitutions. However, the existence of the Bi^{5+} ion has not yet been verified directly. Accordingly, it is not clear at present whether the oxygen sublattice of the pure γ-Bi_2O_3 is occupied completely or not.

The electrical conduction of bcc $Bi_{24}Si_2O_{40}$ single crystal is reported to be p-type electronic at room temperature and to only have a small contribution from oxygen ionic transport at high temperatures [11, 12]. However, $Bi_{24}Pb_2O_{38}$ and the nonstoichiometric $Bi_{24}Si_2O_{40}$ sintered specimen were reported to have much higher oxygen ionic conductivities resulting in a mixed conduction behaviour [12, 13]. Harwig and Gerards [14] also suggested that the oxygen ionic conduction is predominant in the pure γ-Bi_2O_3 based on the frequency dispersion of impedance. However, details of electrical conduction of the pure and doped γ-Bi_2O_3 are not clear.

The present authors reported previously that the γ-form sintered specimen can be obtained at room temperature by doping a few mol % of Sb_2O_3 [15, 16]. In the present study, the electrical conduction in γ-Bi_2O_3 doped with Sb_2O_3 was investigated by measuring electrical conductivity, as a function of temperature and oxygen partial pressure, and ionic transference number.

2. Experimental procedure

The raw materials were monoclinic α-Bi_2O_3 and Sb_2O_3 (both 99.99% pure). The powders were mixed, calcined in air at 730° C for 2 h in a platinum crucible, finely ground, and pressed into pellets (10 mm in diameter × 3 mm in depth) or rods (5 mm × 3 mm × 10 mm) under 54 MPa. The pressed bodies were sintered at 800° C for 5 h in air and furnace-cooled.

Polymorphic forms and lattice constants were determined by X-ray diffraction (XRD). Polymorphic transformations were examined by high-temperature XRD and differential thermal analysis (DTA). The concentration of Sb^{3+} and Sb^{5+} ions in γ-Bi_2O_3 were determined by wet chemical analysis.

Electrical conductivity was measured by a complex impedance method at 5 to 13 MHz and a four-probe d.c. method. The four-probe d.c. method was used for the determination of the oxygen partial pressure (P_{O_2}) dependence of conductivity. No significant deviation in conductivity was observed for both methods. In order to control P_{O_2}, Ar–O_2 mixed gas was passed as a carrier gas and stabilized zirconia cells were used for reducing and monitoring P_{O_2}.

Ionic transference number was determined by a d.c.

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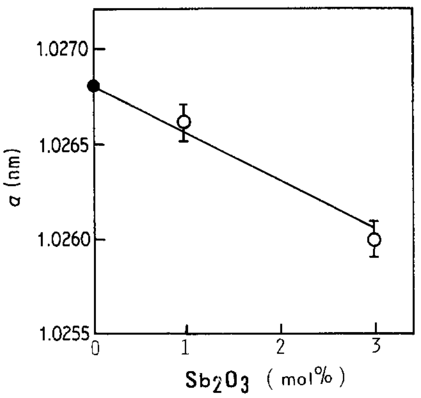

Figure 1 Lattice constant of γ-Bi_2O_3 doped with Sb_2O_3 (●; [6]).

polarization method. A sputtered gold cathode was covered with indium metal as a blocking electrode, and a gold anode was exposed to air. The following equation was used to calculate the transference number t_i;

$$t_i = 1 - \sigma(\infty)/\sigma(0) \qquad (1)$$

where $\sigma(0)$ and $\sigma(\infty)$ are the d.c. conductivity at initiation of biassing and after polarization, respectively. The experimental set-ups are shown elsewhere [13, 17].

3. Results and discussion

Samples of bcc γ-Bi_2O_3 were obtained by doping with 1 to 3 mol% Sb_2O_3. Minor monoclinic XRD peaks were detected only in the 1 mol% specimens. Doping with more than 3 mol% gave rise to another metastable tetragonal β-form. The apparent density of the sintered specimens in the γ-form was 88 to 92% of the theoretical value.

The lattice constant decreased with an increase of Sb_2O_3 content as shown in Fig. 1. This indicates that Sb_2O_3 dissolves into γ-Bi_2O_3 in the present composition. Wet chemical analysis showed that more than 80% of antimony ions are pentavalent in 2 mol% Sb_2O_3 doped γ-Bi_2O_3. Fig. 2 shows DTA curves of γ-Bi_2O_3 doped with 2 mol% Sb_2O_3 and XRD patterns at the indicated temperatures. It was shown that γ-form transforms into α-form at about 560° C and then into the δ-form at about 710° C on increasing temperature. On cooling, the δ-form transformed directly into the γ-form.

Fig. 3 shows typical impedance plots of γ-Bi_2O_3 doped with 32 mol% Sb_2O_3 at 356 and 425° C. One semicircle in contact with the zero point at high frequencies and a section of semicircle at low frequencies can be observed. The low frequency region (below 1 kHz in Fig. 3) can be explained by electrode impedance [18]. There was no semicircle associated with the grain boundary, which often appears in middle frequency region for oxygen ionic conductors such as stabilized zirconia [19]. It is not clear whether this is due to the very small grain-boundary impedance or to the identical time constants in grain and grain-boundary impedances, which prevents the spliting of both contributions in the impedance plot. However, in the present study, the end-point of the first semicircle was taken as the bulk resistance to calculate conductivity.

The temperature dependences of the conductivity for Sb_2O_3 doped Bi_2O_3 on heating are shown in Fig. 4. The polymorphic transformations into the α and δ-forms are accompanied by abrupt conductivity changes. The composition dependence of the conductivity in the γ-form will be discussed later.

Ionic transference numbers in the Sb_2O_3 doped Bi_2O_3 are shown in Fig. 5. In the present method, the applied voltage was controlled to be below 50 mV. Accordingly, the measured transference numbers correspond to the average value under a P_{O_2} of between $10^{4.33}$ (air) and $10^{2.7}$ Pa. The transference numbers were almost unity in the bcc γ-form (below 550° C) and fcc δ-form (above 720° C), whereas they were almost zero in the monoclinic α-form. After the polarization measurements, morphological changes in the specimens were not found; those would be expected if charge transport by cations had occurred.

The dependence of conductivity on P_{O_2} for γ-Bi_2O_3 doped with 1 to 3 mol% Sb_2O_3 at 500° C are shown in Fig. 6. The conductivities were kept constant under the P_{O_2} of 10^5 to 10^{-9} Pa. The results for the ionic transference number and P_{O_2} dependence of conductivity demonstrate that the γ-Bi_2O_3 doped with 1 to 3 mol% Sb_2O_3 is an oxygen ionic conductor in the wide range of P_{O_2}.

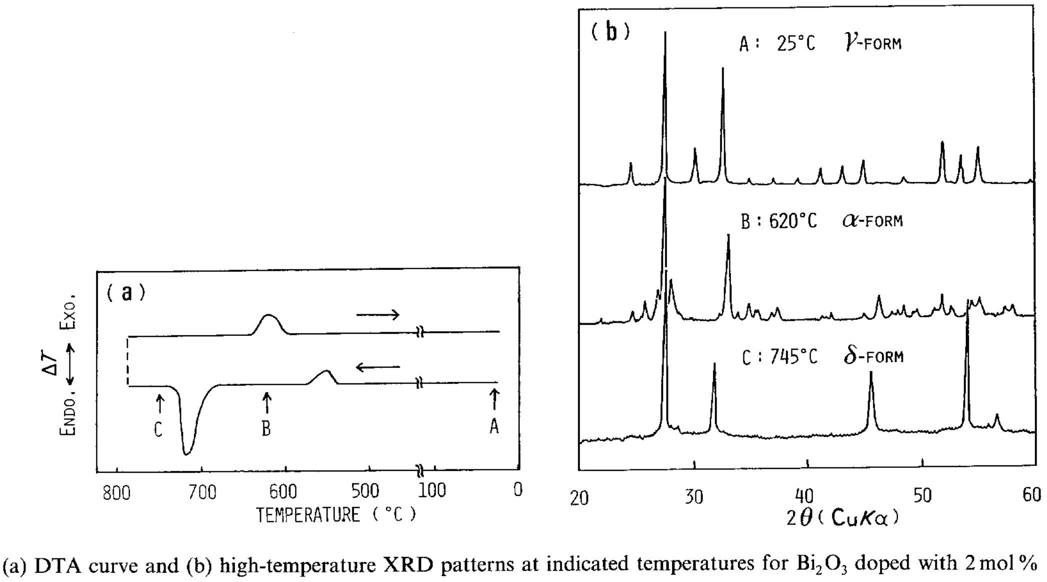

Figure 2 (a) DTA curve and (b) high-temperature XRD patterns at indicated temperatures for Bi_2O_3 doped with 2 mol% Sb_2O_3.

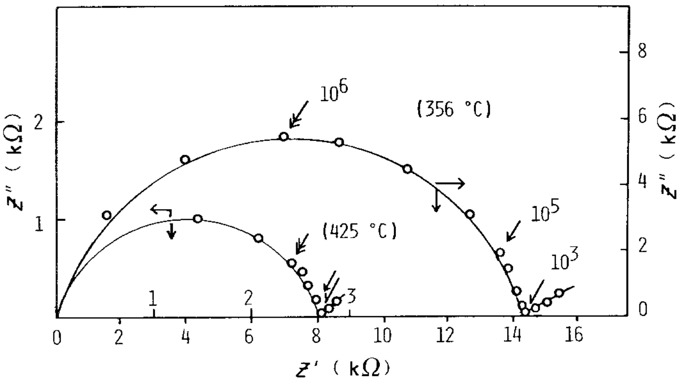

Figure 3 Complex impedance plots of γ-Bi_2O_3 doped with 3 mol % Sb_2O_3 at 356 and 425° C. Indicated numbers are the measuring frequency (Hz).

Fig. 7 shows the dependence on Sb_2O_3 content of conductivity σ, activation energy E and pre-exponential term σ_0, when they are expressed as $\sigma = \sigma_0 \exp(-E/kT)$ where k is the Boltzmann constant and T the absolute temperature. The conductivity showed a maximum at 2.5 mol % Sb_2O_3. The activation energy remained almost unchanged and hence it is clear that the change of σ is due to that of σ_0.

It is proposed that pure γ-Bi_2O_3 contains $Bi_{26}O_{39}$ or $Bi_{25}^{3+}Bi^{5+}O_{40}$ in the unit cell [1, 7–9]. However, if the oxygen sublattice is completely occupied, γ-Bi_2O_3 would not show such a high conductivity. In fact, estimated oxygen ionic conductivity at 500° C in $Bi_{24}Si_2O_{40}$ and non-stoichiometric $Bi_{24}Si_{2-x}O_{40-2x}$ ($x = 0.1$ to 0.14) are reported to be 3×10^{-10} and $4 \times 10^{-5}\,\Omega^{-1}\,cm^{-1}$, repectively [12, 13]. Those are much lower than that of γ-Bi_2O_3 doped with Sb_2O_3. In addition, the reported density of pure γ-Bi_2O_3, 9.21 g cm^{-3} [7], is smaller than the calculated density of 9.29 for $Bi_{26}O_{39}$ and 9.315 g cm^{-3} for $B_{26}O_{40}$ (using 1.0268 nm as the lattice constant), but larger than 8.575 g cm^{-3} for $Bi_{24}O_{36}$ assuming that all tetrahedrons are vacant. Accordingly, it is assumed that the oxygen sublattice in pure γ-Bi_2O_3 is only partially occupied and consequently the large vacancy concentration brings about a high oxygen ionic conductivity. However, it is not clear whether those vacancies are caused only by Bi^{3+} occupation at tetrahedral Si^{4+} sites or by some Shottky-type defects of Bi^{3+} (or Bi^{5+}) and oxygen vacancies [13].

As shown in Fig. 7, the pre-exponential term σ_0 increased with increasing Sb_2O_3 content up to 2.5 mol %. This indicates an increase in the oxygen vacancy concentration effective for ionic conduction [20]. Reported ionic radii (6-coordinated) are 0.103 and 0.076 nm for Bi^{3+} and Bi^{5+}, 0.076 and 0.060 nm for Sb^{3+} and Sb^{5+}, and 0.040 nm for Si^{4+}, respectively, based on 0.140 nm for O^{2-} [21]. The oxygen vacancies in γ-Bi_2O_3 must be bound or ordered around Bi^{3+} (or Bi^{5+}) at tetrahedral sites, which are too large to occupy those sites. The incorporated smaller Sb^{5+} ions would probably substitute preferentially at the tetrahedral sites and subsequently the concentration of the bound vacancies would be decreased resulting in an increase in σ_0.

On the other hand, the bcc lattice approaches the perfect structure as the oxidized Sb^{5+} ions and corresponding oxygen ions are further incorporated. When incorporated Sb_2O_5 content is 3.85 mol %, composition becomes stoichiometric $Bi_{24}^{3+}(Bi^{3+}Sb^{5+})O_{40}$, although its presence is not yet confirmed. Accordingly, the decreases in σ_0 and σ at above 2.5 mol % Sb_2O_3 shown in Fig. 7 appear to be due to a decrease in the total oxygen vacancy concentration.

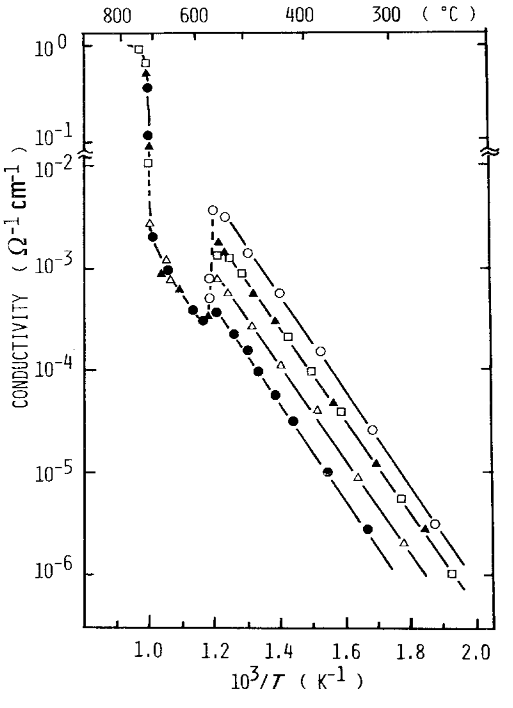

Figure 4 Temperature dependence of conductivity of γ-Bi_2O_3 doped with Sb_2O_3; (●) 1, (△) 1.5, (▲) 2, (○) 2.5, (□) 3 mol % Sb_2O_3.

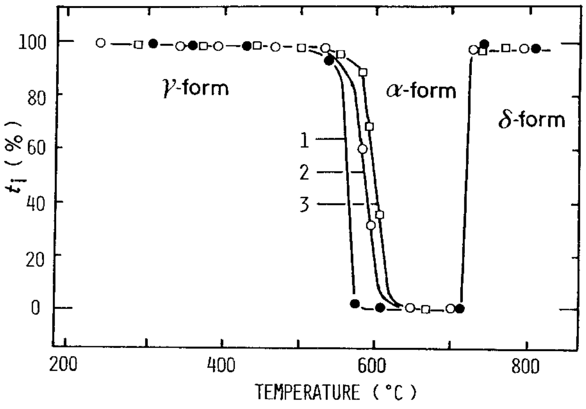

Figure 5 Ionic transference numbers in Sb_2O_3 doped Bi_2O_3. Indicated numbers show Sb_2O_3 content (mol %).

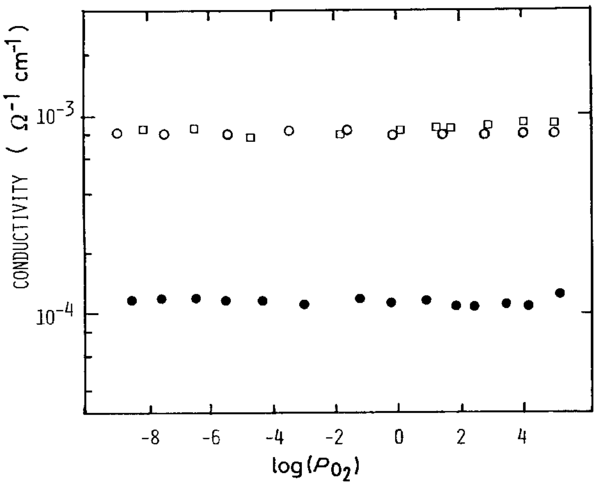

Figure 6 P_{O_2} dependence of conductivity at 500° C for γ-Bi_2O_3 doped with Sb_2O_3; (●) 1, (○) 2, (□) 3 mol % Sb_2O_3.

4. Conclusions

Body centred cubic γ-Bi_2O_3 doped with 1 to 3 mol % Sb_2O_3 was stable up to 550° C but transformed into monoclinic α and fcc δ-Bi_2O_3 at high temperatures.

In the Sb_2O_3 doped γ-Bi_2O_3, the oxygen ionic conduction was predominant in the P_{O_2} range of 10^5 to 10^{-9} Pa. As the Sb_2O_3 content increased, oxygen ionic conductivity increased up to 2.5 mol % Sb_2O_3 reaching a maximum of $1.8 \times 10^{-3} \Omega^{-1} cm^{-1}$ at 500° C and then decreased. However, the activation energy for ionic conduction remained almost unchanged.

It was confirmed that more than 80% of antimony ions are pentavalent in γ-Bi_2O_3. Those Sb^{5+} ions appear to affect the concentraion of oxygen vacancies effective for ionic conduction.

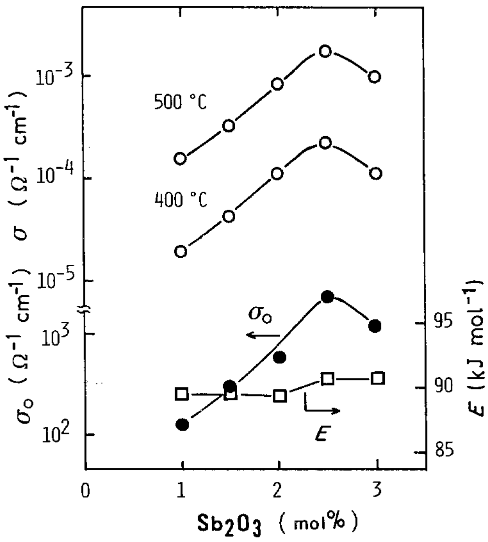

Figure 7 Sb_2O_3 content dependences of conductivity σ (at 400 and 500° C), activation energy E and pre-exponential term σ_0.

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