JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 31–35

Oxide ion conduction in the sintered oxides of MoO_3-doped Bi_2O_3

T. TAKAHASHI, T. ESAKA, H. IWAHARA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Received 14 November 1975

In order to examine the conduction behaviour in the sintered oxides of MoO_3-doped Bi_2O_3, the electrical conductivity in air and the EMF of oxygen gas concentration cell were measured with respect to the phase relation determined by X-ray diffraction.

The tetragonal single phase oxide containing 22 mol% MoO_3 was found to be a high oxide ion conductor, the conductivity of which was comparable to those of stabilized zirconias. The partial electronic conduction in this phase was negligibly small at relatively high oxygen pressure. The oxide ion conduction was considered to be attributable to an appreciable amount of oxygen vacancies present in the crystal. In the monoclinic compound $3Bi_2O_3 \cdot 2MoO_3$, the oxide ion conduction was also observed. Although the conductivity of this phase was somewhat lower than that of the tetragonal phase, the activation energy for conduction (53·5 kJ mol^{-1}) was much lower than the values for usual oxide ion conductors.

---

1. Introduction

Many workers have investigated the high oxide ion conduction in the solid solutions based on tetravalent metallic oxides such as stabilized zirconias and doped thorias [1–4]. These 'defect' fluorite-type oxides have an appreciable number of oxide ion vacancies. In addition, the authors reported the high oxide ion conduction in the sintered oxides based on Bi_2O_3 [5–8]. The high temperature form of pure Bi_2O_3 (δ-Bi_2O_3) shows very high oxide ion conductivity in a temperature range of 730 ~ 825° C (m.p.). This form is considered to have the defect fluorite-type structure (fcc) like stabilized zirconias [9–12]. However, this phase is unstable below 730° C, If the fcc form corresponding to δ-Bi_2O_3 can be stabilized at a lower temperature, high oxide ion conductivity must be retained even below 730°C. The authors found that this could be realized by adding WO_3 to Bi_2O_3 [6]. For example, $(Bi_2O_3)_{0·78}(WO_3)_{0·22}$ has the fcc structure over a wide range of temperature and the oxide ion conductivity is $2·8 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at 600° C, which is higher than the value of yttria-stabilized zirconia at the corresponding temperature.

Molybdenum as well as tungsten belongs to the VIb group of the periodic table, and ionic radius, electronegativity, and other physical properties are almost the same as a result of the lanthanoid contraction. Therefore, sintered oxides of MoO_3-doped Bi_2O_3 were expected to show high oxide ion conductivity as was the case of the system Bi_2O_3–WO_3.

The system Bi_2O_3–MoO_3 has been investigated in the field of catalysis; both $Bi_2O_3 \cdot 2MoO_3$ and $Bi_2O_3 \cdot MoO_3$ are known to have a good catalytic activity and selectivity for oxidation of hydrocarbons [13, 14]. However, the oxide ion conduction in the system Bi_2O_3–MoO_3 has not yet been reported. From this point of view, the authors have investigated the oxide ion conduction in the sintered oxides of MoO_3-doped Bi_2O_3. As a result, a tetragonal phase was observed in this system which showed high oxide ion conductivity.

2. Experimental

2.1. *Preparation of samples*

Bismuth nitrate (JIS special grade) was decom-

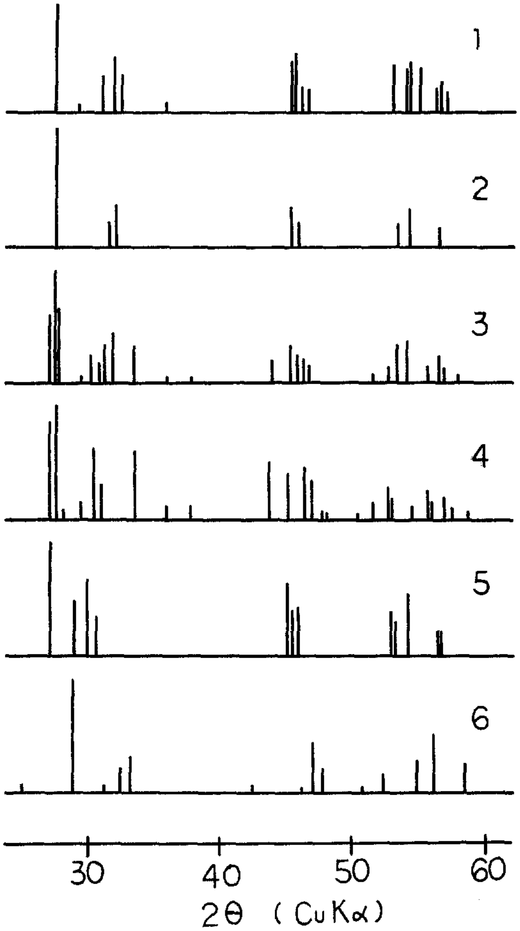

Fig. 1. X-ray diffraction patterns of $(Bi_2O_3)_{1-x}(MoO_3)_x$ cooled slowly from sintering temperature to room temperature

No.	1	2	3	4	5	6
x	0·20	0·25	0·35	0·40	0·50	β-Bi_2O_3

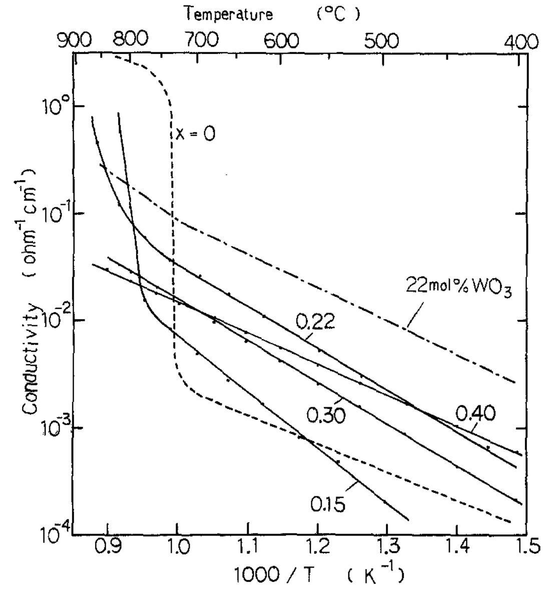

Fig. 2. Conductivity versus reciprocal of the absolute temperature curves for $(Bi_2O_3)_{1-x}(MoO_3)_x$ in air.

posed into Bi_2O_3 at 700° C. A mixture of Bi_2O_3 and MoO_3 (99·5%) was ground, and fired at about 800° C in air. The pre-fired sample was powdered, moulded at a pressure of 3 ton cm^{-2} into a cylinder shape (5 mm ϕ x 12 mm) and disk (12 mm ϕ x 3 mm), and fired again at 800 ~ 1000° C in air for 10 h. The firing temperature was raised with increasing MoO_3 content in order to obtain well-sintered specimens. By this process a density of ≈ 94% of the theoretical was obtained. The sample composition was considered not to change, because TG data showed no weight decrease during firing.

The crystal structure was identified by X-ray diffraction using CuKα radiation with a nickel filter. The density was measured by standard pycnometer method using n-butanol.

2.2. *Measurement of ionic conduction*

The electrical conductivity was measured by 2-probe a.c. method at a frequency of 10 kHz. Ionic transference number was examined by measuring the e.m.f of the following oxygen gas concentration cell using specimen disk as electrolyte;

$$O_2\,(P_{O_2}, a),\ \text{Pt}|\text{specimen disk}|\text{Pt},\ O_2\,(P_{O_2}, c) \qquad (1)$$

where $P_{O_2}, a = 0{\cdot}21$ atm (air) and $P_{O_2}, c = 1{\cdot}00$ atm (pure oxygen). These experimental procedures are the same as those described in the previous papers [5, 6].

3. Results and discussion

3.1. *X-ray diffraction*

Fig. 1 shows the X-ray diffraction patterns of samples which were cooled slowly from sintering temperatures to room temperature for 15 h. A tetragonal single phase and orthorhombic koechlinite (Bi_2MoO_6) were observed for 25 mol % and 50 mol % MoO_3 specimens, respectively. The tetragonal phase was found in a composition range of 22 mol

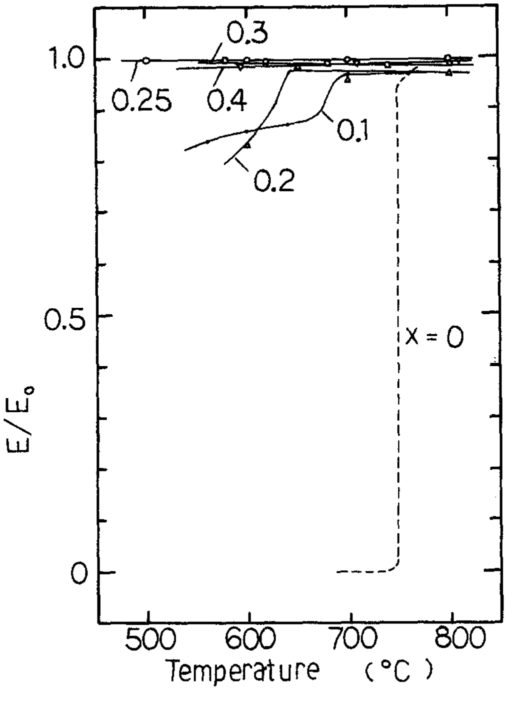

Fig. 3. Ratio of the measured EMF (E) to the theoretical value (E_0) of the following cell, O_2 (0·21 atm), Pt|$(Bi_2O_3)_{1-x}(MoO_3)_x$|Pt, O_2 (1·0 atm).

~ 28 mol % MoO_3. The specimen having 40 mol % MoO_3 corresponded to the monoclinic compound ($3Bi_2O_3 \cdot 2MoO_3$) which was reported by Miyazawa *et al.*, [15]. In the other ranges of composition, a mixture of two phases was seen.

When the samples containing less than 25 mol % MoO_3 were quenched from sintering temperature to room temperature, the X-ray diffraction patterns showed the fcc crystal system. Therefore, the fcc phase similar to δ-Bi_2O_3 is considered to be present in the Bi_2O_3-rich composition ranges as a high temperature modification.

3.2. *Ionic conduction*

Fig. 2 represents an Arrhenius plot of conductivity measured in air. As shown in the case of 15 mol % MoO_3, the system having low MoO_3 content indicated the abrupt conductivity rises which were similar to the conductivity behaviour of pure Bi_2O_3. The conductivity of the 22 mol % MoO_3 specimen was high compared with that of Bi_2O_3 below 730° C and the extent of the conductivity jump was smaller than that of the pure specimen. In the case containing more than 30 mol % MoO_3, no abrupt conductivity change was observed over the temperature range measured (~ 850° C). The abrupt conductivity change was considered to be due to the phase transition into high temperature phase (fcc) because different X-ray diffraction patterns were observed between quenched and annealed samples as mentioned above, and the endothermic reaction was observed on the DTA chart at the temperature of the conductivity jump during heating.

The slope for the 40 mol % MoO_3 sample (monoclinic compound) in Fig. 2 was gentle compared with that for tetragonal phase (22 mol % MoO_3), and both conductivities were comparable at lower temperatures. The conductivity of the 50 mol % MoO_3 sample was less than $10^{-4}\,\Omega^{-1}\,cm^{-1}$ at 750° C.

Fig. 3 shows the ratio of measured EMF of the cell (1) to the theoretical value. As the charge carrier in Bi_2O_3 changes from electron hole to oxide ion at 730° C, an abrupt change is observed in the E/E_0 data at the corresponding temperature. Similar behaviour was observed in the specimen having less than 20 mol % MoO_3. Therefore, in this range of composition, the contribution of partial electronic conduction is present at temperatures lower than 650° C. E/E_0 of the specimens containing more than 22 mol % MoO_3 is above 0·95 over the measured temperature range, indicating predominantly ionic conduction. The steady current could be drawn from the cells and neither decomposition nor corrosion was observed in the specimens after discharge. The conductivity calculated from the i–V relation corresponded to the value measured by the a.c. bridge. These results indicate that the conduction is due to the oxide ion which can react at both electrodes reversibly. As a result, the specimen having tetragonal and monoclinic structures can be concluded to show the predominant oxide ion conduction in the temperature region measured (~ 850° C), but the partial electronic conduction contributes to the total conductivity for the sample containing less than 20 mol % MoO_3 at relatively low temperature.

Fig. 4 shows conductivity versus composition data. In the tetragonal single phase (22 mol ~ 28 mol % MoO_3), the sample having the lowest content of MoO_3 shows the highest oxide ion conductivity. The oxide ion conductivity of monoclinic compound (40 mol % MoO_3) is comparable to the

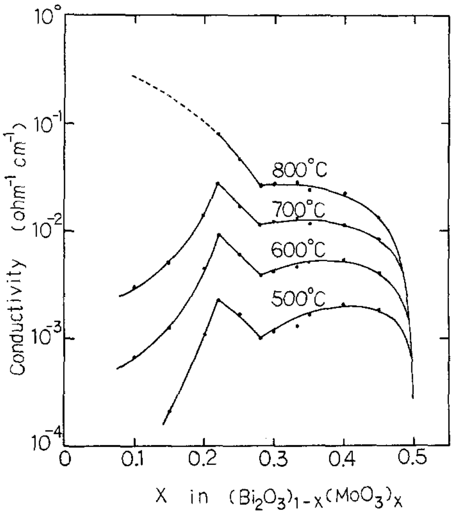

Fig. 4. Conductivity versus composition curves for $(Bi_2O_3)_{1-x}(MoO_3)_x$.

value of the 22 mol% MoO_3) specimen at 500°C, and the activation energy for oxide ion conduction calculated from Fig. 1 is 53·5 kJ mol^{-1}, which is a lower value than that of general oxide ion conductors.

3.3. *Oxygen deficient structure in the tetragonal phase*

Bi_2O_3 is known to have four modifications, in which the metastable β-form is tetragonal [10, 16] and it is known to be stabilized by adding ZrO_2 [17]. In the system Bi_2O_3–MoO_3, a tetragonal single phase was observed in the composition range 22 mol ~ 28 mol% MoO_3. Therefore, the tetragonal phase present in this system may be considered to be analogous to β-Bi_2O_3.

The unit cell parameters of this tetragonal phase ($3Bi_2O_3\cdot MoO_3$) were calculated to be as follows,

$$a = 5{\cdot}62 \pm 0{\cdot}01\ \text{Å}$$

$$c = 5{\cdot}73 \pm 0{\cdot}01\ \text{Å}.$$

This value of a is comparable to the lattice constant (5·604 ± 0·004 Å) of $3Bi_2O_3\cdot WO_3$, which shows the high oxide ion conductivity [6], but the lattice expands to some extent along its c-direction in this case. The pycnometric density for $x = 0{\cdot}25$ was 7·96 ± 0·10 g cm^{-3}. This value coincided within the limits of experimental error, with the density (8·08 ± 0·04 g cm^{-3}), which was calculated assuming that all cation sub-lattice sites of β-Bi_2O_3-type crystal were filled by Bi^{3+} and Mo^{6+} and some oxygen sub-lattice sites were vacant, that is, the unit cell formula could be written as

$$Bi_{4(2-2x)/(2-x)}Mo_{4x/(2-x)}O_{12/(2-x)}\square_{4(1-2x)/(2-x)},$$

where $\square$ shows an oxygen vacant site. This result denotes that the tetragonal phase has an appreciable amount of oxygen vacancies like fcc $3Bi_2O_3\cdot WO_3$. The oxygen vacancies in this phase were considered to distribute randomly, because the X-ray diffraction patterns of this phase showed no characteristic peaks to ordered distribution of atoms (see Fig. 1). These vacancies can contribute to oxide ion conduction in these materials as in the case of stabilized zirconias.

3.4. *Conduction in the co-precipitated samples*

As has been reported by the authors of this paper, the fcc phase of Bi_2O_3-based oxides was generally a high oxide ion conductor. In the sintered specimens of the system Bi_2O_3-MoO_3, this phase was unstable at room temperature. Gattow *et al.* reported, however, that $2Bi_2O_3\cdot MoO_3$ and $Bi_2O_3\cdot MoO_3$ prepared by co-precipitation showed the fcc crystal system at room temperature [18]. $Bi_2O_3\cdot 2MoO_3$ and $Bi_2O_3\cdot 3MoO_3$ which are known as catalysts for the oxidation of hydrocarbons are also prepared by co-precipitation. This preparation method was followed to examine the conduction properties of the powder obtained. The oxides were co-precipitated from the nitrate solution of Bi and Mo using NH_4OH as precipitant, and pressed into a pellet under a pressure of 3 ton cm^{-2}.

The $2Bi_2O_3\cdot MoO_3$ and $Bi_2O_3\cdot MoO_3$ obtained thus showed X-ray diffraction patterns of the fcc crystal system. However, the pressed oxides were not high oxide ion conductors ($> 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 400° C) and transformed at about 500° C into the phase prepared by solid state reaction. Furthermore, $Bi_2O_3\cdot 2MoO_3$ and $Bi_2O_3\cdot 3MoO_3$ in an amorphous state suitable for a catalyst showed no ionic conduction in our experiment.

4. Summary

The authors investigated the conduction in the system Bi_2O_3-MoO_3, and obtained the following results.

(1) Instead of the fcc phase shown in the Bi_2O_3–WO_3 system [6], the tetragonal single phase is stable for the system Bi_2O_3–MoO_3 in the corresponding composition range (22 mol ~ 28 mol %).

(2) The conduction in the tetragonal phase is ascribed predominantly to the oxide ion. This oxide ion conduction is considered to be due to the migration of oxygen vacancies present in the crystal. The conductivity is $9{\cdot}0 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ at 600° C, which is somewhat lower than the value of the fcc phase in the system Bi_2O_3–WO_3, but is higher than that of stabilized zirconia.

(3) For MoO_3 content of less than 20 mol %, the oxides show a monoclinic (α-Bi_2O_3) and tetragonal mixed phase, in which partial electronic conduction was observed.

(4) In the composition range of 30 mol ~ 45 mol% MoO_3, the conduction is also attributed predominantly to oxide ion. Though the monoclinic compound $3Bi_2O_3 \cdot 2MoO_3$ shows somewhat lower conductivity than that of the tetragonal phase, the activation energy for conduction is 53·5 kJ mol^{-1}, which is much lower than the values of the usual oxide ion conductors.

References

[1] R. Hartung, *Z. phys. Chem (Leipzig)* **254** (1973) 393.
[2] T. H. Etsell and S. N. Flengas, *J. Electrochem. Soc.* **119** (1972) 1.
[3] F. J. Salzano, C. Auerbach, H. S. Isaacs and B. Minushkin, *ibid* **118** (1971) 416.
[4] J. B. Hardaway, J. W. Patterson, D. R. Wilder and J. D. Schieltz, *J. Amer. Ceram. Soc.* **54** (1971) 94.
[5] T. Takahashi, H. Iwahara and Y. Nagai, *J. Appl. Electrochem.* **2** (1972) 97.
[6] T. Takahashi and H. Iwahara, *ibid* **3** (1973) 65.
[7] T. Takahashi, H. Iwahara and T. Arao, *ibid* **5** (1975) 187.
[8] T. Takahashi, T. Esaka and H. Iwahara, *ibid* **5** (1975) 197.
[9] G. Gattow and H. Schröder, *Z. anorg. Chem.* **318** (1962) 176.
[10] G. Gattow and D. Schütze, *ibid* **328** (1964) 44.
[11] M. G. Hapase and V. B. Tare, *Indian J. Pure Appl. Phys.* **5** (1967) 401.
[12] R. S. Sethi and H. C. Gaur, *Indian J. Chem.* **3** (1955) 177.
[13] A. P. Gorshkov, G. V. Isagulyants, Yu. I Derbentsev, L. Ya. Margolis and I. K. Kolchin, *Dokl. Akad. Nauk. SSSR* **186** (1969) 827.
[14] Ph. A. Batist, A. H. W. M. der Kinderen, Y. Leeuwenburgh, F. A. M. G. Metz and G. C. A. Schuit, *J. Catal.* **12** (1968) 45.
[15] S. Miyazawa, A. Kawana, H. Koizumi and H. Iwasaki, *Mat. Res. Bull.* **9** (1974) 41.
[16] F. Hund, *Z. anorg. Chem.* **333** (1964) 248.
[17] D. Becherescu, R. Cipau and F. Marx, *Keram. Z.* **23** (1971) 387.
[18] G. Gattow, *Z. anorg. Chem.* **298** (1959) 64.