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High oxide ion conduction in sintered oxides of the system Bi_2O_3–WO_3

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The ionic conduction in sintered oxides of the system Bi_2O_3–WO_3 was investigated by measuring conductivities and ion transference numbers under various conditions. The ion transference number was measured by an oxygen concentration cell employing the specimen tablet as the electrolyte.

It was found that a compound $3Bi_2O_3$ WO_3 and its solid solution were high oxide ion conductors, the conductivities of which were about one order of magnitude higher than those of the well-known oxide ion conductors such as stabilized zirconias. In contrast to pure Bi_2O_3 which is a completely electronic conductor below 730°C, these materials showed high oxide ion conduction even below 700°C accompanied by little electronic conduction. $3Bi_2O_3$ WO_3 has the face centered cubic structure, probably of the fluorite type, and the oxide ion conduction was thought to be attributed to the migration of oxide ion vacancies in the crystal.

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1. Introduction

As previously reported by the present authors[1], sintered Bi_2O_3 containing a certain amount of SrO, CaO or La_2O_3 shows high oxide ion conduction under ordinary atmospheres, the conductivities being several times higher than those of the well-known stabilized zirconias. These materials belong to or contain the solid solution of rhombohedral phase which was first proposed by Sillén [2] to have a relatively large number of oxide ion vacancies in the crystal.

Although a number of references on the electrical properties of solid electrolytes are quoted in a recent review [3], highly conductive pure oxide ion conductors studied so far are mainly the fluorite-type solid solutions based on the oxides of tetravalent metals containing some lower valent metallic oxides. These fluorite-type oxide solid solutions have also an appreciable number of oxide ion vacancies in the crystal lattice, which belongs to the face centered cubic structure with respect to cations.

It may be expected, therefore, that face centered cubic-type oxides based on Bi_2O_3 should have high oxide ion conduction, since a substantial quantity of oxide ion vacancies may be anticipated in the f.c.c.-type crystal of tri-valent metallic oxides. In fact, the high temperature modification (>730°C) of pure Bi_2O_3 is known to have a face centered cubic structure, probably of the fluorite-type [4, 5], and its high electrical conduction is thought to be attributable to the migration of oxide ions through the vacancies as previously reported [1, 6, 7]. High oxide ion conduction in this material, however, is only well-defined above 730°C, and electronic conduction predominates below this temperature where the monoclinic structure (α-phase) is stable.

Gattow *et al.* [5] reported that $2Bi_2O_3$ WO_3 had a f.c.c. crystal structure (δ^*-phase) stable even at temperatures below 700°C, the X-ray diffraction pattern of which was related to that of the high temperature modification of pure Bi_2O_3 (δ-phase). Galiperin *et al.* [8] reported that the δ^*-phase was stable in the compositions from $(Bi_2O_3)_{0\cdot67}$ $(WO_3)_{0\cdot33}$ to $(Bi_2O_3)_{0\cdot88}$ $(WO_3)_{0\cdot22}$ over a wide range of temperature. On the other hand, according to the phase diagram of Bi_2O_3–WO_3 drawn by Speranskaya [9], the f.c.c.-type phase was recognized only in the narrow composition range near the compound $3Bi_2O_3\ WO_3$. In either case, at any rate, the system Bi_2O_3–WO_3 is known to contain the phase of the face centered cubic structure, and, therefore, these materials may possibly exhibit high-oxide ion conduction over a wide range of temperature.

From these points of view, the present authors investigated ionic conduction in the system Bi_2O_3–WO_3 over a wide range of composition and under various conditions.

2. Experimental

2.1. *The preparation of the specimens*

The raw materials were tungstic acid and bismuth sesquioxide which was obtained by the thermal decomposition of bismuth nitrate (JIS; special grade) at 700°C for 2 h. The powders of these substances were mixed well and were calcined at 700~800°C for 10 h in air. The calcined materials were ground fine and pressed into rods (dia.; 0·5~0·6, length; 0·5~1·0 cm) or tablets (dia.; 1·3, thickness; 0·2~0·3 cm) under a pressure of 3~4 ton/cm^2 and finally sintered in air for 10 h. The temperatures in the final sintering were changed from 750°C to 950°C according to the compositions of the specimens as represented in Table 1, the greater the WO_3 content the higher the sintering temperature.

Table 1. Temperature of final sintering

composition *x in* $(Bi_2O_3)_{1-x}(WO_3)_x$	*temperature* (°C)
0·00	750
0·05	820
0·10	850
0·15	850
0·20	900
0·33	900
0·50	950

The X-ray diffraction of the sintered oxides or their powders was carried out with Cu*Kα* radiation, and, for the measurement of the density, the picnometric method using n-butanol at 25°C was adopted.

2.2. *Measurement of ionic conduction*

The ionic conduction in the specimens was investigated by measuring the electrical conductivity and the ion transference number under various conditions.

The measurement of conductivity was made by an A.C. bridge equipped with a capacity compensator. The column-shaped specimens were used in this case and platinum paste was adopted as the electrode material. 10 k Hz was employed as the frequency of the A.C. applied to the bridge, since the dependence of measured conductivity on frequency is sometimes fairly marked in the frequency range lower than 5 k Hz.

The relative contribution of ions and electrons to the total conductivity, that is, the ion transference number, was measured mainly by the concentration cell method [10]. The following cell was constructed using the specimen tablet as the electrolyte.

$$O_2\,(P_{O_2,a}),\ Pt\ \left|\begin{array}{l}\text{Specimen}\\ \text{tablet}\end{array}\right|\ Pt,\ O_2\,(P_{O_2,c}) \quad (1)$$

If the conduction in the specimen is purely ionic, the e.m.f. of the cell, E_0, is given by

$$E_0 = \frac{RT}{4F}\ln\frac{P_{O_2,c}}{P_{O_2,a}} \quad (2)$$

where R, T and F have their usual meanings.

In the mixed conductor, in which the conduction is both ionic and electronic, the e.m.f. is lowered from E_0 to some extent because of the discharge of the cell due to the electronic conduction in it. In this case, the ratio of the ionic conductivity σ_i to the total value $\sigma = \sigma_i + \sigma_e$ (where σ_e is the electronic conductivity), that is, the ion transference number t_i, can be determined as a ratio of the measured e.m.f. ,E, to the theoretical value, E_0,

$$t_i = \frac{\sigma_i}{\sigma_i + \sigma_e} = \frac{E}{E_0} \quad (3)$$

when the reversibility of the electrode reaction is good.

The construction of the cell in the present experiment was the same as that previously reported [1, 11]. Pure oxygen at 1 atm. was used as cathode gas. Air free from H_2O and CO_2 was usually adopted as anode gas, and sometimes, a mixture of oxygen and argon gas was used in order to prepare relatively low partial pressures of oxygen ($10^{-2} \sim 10^{-5}$ atm.). In the latter case, the same gas as that of the anode was flowed through the outside space of the cell to prevent a change in the oxygen partial pressure of the anode gas due to mechanical leakage at the gasket.

The reversibility of the electrode was examined by discharging the concentration cell through the outer circuit.

3. Results

3.1. *Specimen preparation*

The specimens prepared in the way described above could be sintered well; the porosity was less than 5% and open pores allowing the penetration of gases were not recognized. The colour of the specimens changed from deep yellow to pale yellow with increase of WO_3 content.

Fig. 1 shows X-ray diffraction patterns of the specimens which were cooled from the sintering temperature (>750°C) to 650°C, where they were kept for 15 h and then cooled slowly to room temperature. The single phase of f.c.c.-type (δ^*-phase) was observed in the specimen containing 25% WO_3 ($3Bi_2O_3$ WO_3). The homogeneous δ^*-phase was observed in the compositions ranging about 3% in both sides of $3Bi_2O_3$ WO_3 and, therefore, it is better to regard this compound as having a rather narrow range for the formation of solid solutions. This result is in accordance with the Speranskaya's phase diagram [9] but differs from the results obtained by Gattow [5] and Galiperin [8]. The specimens containing less than 10% WO_3 showed the mixed phase of monoclinic (α-phase) and orthorhombic (η^*-phase after Galiperin) structure, while the specimens containing $10 \sim 20\%$ WO_3 showed the mixed phase of η^* and δ^*. Although the compound $6Bi_2O_3$ WO_3 is said to exist according to the phase diagram reported by Speranskaya [8], this composition was observed to be a mixture of η^*- and δ^*-phase in our experiments. An appreciable amount of orthorhombic phase (γ-phase after Galiperin [8]) which differed from the η^*-phase appeared in $(Bi_2O_3)_{0.67}$ $(WO_3)_{0.30}$; the specimen having 50% WO_3 showed the γ^* single phase.

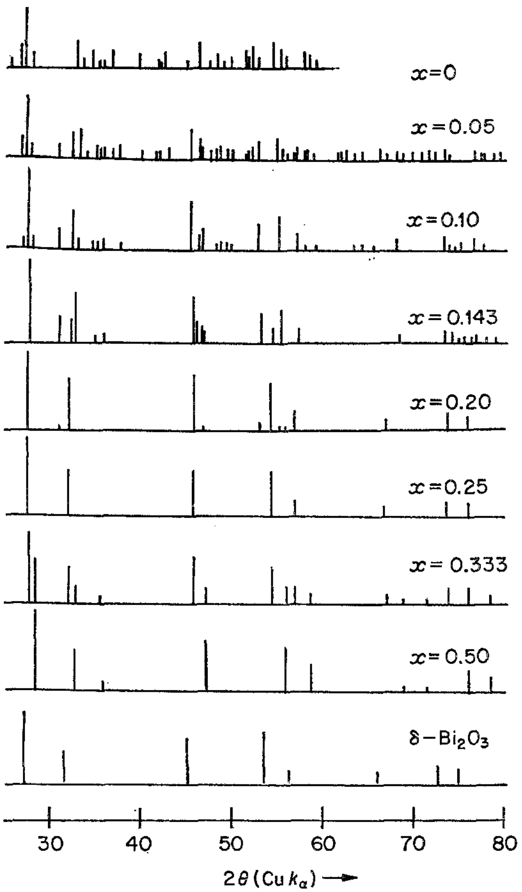

Fig. 1. X-ray diffraction patterns of $(Bi_2O_3)_{1-x}(WO_3)_x$.

3.2. *Ionic conduction*

The conductivities of the sintered Bi_2O_3–WO_3 system measured in air are represented in Fig. 2 in the form of Arrhenius plots. As previously reported [1], the conductivity of pure Bi_2O_3 is relatively low below 730°C, and the sudden increase in conductivity at this temperature corresponds to the transformation from monoclinic (α-phase) to cubic (δ-phase) structure [12]. $(Bi_2O_3)_{0.75}$ $(WO_3)_{0.25}$, on the contrary, showed no jump in conductivity up to 850°C, and its value below 730°C was markedly high compared with that of pure Bi_2O_3. This can be accounted

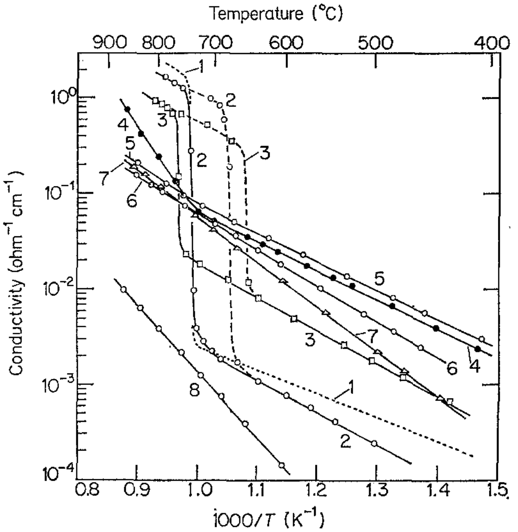

Fig. 2. Electrical conductivities of $(Bi_2O_3)_{1-x}(WO_3)_x$ in air.

No.	*x*	*No.*	*x*
1.	0·00	5.	0·22
2.	0·05	6.	0·25
3.	0·143	7.	0·333
4.	0·20	8.	0·50

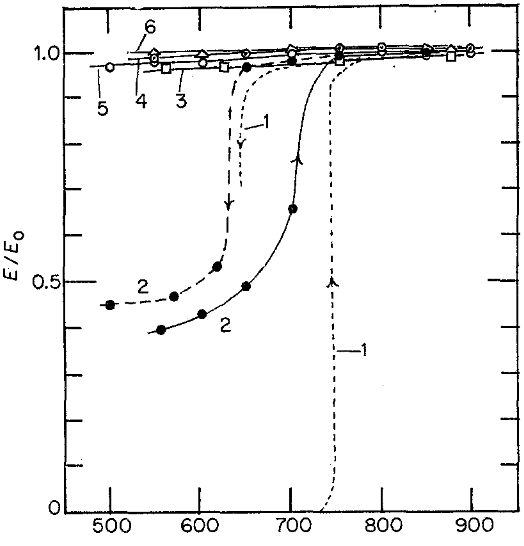

Fig. 3. Ratios of the measured e.m.f. E to the theoretical value E_0 of the following cell:
O_2 (0·21 atm.), Pt | $(Bi_2O_3)_{1-x}$ $(WO_3)_x$ | Pt, O_2 (1 atm.)

No.	*x*	*No.*	*x*
1.	0·00	4.	0·22
2.	0·05	5.	0·25
3.	0·143	6.	0·333 0·50

for in terms of the homogeneous phase of the compound $3Bi_2O_3$ WO_3 which has the f.c.c. structure over a wide range of temperature up to, at least, 850°C. The composition which showed a maximum conductivity in the temperature range below 700°C was $(Bi_2O_3)_{0{\cdot}78}$ $(WO_3)_{0{\cdot}22}$ which corresponded to a limiting composition of the solid solution range based on the compound $3Bi_2O_3$ WO_3.

The specimens having a content of WO_3 less than that of the limit composition showed a sudden jump in conductivity at about 720~770°C, where the phase transition to cubic structure would take place according to the phase diagram [9]. The degree of the jump in conductivity grew remarkably as the content of WO_3 decreased. In the low temperature range below 700°C, the conductivities of these specimens increased as the content of WO_3 increased; and they decreased with increasing content of WO_3 in the high temperature range. A thermal hysteresis in conductivity was observed in these specimens. As indicated in Fig. 2, with dotted line for $(Bi_2O_3)_{0{\cdot}95}$ $(WO_3)_{0{\cdot}05}$ and $Bi_2O_3)_{0{\cdot}857}$ $(WO_3)_{0{\cdot}143}$, the conductivity during the cooling process from 800°C decreased along the extrapolated line of the conductivity curve in the high temperature range, and it dropped rapidly at a temperature 50~100°C lower than the temperatures of the conductivity jump during the heating process.

In the specimens having the WO_3 content higher than 22%, the conductivities decreased with increasing the content of WO_3. Their Arrhenius plots showed straight lines over a wide range of temperature, and both the rapid jump and the thermal hysteresis in conductivity were not recognized.

Fig. 3 represents the ratio of the measured e.m.f. to the theoretical value of the oxygen concentration cell using the sintered tablet as the electrolyte under the condition of $P_{O_2,a} = 0{\cdot}21$ and $P_{O_2,c} = 1{\cdot}0$ atm. As previously reported, the e.m.f. of the cell using pure Bi_2O_3 as the electrolyte could not be recognized up to 730°C, where it appeared suddenly and increased rapidly to the theoretical value. This temperature is in accordance with the temperature at which the jump in conductivity occurs and, therefore, the monoclinic-cubic transformation takes place.

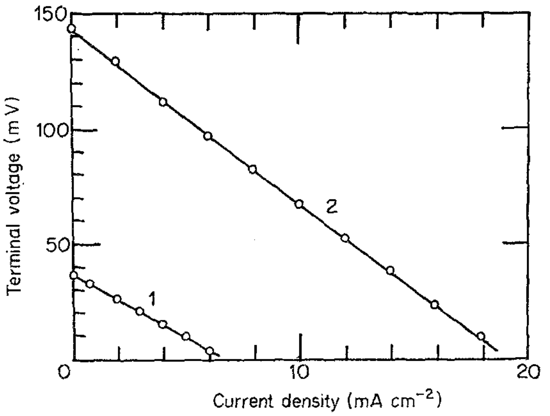

Fig. 4. The discharge curve of the following cell at 800°C: $O_2(P_{O_2,a})$, Pt | $(Bi_2O_3)_{0\cdot 76}$ $(WO_3)_{0\cdot 24}$ | Pt, O_2 (1 atm.)
1. $P_{O_2,a} = 0\cdot 21$ atm.
2. $P_{O_2,a} = 1\cdot 89\times 10^{-3}$ atm.

In contrast, the specimens containing a certain amount of WO_3 showed the e.m.f. even in the temperature range below 700°C, indicating the existence of considerable ionic conduction. Especially in the specimens having more than 14·3% WO_3, the ratio of E to E_0 is higher than 0·9 over a wide range of temperature, which means that they are essentially ionic conductors.

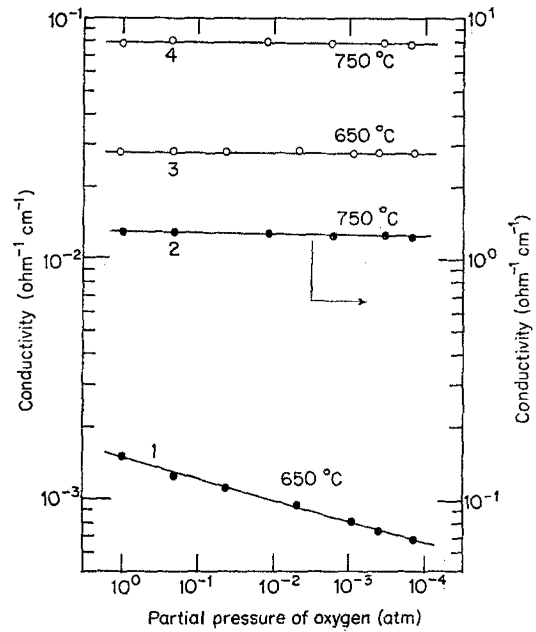

Fig. 5. The dependence of conductivities on oxygen partial pressure

1. 2. } $(Bi_2O_3)_{0.95}(WO_3)_{0.05}$
3. 4. } $(Bi_2O_3(_{0.75})WO_3)_{0.25}$

High but stable currents could be drawn from these concentration cells. Fig. 4 shows the terminal voltage and current density for the specimen containing 24% WO_3 under the condition of P_{2O}, $a = 0\cdot 21$ and $1\cdot 9\times 10^{-3}$ atm. keeping P_{O_2}, $c = 1\cdot 0$ atm. at 800°C. The cell characteristics were reproducible even after the cell had been short-circuited for a long time. These results indicate that the ion contributing to the conduction should be the oxide ion. For, if cations were the charge carriers, polarization would appear because of the irreversibility of the electrode reaction, and a high stable current density could not be drawn from the cell. As a result, the conductivities represented in Fig. 2 are oxide ion conductivities except those of pure Bi_2O_3 and $(Bi_2O_3)_{0\cdot 95}$ $(WO_3)_{0\cdot 05}$ below 700°C which arise completely or partially from electronic conduction. The oxide ion conductivities of these materials are markedly higher than those of the conventional oxide ion conductors such as stabilized zirconias. For example, the conductivities of $(Bi_2O_3)_{0\cdot 78}$ $(WO_3)_{0\cdot 22}$ are $1\cdot 0\times 10^{-2}$ohm^{-1}cm^{-1} at 500°C and $6\cdot 2\times 10^{-2}$ ohm^{-1}cm^{-1} at 700°C which are about ten times higher than those of the well-known $(ZrO_2)_{0\cdot 9}$ $(Y_2O_3)_{0\cdot 1}$ at the same temperatures.

As represented in Fig. 3, relatively low values of E/E_0 were found for $(Bi_2O_3)_{0\cdot 95}$ $(WO_3)_{0\cdot 05}$ below 700°C where monoclinic (α) and cubic (δ) phases coexisted; E/E_0 increased up to nearly unity at about 730°C in accordance with the conductivity behaviour shown in Fig. 2. On the other hand, E/E_0 for $(Bi_2O_3)_{0\cdot 857}$ $(WO_3)_{0\cdot 143}$ was higher than 0·9 even below 700°C where the η^* and δ^* phases coexisted according to our X-ray diffraction analysis. The rapid change and thermal hysteresis in E/E_0 were not observed in this case although the conductivities did vary in this way. The specimens having γ^* as the main phase, as in $(Bi_2O_3)_{0\cdot 5}$ $(WO_3)_{0\cdot 5}$, were also the pure oxide ion conductors though the conductivity was not so high.

Fig. 5 shows the dependence of the conductivity on the oxygen partial pressure surrounding the sample. In the specimens, such as $(Bi_2O_3)_{0\cdot 75}$ $(WO_3)_{0\cdot 25}$, which belong to δ^*-phase and for which E/E_0 is almost unity, the conductivities were independent of the partial pressure of oxygen over a range from 1 atm. to at least 10^{-4} atm. and over a wide range of temperature. In the specimens which showed low E/E_0 values, a marked dependence of the conductivity on the oxygen pressure was observed at temperatures below 700°C before the jump in conductivity took place. All specimens investigated, however, showed no pressure dependence at the temperatures where E/E_0 values were almost unity. The dependence of conductivity of metallic oxide on oxygen partial pressure is, in general, given by

$$\sigma = \sigma_i + \sigma_e^0 P_{O_2}^{-1/n} + \sigma_h^0 P_{O_2}^{1/m} \qquad (4)$$

where P_{O_2} is the oxygen partial pressure, n and m positive integers which are determined by the kind of lattice imperfection, and $\sigma_e{}^\circ$ and $\sigma_h{}^\circ$ are the constants with respect to the conduction of excess electrons and electron holes respectively [13]. σ_i represents the ionic conductivity and is, in general, independent of the oxygen partial pressure, whereas the conduction due to excess electrons or electron holes, which is given by the second or third terms in Equation (4), is pressure-dependent. Our results showed that the conduction in the δ^*- or η^*-phase is essentially due to oxide ion, and the phases which contained monoclinic structures had considerable electronic conduction due to electron holes (p-type conduction).

In this mixed conduction range, it was also confirmed that the oxide ion conductivity remained constant with respect to the oxygen partial pressure at constant temperature. The oxygen concentration cell using $(Bi_2O_3)_{0\cdot95}$ $(WO_3)_{0\cdot05}$ as the electrolyte was examined at 700°C under different partial pressures of oxygen at the anode, keeping the cathode pressure at 1 atm. The first column in Table 2 shows the ion transference numbers obtained from the e.m.f. of the cell under different partial pressures at the anode. The values increase with decreasing P_{O_2} at the anode indicating that the electrolyte has a p-type electronic conduction. In the second column, the total conductivities σ of the electrolyte are listed, and the third column represents the oxide ion conductivities which are calculated from Equation (3) by

$$\sigma_i = t\sigma = \frac{E}{E_0}\,\sigma \qquad (5)$$

Table 2. The dependence of E/E_0 and σ_i on the oxygen partial pressure at the anode of the following cell (700°C): O_2, $(P_{O_2,a})$, $Pt\,|\,(Bi_2O_3)_{0\cdot95}(WO_3)_{0\cdot05}\,|\,Pt$, O_2 (1 atm)

$P_{O_2,a}$ (atm.)	E/E_0	$\sigma \times 10^3$ (ohm^{-1})	$\sigma_i \times 10^3$ (ohm^{-1})
$2\cdot10 \times 10^{-1}$	0·652	5·83	3·80
$5\cdot19 \times 10^{-2}$	0·675	5·65	3·81
$1\cdot78 \times 10^{-2}$	0·710	5·56	3·94
$2\cdot68 \times 10^{-3}$	0·731	5·39	3·94
$4\cdot54 \times 10^{-4}$	0·727	5·28	3·84

It is clear from this result that the oxide ion conductivity of the mixed conductor is almost constant in the pressure range listed in the Table.

On the basis of Fig. 5, the oxide ion transference number in the specimen having single δ^*-phase should approach unity and be independent of oxygen partial pressure at the anode of the concentration cell. This was so for $(Bi_2O_3)_{0\cdot76}$ $(WO_3)_{0\cdot24}$ at 800°C (see Table 3). This material is essentially an oxide ion conductor at 600°C even under a pressure of 10^{-15} atm. At 800°C, however, it is apt to be reduced under atmospheres such as CO–CO_2 mixed gas, and considerable n-type electronic conduction appears as a result of the reduction of the host oxide Bi_2O_3, although detailed investigation has not been carried out.

4. Discussion

From the results described above, it can be said that, in the Bi_2O_3–WO_3 system, the phase δ^*

Table 3. E.m.f. and E/E_0 of the following cell under various oxygen partial pressure at the anode (800°C_{O_2}): $(P_{O_2,a})$, $Pt\,|\,(Bi_2O_3)_{0\cdot76}(WO_3)_{0\cdot24}\,|\,Pt$, (1 atm.)

$P_{O_2,a}$ (atm.)	measured e.m.f. E (mV)	theoretical e.m.f. E_0 (mV)	E/E_0
$2\cdot10 \times 10^{-1}$	36·3	36·2	1·00
$2\cdot04 \times 10^{-2}$	86·0	90·0	0·96
$1\cdot98 \times 10^{-3}$	144	146	0·99
$1\cdot75 \times 10^{-4}$	198	201	0·98
$5\cdot98 \times 10^{-5}$	223	227	0·98

(f.c.c.) is a high oxide ion conductor; the η^*-phase (orthorhombic) is also an oxide ion conductor though it has relatively low conductivity, and the α-phase shows appreciable electronic conduction, but the conductivity in this case is not so high. The specimen having γ-phase (orthorhombic) as a main phase is thought to be an oxide ion conductor with fairly low conductivity.

In pure δ-Bi_2O_3 which has the fluorite-type structure, two of the eight lattice sites for the oxide ions per unit cell (Bi_4O_6) are on average vacant, since the formula of the perfect fluorite-type oxide is represented as M_4O_8 (M = cation) for a unit cell. The high oxide ion conduction in this material can be attributed to easy migration of these vacancies, just as in the case of stabilized zirconias [5]. A compound $3Bi_2O_3\ WO_3$ has the face-centered cubic structure (δ^*-phase), the X-ray diffraction pattern of which corresponds to that of δ-Bi_2O_3 as represented in Fig. 1. Thermogravimetric analysis of the solid state reaction:

$$3Bi_2O_3 + WO_3 \rightarrow 3Bi_2O_3\ WO_3$$

demonstrated a negligible change in weight, indicating that the total valencies of the cations remained unchanged in the compound. These facts should suggest that this compound and its solid solution also have the fluorite-type like structure. If it is true, and all cations occupy their normal sites in the fluorite-type crystal lattice, 1·14 of the eight oxide ion lattice sites will be vacant on average in the compound $3Bi_2O_3\ WO_3$, i.e. its formula per unit cell can be represented as $Bi_{24/7}\ W_{4/7}\ O_{48/7}\ \square_{8/7}$, where $\square$ is the oxide ion vacancy. The theoretical densities of this material were calculated from its lattice constant assuming the following two cases;

(i) all cations occupy their normal sites in the fluorite-type lattice and 1·14 of the eight oxide ion sites per unit cell are vacant,

(ii) all oxide ions occupy their normal sites and the excess cations are situated on the interstitial sites.

The calculated values using the measured lattice constant of 5·604±0·004 Å were 8·78 g/cm^3 for (i) and 10·25 g/cm^3 for (ii). The observed picnometric density was 8·66 g/cm^3 which was rather close to that for the case (i), suggesting that the number of oxide ion vacancies might be close to the theoretical value.

Thus the oxide ion conduction in this material can be ascribed to the vacancy mechanism. Since the δ^*-phase of $3Bi_2O_3\ WO_3$ is stable over a wide range of temperature, the Arrhenius plot of the oxide ion conductivity is a straight line and, therefore, the material is a high oxide ion conductor even at relatively low temperatures below 700°C. The high oxide ion conduction in this substance may apparently result from the stabilization of a high oxide ion-conductive phase of pure Bi_2O_3 (δ-phase >730°C) by WO_3 although $3Bi_2O_3\ WO_3$ is not the solid solution based on Bi_2O_3.

The result that the composition showing the highest oxide ion conductivity is $(Bi_2O_3)_{0\cdot78}(WO_3)_{0\cdot22}$, which corresponds to the limit of the solid solution formation range based on $3Bi_2O_3\ WO_3$, is in accordance with the general tendency for the stabilized zirconias that the composition giving the highest oxide ion conductivity corresponds to the lowest content of the second cation within the solid solution formation range. The fact that the activation energy of conduction in the δ^*-phase decreased from 0·74 eV for $(Bi_2O_3)_{0\cdot75}(WO_3)_{0\cdot25}$ to 0·59 eV for $(Bi_2O_3)_{0\cdot78}(WO_3)_{0\cdot22}$ should indicate that the migration of oxide ion grew easier as the content of W decreased. The values 0·59∼0·74 eV are somewhat low compared with those of the conventional oxide ion conductors (0·8∼1·2 eV for most stabilized zirconias), showing that the oxide ions in the materials based on Bi_2O_3 may be more mobile than those of any other oxides ever known.

Face centered cubic phases, which are stable at relatively low temperatures, should exist in other compounds or solid solutions based on Bi_2O_3. The ionic conduction of these materials is under investigation in our laboratory.

5. Conclusion

The sintered oxides of the system Bi_2O_3–WO_3 were found to be oxide ion conductors. In particular, $3Bi_2O_3\ WO_3$ and its solid solution are high oxide ion conductors, the conductivities of which are about one order of magnitude higher than those of any oxide ion conductors ever known, such as stabilized zirconias. In contrast to pure Bi_2O_3, which is a completely electronic conductor below 730°C, these materials show a high oxide ion conduction even below 700°C accompanied by little electronic conduction. $3Bi_2O_3$ WO_3 has the face centered cubic structure, probably of the fluorite-type, and the oxide ion conduction can be attributed to the migration of oxide ion vacancies present in the crystal.

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