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Activity of Bi_2O_3 in Bi_2O_3–Y_2O_3 Oxygen Ion Conductor

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Dense bodies (>96% theoretical density) of Bi_2O_3–Y_2O_3 oxygen ion conductor in the compositional range 50–85 mol% Bi_2O_3 were prepared. The activities of Bi_2O_3 in this system were measured using a solid electrolyte galvanic cell. The results show that the activity of Bi_2O_3 with 70 mol% Bi_2O_3 at 871 K is 0.084, and the equilibrium oxygen partial pressures are 10^{-15} to 10^{-16} atm, which are one or two orders of magnitude lower than that of pure Bi_2O_3 at the corresponding temperature

Introduction

The high-temperature phase (δ phase) of bismuth sesquioxide is known to show the defect fluorite-type (fcc) crystal structure and to be a highly conductive oxide ion conductor (*1*). This phase is, however, unstable below 730°C and transforms to the monoclinic phase (α phase) (*2*), whose conduction is low and electronic. Takahashi and Iwahara (*3*) reported that the highly conductive phase δ could be retained below 730°C by adding particular di-, tri-, penta-, or hexavalent metal oxides with electric conductivity one order of magnitude higher than that of the stabilized zirconia at corresponding temperatures. Due to the above advantage, we hope to use these kinds of materials as sensing elements in oxygen sensors, oxygen pumps and high temperature fuel cells. However, there exist differences in the range of oxygen partial pressure for the use of Bi_2O_3-based materials. Takahashi *et al.* (*4, 5*) proposed that Bi_2O_3–Y_2O_3 solid solution exhibited the equilibrium oxygen partial pressure (10^{-13} atm at 600°C), which is equal to that of the pure Bi, Bi_2O_3 mixture. But Wang *et al.* (*6*) found that there was no bismuth reduction in the process of conductivity measurement, which extended the interval of the oxygen partial pressure to 10^{-21} atm. In order to provide the theoretical base for use of Bi_2O_3-based materials, the activity of Bi_2O_3 in the Bi_2O_3–Y_2O_3 system should be measured.

Experimental

The Bi_2O_3–Y_2O_3 solid solutions with 50–85 mol% Bi_2O_3 were prepared as proposed by Takahashi *et al.* (*4*). X-ray diffraction was carried out using Cu*K*α radiation to determine the structure.

The activity of Bi_2O_3 was determined using a solid electrolyte galvanic cell:

$$(-)\mathrm{Mo} \mid \mathrm{Bi},\ \mathrm{Bi_2O_3(ss)} \mid \mathrm{ZrO_2(Y_2O_3)} \mid \mathrm{Bi_2O_3\ (s),\ Bi} \mid \mathrm{Mo}(+).$$

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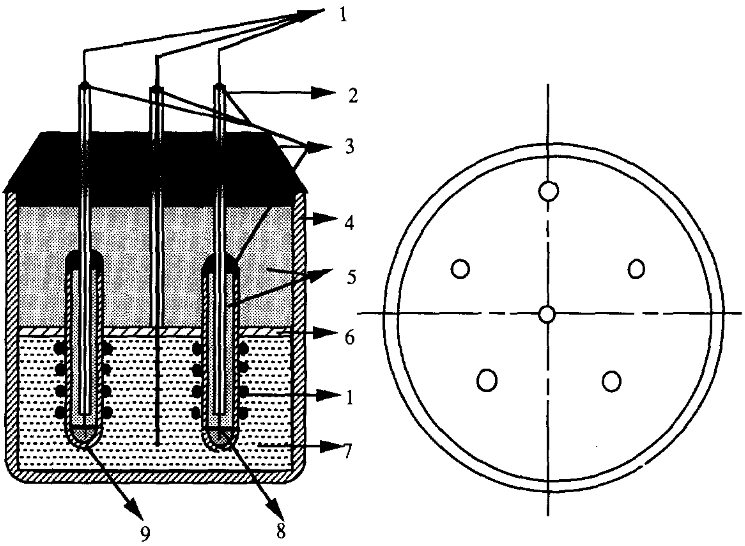

1. Mo leads
2. alumina rod
3. cement
4. alumina crucible
5. alumina powder
6. Mo disk
7. reference electrode
8. working electrode
9. zirconia tube

FIG. 1. The cross section of the cell assembly.

The overall reaction of the cell is $Bi_2O_3(s) = Bi_2O_3(ss)$, resulting in a free energy change of

$$\Delta G = \Delta G_{Bi_2O_3(ss)} - \Delta G^0_{Bi_2O_3} = RT \ln a_{Bi_2O_3}. \quad (1)$$

However, the change in free energy may also be expressed by

$$\Delta G = -nFE, \quad (2)$$

where $n = 6$ for the passage of oxygen ion through the cell, E is the electromotive force, F is Faraday's constant, and R is the gas constant. Therefore

$$a_{Bi_2O_3} = \exp(-6EF/RT). \quad (3)$$

In a typical experiment, $Bi_2O_3(s)$ + Bi (>99.99%) was used as common reference electrode of the cell and placed in an alumina crucible (Ø50 × 40 × 50 mm). The working electrode $Bi_2O_3(ss)$ + Bi was placed in a solid electrolyte tube (Ø5 × 6 × 30 mm) of yttria-stabilized zirconia. The volume ratios of Bi to $Bi_2O_3(s)$ in the reference electrode and Bi to $Bi_2O_3(ss)$ in the working electrode were both taken as 5 : 1. The molybdenum lead wire could be allowed to remain in contact with both electrodes for the entire duration of the experiment, since no reaction between molybdenum and bismuth was observed. The cell assembly is shown in Fig. 1.

The system was slowly heated to above 550°C in an argon atmosphere, and the EMF measurement was started. A Keithley 192 DVM was used to measure the open-circuit cell EMF to a precision of 0.1 mV by a change-over switch. The high input impedance of this voltmeter prevented loading of the cell and allowed reversible measurement. Thus the EMF values of five cells containing different compositions in the range of 50–85 mol% Bi_2O_3 were measured simultaneously at one specific temperature (referring to Fig. 1). On reaching the desired tempera-

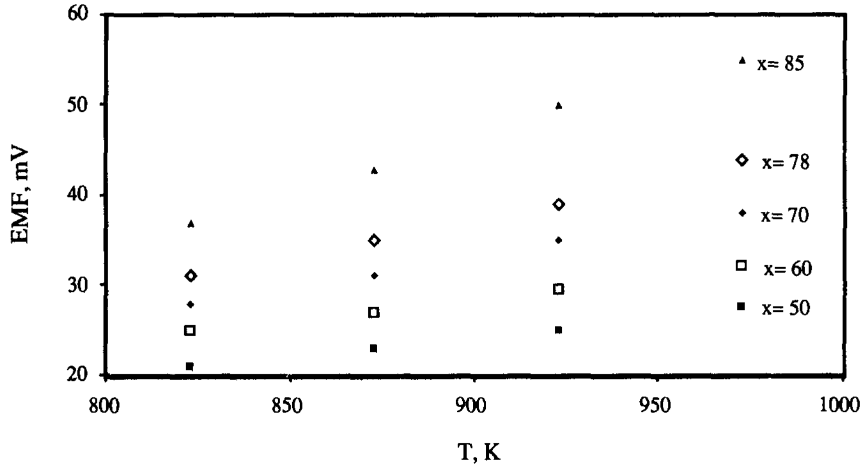

FIG. 2. Relationship between measured EMF and temperature; x is mol% of Bi_2O_3 in Bi_2O_3–Y_2O_3.

ture, the cell EMF assumed a stable value within about ½ hr. The EMF remained constant to within ±1 mV for 24 hr or longer if allowed. The reversibility of the measured EMF was checked frequently by shorting the cell for about 10 sec and then allowing the EMF to return to the original value within 1 min. Once a constant cell EMF was obtained for a controlled temperature, the set point of the controller was changed to a new value and the sequence of measurements was repeated. In the present investigation, the cell temperatures could be controlled to within ±1°C using a Pt/PtRh10 thermocouple. All EMF values were measured in order to increasing temperature. The reference and working electrode were both checked by X-ray diffraction after each run.

Results and Discussions

The results of X-ray diffraction agreed well with those of Takahashi *et al.* (*4*). Vegard's rule almost held in the composition range from 46–85 mol% Bi_2O_3, though some curvature was observed.

Figure 2 presents the EMF-temperature relationship with a standard deviation of ±1

TABLE I

ACTIVITY AND EQUILIBRIUM OXYGEN PARTIAL PRESSURE OF Bi_2O_3 AT DIFFERENT TEMPERATURES

(X is mol% of Bi_2O_3)

T (K)	X	100	85	78	70	60	50	Factor
823	$a_{Bi_2O_3}$	1.00	0.169	0.121	0.094	0.073	0.044	
	Po_2/atm	6.75	1.15	0.810	0.635	0.493	0.297	$\times 10^{-16}$
871	$a_{Bi_2O_3}$	1.00	0.160	0.116	0.084	0.061	0.032	
	Po_2/atm	14.9	2.38	1.73	1.25	0.909	0.477	$\times 10^{-15}$
921	$a_{Bi_2O_3}$	1.00	0.152	0.112	0.071	0.053	0.023	
	Po_2/am	26.7	4.06	2.99	1.89	1.42	0.614	$\times 10^{-14}$
968	$a_{Bi_2O_3}$	1.00	0.145	0.101	0.066	0.043	0.019	
	Po_2/am	30.6	4.44	3.09	2.02	1.32	0.581	$\times 10^{-13}$

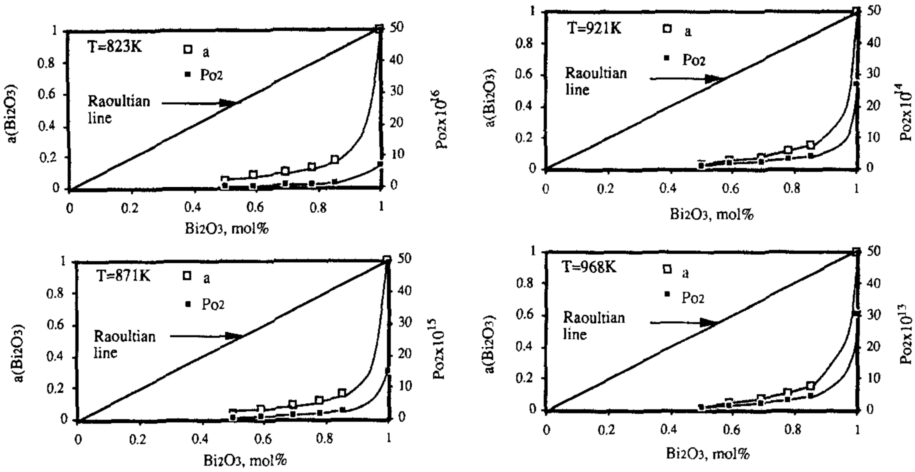

FIG. 3. The relationships of activity–composition and oxygen pressure–composition of Bi_2O_3 in solid solution.

mV. The activities were calculated from the EMF–temperature data using Eq. (3) and the equilibrium oxygen partial pressures of solid solutions were calculated using Eq. (4), all data listed in Table I,

$$Po_2(\mathrm{II}) = Po_2(\mathrm{I})*a_{Bi_2O_3} \qquad (4)$$

where, Po_2(II) is the equilibrium oxygen partial pressure of the solid solution and Po_2(I) is equilibrium oxygen partial pressure of pure Bi_2O_3, which is taken from (7),

$$\Delta G_{f,Bi_2O_3} = 137{,}890\text{-}63.43T \text{ cal mol}^{-1}.$$

Figure 3 shows the activity–composition and oxygen pressure–composition relationships of the Bi_2O_3 component in the solid solution. The results indicate a great negative departure of the solid solution from Raoultian behavior which means the solid solution has a higher stability than pure Bi_2O_3. The equilibrium oxygen partial pressures of the solid solution at one specific temperature calculated from Eq. (4) are one or two orders of magnitude lower than that of pure Bi_2O_3 at the corresponding temperature. The working electrode and reference electrode were both Bi_2O_3(ss) + Bi and Bi_2O_3(s) + Bi, respectively, using X-ray diffraction. No phase transformations were observed.

Conclusion

The activity of Bi_2O_3 in a Bi_2O_3–Y_2O_3 oxygen ion conductor were measured using a solid electrolyte galvanic cell. The results show that the activity of Bi_2O_3 with 70 mol% Bi_2O_3 at 871 K is 0.084, and the equilibrium oxygen partial pressures are 10^{-15} to 10^{-16} atm, which are one or two orders of magnitude lower than that of pure Bi_2O_3 at the corresponding temperature.

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