BISMUTH-LEAD OXIDE, A NEW HIGHLY CONDUCTIVE OXYGEN MATERIAL

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The transport properties of an oxygen-deficient solid solution containing lead and bismuth oxides have been investigated. The conductivity is larger than $1(\Omega \times \text{cm})^{-1}$ at 600 °C. Thermogalvanic measurements confirm that no significant electronic contribution occurs in the range $1-10^{-3}$ atm p O_2 . The heat of transport of O^{2-} ions is calculated and is in agreement with the activation energy of conduction.

INTRODUCTION

High oxide ion mobilities at moderate temperature have already been reported in bismuth oxide (1) and bismuth-based mixed oxides (2-4). The reported conductivities are often several orders of magnitude higher than in the well-known stabilized-zirconia, at the same temperature. Similar behaviour was also encountered in mixed fluorides (5). Enhancement of conduction properties is generally attributed to the high polarizability of bismuth ion. As a consequence, it was decided to investigate conduction properties of some lead-bismuth oxides in which the polarizabilities of the cations are very similar.

A general study of the lead oxide-bismuth oxide system was carried out in our laboratory a few years ago (6) and preliminary results of conductivity measurements were published earlier (7). In the present work, we focussed our attention on a body-centered cubic solid solution (called β) with a wide range of homogeneity ($0.30 \leq n \leq 0.70$ with n = molar fraction of PbO). The temperature stability range strongly depends on the composition (Fig. 1). The b.c.c. structure cannot be quenched: rapid cooling results in two different metastable solid solutions depending on n . When $n < .5$, β turns into a monoclinic solid solution

Figure 1

called β_1 (8); when $n > .5$, a tetragonal solid solution which is called β_2 appears. We report here the results obtained on mixed oxides in the $n > .5$ region. A special attention has been drawn to the composition $n = 0.555$ since it corresponds to a material which always remains monophasic.

HIGH-TEMPERATURE X-RAY INVESTIGATIONS

Fig. 2 shows the high-temperature X-Ray spectrum of a metastable β_2 sample corresponding

Figure 2

* Reflexions due to the gold sample holder

ding to $n = 0.555$. Between room temperature and 450°C , the diffraction pattern is characteristic of the tetragonal β_2 phase ($a = 4.041(1)$, $c = 5.023(1)\text{\AA}$ at room temperature). At 450°C , the decomposition of β_2 leads to the definite compound $\text{Bi}_8\text{Pb}_5\text{O}_{17}$. The transformation of the latter into β is observed at 590°C in accordance with the phase diagram (Fig. 1).

CONDUCTIVITY MEASUREMENTS

Both d.c. and a.c. measurements were performed on polycrystalline samples. Cylindrical and parallelepipedic pellets were cold-pressed (1T.cm^{-2}) and sintered at 620°C . Apparent densities of about 90% the theoretical ones were easily obtained. X-Ray analysis of air-quenched specimens revealed the presence of the β_2 phase. A.C. measurements were carried out by the complex impedance method with a 1174 Frequency Response Analyser Solartron, in the range 1Hz – 1MHz , on cylindrical pellets (6 to 10 mm diameter, 4 to 6 mm height). Gold electrodes were vacuum-deposited on mechanically polished faces. D.C. measurements were performed by the four-probes method on a small bar ($13 \times 2 \times 2\text{ mm}^3$). Pt leads were used as probes. Thermoelectric effects were eliminated by reversing the current in the sample. Results of a.c. and d.c. measurements are in

Figure 3

good agreement. As an example, the results of a typical heating-cooling cycle for a sample with the composition $\text{Bi}_8\text{Pb}_5\text{O}_{17}$ ($n = 0.555$) are shown in Fig. 3, where $\log \sigma$ is plotted versus $1000/T$.

In the low-temperature region of the heating curve, the conductivity of the tetragonal β_2 phase shows an Arrhenius-type behaviour. It is obvious from a comparison with the high-temperature X-Ray spectrum that the decrease observed in corresponds to the decomposition of β_2 into the compound $\text{Bi}_8\text{Pb}_5\text{O}_{17}$. At 590°C , the considerable increase in conductivity is related to the appearance of the cubic-centered β phase. In the high temperature region, the conductivity is larger than $1(\Omega\text{cm})^{-1}$ and exhibits also an Arrhenius-type behaviour. On cooling, a rather large hysteresis phenomenon is observed: the decrease in conductivity, resulting from the decomposition of β , is currently observed 40°C below the temperature of the heating sequence. In the low-temperature region, either β_2 or $\text{Bi}_8\text{Pb}_5\text{O}_{17}$ can be obtained, depending upon the rate of cooling.

Activation energies of β_2 solid solution and $\text{Bi}_8\text{Pb}_5\text{O}_{17}$, taken from the heating curve, are rather large. Values in the range 1.40 – 1.50 eV are observed. Activation energies for the highly conductive β phase were taken from the cooling curve, in order to increase the number of experimental points. Values in the range 0.4 – 0.5 eV are obtained. Such low values have already been observed on Bi_2O_3 (1) and $\text{Bi}_{12}\text{PbO}_{19}$ (9) in their high-temperature form.

THERMOCALVANIC MEASUREMENTS IN THE β PHASE

Ionic transference number measurements were carried out by means of a concentration cell using air and oxygen as potential reference gases. Details will be published elsewhere. While t_i deviates significantly from 1 in the low temperature region, the transference number of the β phase appears to be about 1. Nevertheless, it was decided to repeat this investigation of transport properties of the β phase by means of thermogalvanic (or Seebeck coefficient) measurements. These are much more sensitive to minority electronic contributions to conductivity than concentration cell measurements do.

Sintered samples about 6 mm in diameter and 6 mm in height were provided with sputtered gold electrodes about 300 nm thick and placed between gold foil electrodes in a pyrex cell. This cell will be described in a following paper.

Thermogalvanic measurements reported here were carried out between about 590 and 625°C in various pO_2 atmospheres and using argon as a carrier. The temperature range is limited because of plastic deformation of the sample at higher temperatures. The direct thermo cell method was used in combination with the cell:

No chemical diffusion of the cations could be detected. The cell voltage withdrew as soon as the temperature difference (2–15°C) was diminished to zero. Therefore it was concluded that no Soret effect took place.

This reduces the complexity of the expression for $\mathcal{E}_T$ considerably. The compositions 0.555 and 0.65 were chosen for the measurements because they are more or less situated at the lower and higher composition limits of the β phase.

Results are reported in tables 1 and 2

pO_2 atm	$\mathcal{E}_{T\text{meas.}}^{-1}$ (μVK^{-1})	$\mathcal{E}_{T\text{calc.}}^*$ (μVK^{-1})
1	-152±3	-149
0.21	-187±3	-183
0.048	-212±3	-215
0.014	-221±4	-241
0.001	-289±5	-298

Table 1 : EMF of sample n = 0.555 vs pO_2 between 590 and 620°C.

pO_2 atm	$\mathcal{E}_{T\text{meas.}}^{-1}$ (μVK^{-1})	$\mathcal{E}_{T\text{calc.}}^*$ (μVK^{-1})
1	-122±3	-120
0.21	-151±3	-154
0.048	-179±4	-186
0.014	-205±4	-212
0.001	-256±4	-269

Table 2 : EMF of sample n = 0.65 vs pO_2 between 590 and 620°C.

* $\mathcal{E}_T$ calculated as obtained from

$$\mathcal{E}_T(O_2/O^{2-}) = \frac{0}{T} + \frac{2,303.R}{4F} \log pO_2 \mu\text{VK}^{-1}.$$

This expression allows to calculate the influence of changes in pO_2 on $\mathcal{E}_T$. Here $\mathcal{E}_T^0$ contains all temperature-dependent terms in the expression for $\mathcal{E}_{T\text{total}}$ mentioned later in this contribution. The values of $\mathcal{E}_T^0$ used for the calculations of $\mathcal{E}_T$ in Tables 1 and 2 are the measured values of $\mathcal{E}_T$ at pO_2 equal to one atm.

The agreement between measured and calculated $\mathcal{E}_T$ values may be an indication of the reversibility of the electrode reaction (14). The $\mathcal{E}_T$ values measured are negative, this

follows from the experiments where the hottest electrode had a negative potential. Within the small temperature region available for the $\mathcal{E}_T$ measurements in β phase, practically constant $\mathcal{E}_T$ values are found for fixed pO_2 values. This is an indication for the absence of conducting electron in the β_2 phase. Such electrons have usually a relatively strong temperature dependent contribution to $\mathcal{E}_T$. The negative $\mathcal{E}_T$ values and the finding of ionic transport numbers of about 1, mentioned before leads to the conclusion that O^{2-} ions are the mobile species in the β phase for both compositions 0.555 and 0.65 in between 10^{-3} and 1 atm. pO_2 .

Tables 1 and 2 show that $\mathcal{E}_T$ differs considerably for the two samples measured. This difference is considered as significant. The values of $\mathcal{E}_T$ measured at $pO_2 = 1$ atm. are used to estimate the heat of transport of O^{2-} ions ($\approx Q^*$) in the composition 0.555 and 0.65.

Generally when the Soret effect is absent $\mathcal{E}_{T\text{total}}$ consists of three contributions:

$\mathcal{E}_T$ homogeneous O_2 electrolyte + $\mathcal{E}_T$ homogeneous electrode and leads + $\mathcal{E}_T$ heterogeneous electrode reactions

For the electrode reaction:

which is reversible at both identical sputtered gold electrodes, the expression for $\mathcal{E}_{T\text{total}}$ can be reduced to:

$$\mathcal{E}_{T\text{tot}} = \lim_{\Delta T \rightarrow 0} (\Delta \mathcal{E} / \Delta T) \quad (14)$$

$$= (-\frac{1}{2}S^O + \frac{1}{2}R \ln pO_2 - \tilde{S}_{e,Au} + \frac{1}{2}\bar{S}_{O^{2-}} + Q^*/2T)/F$$

S^O = Standard entropy of O_{2g} :
55,2 cal/mol K at 620°C (11)

pO_2 = Oxygen partial pressure in equilibrium with the sample. Suppose $p_{O_2} = 1$ atm.

$\tilde{S}_{e,Au}$ = transport entropy of electrons in gold electrode: $3,77\mu\text{VK}^{-1}$ at 620°C (12)

$\bar{S}_{O^{2-}}$ = partial entropy of oxygen ions (vibration + configuration)

Q^* = heat transport of O^{2-} ions

$\bar{S}_{O^{2-}}$ is estimated from the entropy of $Bi_2O_3(\beta)$ and PbO , data of ref. (11) and accounting for the ionic mass ratio's according to ref. (13).

$$\bar{S}_{O^{2-}} = (1-x)\bar{S}_{O^{2-}}(\beta-Bi_2O_3) + x\bar{S}_{O^{2-}}(PbO)$$

with

$$\bar{S}_{O^{2-}}(\text{Bi}_2\text{O}_3) = 1/5 S_{(\text{Bi}_2\text{O}_3)}^O - 3/5 R \cdot \ln \frac{M_{\text{Bi}}}{M_{\text{O}}} \\ = 44,59 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

and

$$\bar{S}_{O^{2-}}(\text{PbO}) = 1/2 S_{(\text{PbO})}^O - 1/2 R \cdot \ln \frac{M_{\text{Pb}}}{M_{\text{O}}} \\ = 51,19 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

Using the $\mathcal{E}_T$ values found for $pO_2 = 1 \text{ atm}$ in table 1 and 2 for the compositions 0.555 and 0.65, the heat of transport for oxygen ions are found to be 0.44 and 0.48 eV, respectively. These values are in agreement with the activation energies obtained from conductivity data ; such an agreement has already been observed in several ionic conductors derived from the silver iodide structure (15) and for α -AgI itself (16). It may be significant to notice that the β phase has an anti- α -AgI structure, as shown in a parallel structural work to be published later.

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