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The thermoelectric power in Bi_2O_3

A. HONDERS, J. H. W. de WIT

Department of Inorganic Chemistry, State University of Utrecht, Croesestraat 77A, 3522 AD Utrecht, The Netherlands

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The thermo electric power, $\Delta E/\Delta T$, of the cell

$$\underset{(T+\Delta T)}{O_2 + N_2, Pt}/Bi_2O_3\ (\delta\ \text{phase})/\underset{(T)}{Pt, O_2 + N_2}$$

has been measured as a function of oxygen pressure (10^{-4} atm $\leqslant p(O_2) \leqslant 1$ atm) in the temperature range 650–800° C. The experimental result can be described by:

$$[\epsilon(O_2/O^{2-}) - \epsilon(e, Pt)] \quad = [45.6 \pm 5.6 \log p(O_2) - 261]\ (\mu V\ K^{-1})$$

within experimental error, where $\epsilon(O_2/O^2)$, the Seebeck coefficient of δ-Bi_2O_3, stands for $\lim_{\Delta T \to 0} \Delta E/\Delta T$. The change of $\Delta E/\Delta T$ with oxygen pressure corresponds to the change of the partial molar entropy of O_2. The heat of transport of O^{2-} ions is calculated to be 0.13 eV ± 0.01 whereas the activation enthalpy for ionic conduction is 0.30 eV. From this discrepancy it is concluded that the free ion model of Rice and Roth cannot be applied, while the extended lattice gas model of Girvin might explain the results when strong polaron coupling is assumed.

List of symbols

E	potential (V)
p	partial pressure (atm)
S	entropy ($J\ K^{-1} mol^{-1}$)
S^0	standard entropy (at 1 atm)
$\tilde{S}$	transport entropy
$\bar{S}$	partial (ionic) entropy
Q^*	ionic heat of transport (eV)
ϵ	Seebeck coefficient or thermogalvanic power ($V\ K^{-1}$)
R, T, F	usual significance.

1. Introduction

In the search for high ionic conduction in solid materials, Bi_2O_3 was found to be a promising material [1]. The polymorphism and the electrical properties of Bi_2O_3 were recently investigated by Harwig and Gerards [2, 3]. The monoclinic α-phase is the stable phase at room temperature. At 729° C a transition occurs to the high temperature, fcc, δ-phase, that is stable up to the melting point at 824° C. Once established at higher temperatures, this δ-phase can metastably be retained at lower temperatures down to ≈ 650° C. It transforms to the α-phase via one of two intermediate phases. Either the tetragonal β-phase at 650° C, or the bcc γ-phase at 639° C. The electrical conductivity in the α-phase (p-type in air [4]) has a value of about $10^{-5}\ \Omega^{-1}\ cm^{-1}$. The δ-phase exhibits predominantly oxygen ion conduction, with an electrical conductivity of the order of $1\ \Omega^{-1}\ cm^{-1}$, and a low activation enthalpy of 0.30 eV.

The purpose of our investigations is to broaden the stability of the good ionically conducting δ-phase to lower temperatures, in order to increase the feasibility of application. A possible extension of the δ-phase stability range might result from incorporation of other suitable oxides. Y_2O_3 [5] and several oxides of the lanthanide series from Tb to Lu seem able to perform this function [6, 8], even down to room temperature. However, the (ionic) conductivities of these materials are much lower (e.g. about 10^{-2}–$10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 500° C) than would be expected from the extrapolation of the high temperature conductivity in the pure

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δ-phase to these temperatures. In order to find an explanation for these low conductivities, detailed X-ray diffraction, DTA studies and electrical conductivity measurements on these mixed oxides are in progress [6].

As little is known on the transport properties of the oxygen ions in the δ-phase of pure Bi_2O_3, it was also decided to perform Seebeck coefficient measurements on the polycrystalline δ-phase of Bi_2O_3 in the temperature range 650–800° C at various oxygen pressures, the results of which are reported here. The sign of the mobile charge carriers can be deduced from the sign of the thermogalvanic e.m.f. (ΔE), while its oxygen pressure dependency gives information on the reversibility of the O_2/O^{2-} electrode. Furthermore contributions of electronic conduction can be detected with great sensitivity. From the Seebeck coefficient data quantitative information on the heat of transport of the oxygen ions is obtained.

2. Experimental

Nominally pure Bi_2O_3 powder (Kawecki-Billiton 99.99% pure) was used as starting material. Spectrochemical analysis* showed that Si (0.001 wt%) was the main impurity. Except for Fe (0.0002 wt%) and Mg (0.000 05 wt%) no other impurities could be detected. Pellets with a diameter of 0.5 cm and a length of 2 cm were pressed at $10^6\,N\,m^{-2}$ and sintered in air at 680° C for three days, and then slowly cooled ($30\,K\,h^{-1}$) to room temperature. After sintering the apparent density of the sample was approximately 85% of the theoretical density.

The sample was mounted in a quartz cell, as shown schematically in Fig. 1. The platinum electrodes were pressed onto the sample at a constant pressure by means of a spring. No electrode paint was used, to limit the incorporation of electrode material (see Section 3). The detection equipment and the experimental procedures have been described elsewhere [7]. The measurements were always performed after equilibration for 2 h at 800° C, while cooling down to 650 °C at a rate of $6.4\,K\,h^{-1}$; ΔT was kept in the order 10–15 K.

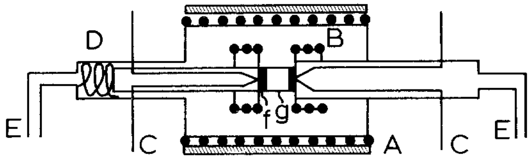

Fig. 1. The quartz cell for the thermoelectric power measurements in a simplified version. A, Kantalwound furnace; B, small inner furnace; C, platinum-platinel (Engelhardt) thermocouple; D, spring; E, gas input and output; f, Pt/O_2 electrode; g, sample.

Oxygen–nitrogen mixtures of various compositions were passed through the cell at a flow rate of $30\,cm^3\,min^{-1}$ (20° C). They were obtained from gasbottles, with a fixed and known high O_2/N_2 ratio. The lower oxygen pressures were established by mixing oxygen gas, that was liberated by electrolytical decomposition of water (6 M KOH) with high purity nitrogen (< 5 ppm O_2).

The composition of each atmosphere was checked by monitoring the exit gas-stream, with a commercial CSZ oxygen concentration cell.

3. Results and discussion

Fig. 2 shows the measured Seebeck coefficient of Bi_2O_3, in the δ-phase in the temperature range 650–800° C and at oxygen pressures of $1–10^{-4}$ atm. Each line was obtained from two independent runs. Two typical curves, showing the spread of the experimental points, are shown in Fig. 3.

For the thermogalvanic cell:

$$\begin{array}{ccc} O_2 + N_2,\ Pt/Bi_2O_3\ (\delta\text{-phase})/Pt, & O_2 + N_2 & \\ (T + \Delta T) & (T) & \qquad (1) \end{array}$$

with the reversible electrode reaction:

$$\tfrac{1}{2}O_2(g) + 2e(Pt) \leftrightarrows O^{2-}(s) \qquad (2)$$

the Seebeck coefficient is given by:

$$\lim_{\Delta T \to 0} \frac{\Delta E}{\Delta T} = \epsilon(O_2/O^{2-}) =$$

$$= \frac{1}{F}\left[-\tfrac{1}{4}S^0(O_2) + \tfrac{1}{4}R\ln p(O_2) - \widetilde{S}(e, Pt) + \tfrac{1}{2}\overline{S}(O^{2-}) + \frac{Q^*(O^{2-})}{2T}\right] \qquad (3)$$

for an assumed transport number $t(O^{2-}) = 1$, i.e. no electronic conduction. To check the oxygen

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* The spectrochemical analysis was kindly performed for us in the Philips Research Laboratories at Eindhoven.

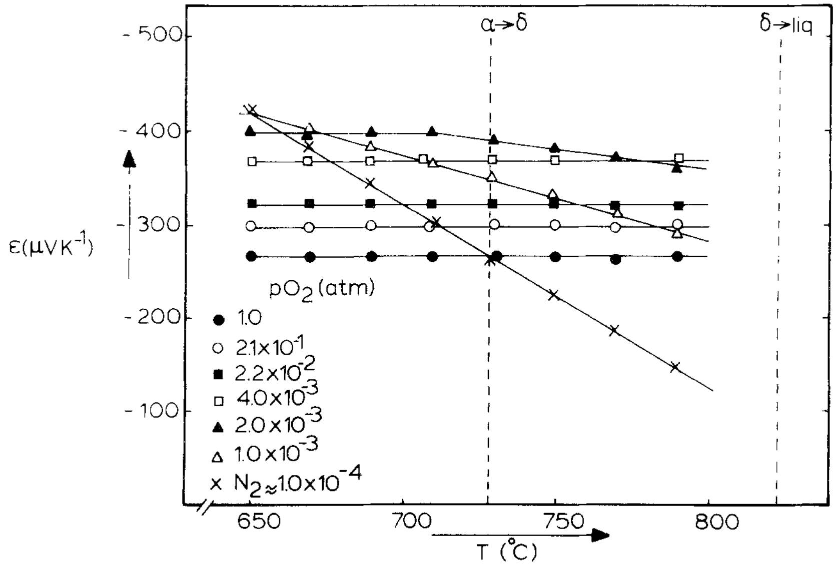

Fig. 2. The thermoelectric power of $\delta\text{-}Bi_2O_3$ $\epsilon_{Bi_2O_3}$ as a function of the temperature and the partial oxygen pressure. The values have been corrected for ϵ_{Pt}.

pressure dependence of the Seebeck coefficient, Equation 3 is written in the form:

$$\epsilon(O_2/O^{2-}) = \epsilon^0(T) + \frac{2.303R}{4F}\log p(O_2) \quad (4)$$

where $\epsilon^0(T)$ includes all (basically) temperature dependent terms in Equation 3.

The location of the 'plateaux' in Fig. 2 is in fair accordance (± 8%) with the 49.6 $\log p(O_2)$ ($\mu V\,K^{-1}$) prediction of Equation 4, as can readily be seen in Fig. 4 where the 'plateaux' ($\mu V\,K^{-1}$) are plotted versus 49.6 $\log p(O_2)$ ($\mu V\,K^{-1}$). From this we conclude that the electrode Reaction 2 is reversible on the platinum electrodes under the conditions mentioned above.

From a practical point of view Equation 4 suggests the use of (oxidic) thermogalvanic cells as a check on the absence of significant electronic conduction and, if so, their use as a '$p(O_2)$ meter' (oxygen gauge) [8]. In comparison to the more conventional isothermal concentration cell technique, the great advantage is the alleviation of gas tightness problems. All Seebeck coefficients in the oxygen pressure range 1–10^{-4} atm are negative

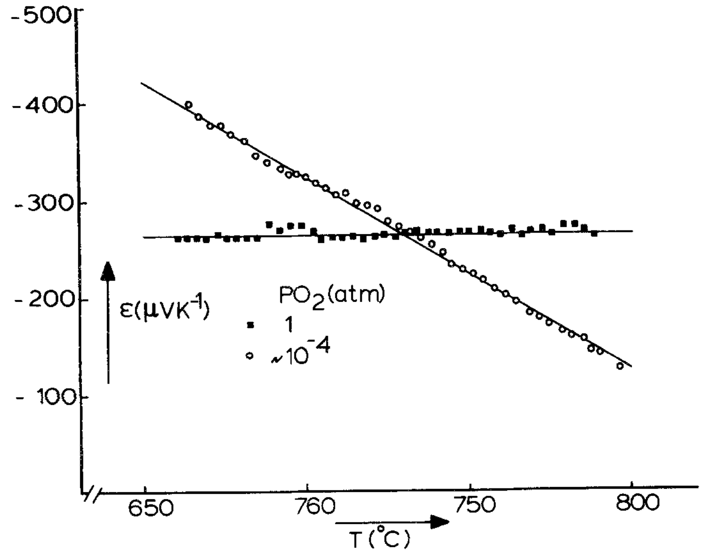

Fig. 3. The thermoelectric power of $\delta\text{-}Bi_2O_3$ for $p(O_2) = 1$ and 10^{-4} atm as a function of the temperature, showing the spread in the experimental points.

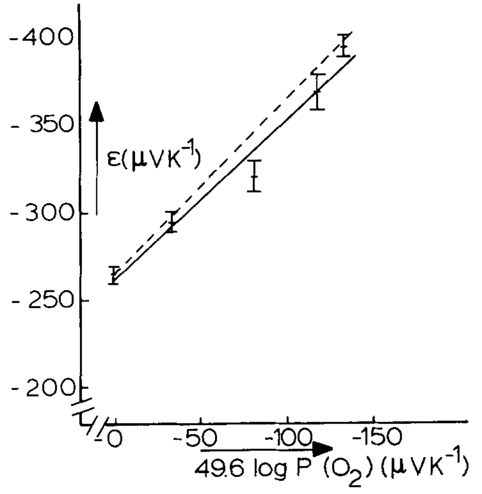

Fig. 4. The temperature independent 'plateaux' in μV K^{-1} as a function of 49.6 log $p(O_2)$ in μV K^{-1} (cf. Equation 4). – – – theoretical curve; —— experimental curve (by linear regression).

('hotter' electrode has negative sign), similar to various other oxygen ion conducting materials, such as the ZrO_2–CaO–Y_2O_3 systems [9–11]. This indicates that oxygen ions are the mobile charge carriers, which can readily be seen from entropy considerations on the electrode Reaction 2; (endothermic) evolution of oxygen will take place at the hotter electrode, while (exothermic) condensation takes place at the colder electrode.

At oxygen pressures from 1 to 4 x 10^{-3} atm the Seebeck coefficient is almost constant in the relevant (ionic) temperature range, similar to some cationic (Ag^+) [12–14] and anionic (O^{2-}) [9–11] 'fast ionic conductors'. At these oxygen pressures the transport number $t(O^{2-}) = 1$. However, at lower oxygen pressures, e.g. $p(O_2) = 10^{-3}$, 10^{-4} atm, no 'plateaux' are observed, and at $p(O_2) = 2 \times 10^{-3}$ atm the Seebeck coefficient is constant only in a small temperature range ($T = 650$–710° C). These phenomena are most likely caused by electronic (n-type) contributions to the conduction. This conduction could in principle be extrinsic, resulting from the incorporation of aliovalent cations (e.g. from the electrode material). After the measurements the originally yellow sample was grey coloured, and a spectrochemical analysis revealed a Pt content of 0.05 wt%, as has been reported earlier by Harwig and Gerards [3]. However, because of the strong oxygen pressure dependency of this electronic contribution, the extrinsic part cannot be very important. In a qualitative sense, an intrinsic n-type contribution due to the process: $O_0^* \rightarrow V_0^{\cdot\cdot} + \frac{1}{2}O_2(g) + 2e'$, may well explain the observed phenomena: (a) This contribution increases with decreasing $p(O_2)$ and increasing T (entropy gain); (b) parasitic loading of the electrochemical process increases in the same directions; (c) mass transport limitations to the reversibility of the electrochemical process become more severe at decreasing $p(O_2)$. These effects all tend to lower the absolute e.m.f. of the galvanic cell in the observed direction. Moreover, migrational contributions of the e carriers proper will give rise to a positive ϵ in terms of the sign convention adopted here, again in accordance with the observed trend.

Though a quantitative interpretation of the apparent linearity in the low pressure ϵ versus T curves cannot be given, we can say that the Seebeck coefficient is very sensitive to electronic contributions, because at these oxygen pressures no electronic contributions could be detected, when measuring the overall conductivity [3]. The kinetically important heat of transport, $Q^*(O^{2-})$ is calculated from the observed $\epsilon^0(T)$, tabulations of $S^0(O_2)$, $\bar{S}(e, Pt)$ [15, 16] and an estimated value for $\bar{S}(O^{2-})$, using entropy data for the oxide [15] and accounting for cationic and anionic mass ratios (cf. Pitzer's approach [17]):

$$\bar{S}(O^{2-}) = \tfrac{1}{5}S^0(Bi_2O_3) - \tfrac{3}{5}R \ln (M_{Bi}/M_O) \quad (5)$$

The results are presented in Fig. 5. The heat of transport is found to be independent of temperature within the experimental error, having a value of 0.13 ± 0.01 eV, whereas the activation enthalpy for electrical conduction is 0.30 eV. The reported agreement between values of the heat of transport and the activation enthalpy for the electrical conduction [18, 19, 23], is in our case not valid, and for other 'fast ionic conductors' not firmly sustained by experiments. The $Q^*(Ag_i^+) = 0.052$ eV in α-AgI, found by Shahi and Chandra [13] seems to be in good agreement with the activation enthalpy of electrical conduction, $\Delta H(Ag_i^+) = 0.051$ eV [20]. However in view of their experimental errors and the neglect of $\bar{S}(e, Ag)$ their conclusions are doubtful. Fischer [9] obtained for

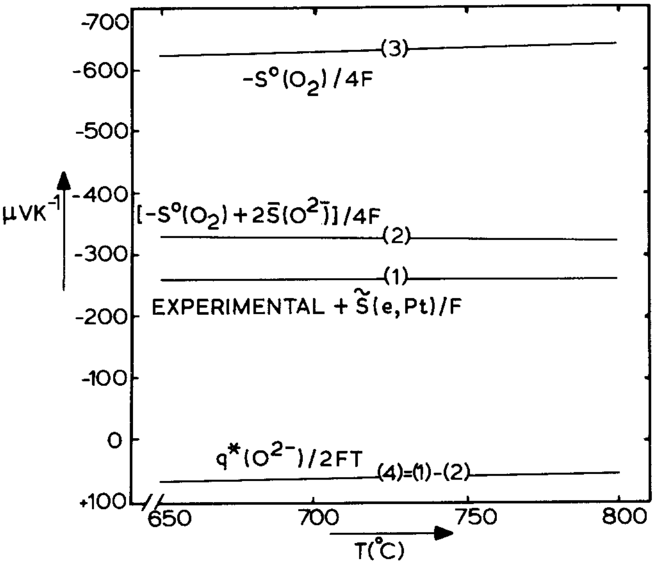

Fig. 5. The contributions to Equation 3 for δ-Bi_2O_3 at 1 atm O_2, yielding $Q^*(O^{2-})$.

the $(ZrO_2)_{0.88}(CaO)_{0.12}$ and $(ZrO_2)_{0.91}(Y_2O_3)_{0.09}$ compounds values for $Q^*(O^{2-})$ of respectively 0.009 and 0.053 eV, in contradiction to the enthalpies of electrical conduction, which are in the order of $\Delta H(O^{2-}) = 0.8$–1.5 eV [18].

As a striking result, all values of the heat of transport for fast ionic conductors are low, which might very well be characteristic for these materials. Because of the discrepancy between $\Delta H(O^{2-})$ and $Q^*(O^{2-})$ the free ion model as proposed by Rice and Roth [18] cannot be applied for Bi_2O_3. The extended lattice gas model proposed by Girvin [19] can be used to explain this phenomenon if it is accepted that the polaron coupling is very strong in δ-Bi_2O_3. This is quite natural for the highly disordered structure of δ-Bi_2O_3. Experimental evidence for the high degree of vibrational freedom in the δ-phase can result from infra-red studies, which are now in progress [21, 23]. From these and thermogalvanic data on various Bi_2O_3–M_2O_3 solid solution, where M = Y, Tb–Lu, more detailed information on the conduction mechanism can be expected in future [22].

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