

HIGH OXYGEN ION CONDUCTION IN SINTERED OXIDES OF THE $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$ SYSTEM

M.J. VERKERK and A.J. BURGGRAAF

Department of Inorganic Materials Science, Twente University of Technology, 7500 AE Enschede, The Netherlands

The conditions leading to optimum conductivity of the $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$ system were investigated. The highest conductivity was found for $\text{Ln} = \text{Er}$ or Tm . Ordering in the oxygen lattice was investigated using neutron diffraction. Correlations were found between the neutron diffraction data and the conductivity.

1. Introduction

In the search for new inorganic compounds which exhibit predominantly oxygen ion conduction at low temperatures, Bi_2O_3 was found a promising material. The conductivity of the δ -phase (fcc), which exists between 1002 K and the melting point at 1097 K, is mainly ionic. The region of the highly ionic conductive phase can be extended to room temperature by introduction of lanthanides [1–5].

At higher temperatures, bismuth sesquioxide shows a tendency to be reduced under low oxygen pressures. Verkerk et al. [6] showed that no increase in the stability against reduction of $\delta\text{-Bi}_2\text{O}_3$ can be achieved by stabilization of $\delta\text{-Bi}_2\text{O}_3$ with lanthanides. At 900 K the equilibrium oxygen pressure of a stabilized Bi_2O_3 is 10^{-12} atm. This makes the material a potential candidate for devices such as oxygen pumps, oxygen gauges and other applications under non-strongly reducing conditions.

We have studied the $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$ system since the conductivity of stabilized bismuth sesquioxides is one decade or more higher than that of stabilized zirconias. Our investigations were focused on the following aspects:

- (1) optimization of the conductivity;
- (2) defect structure of stabilized Bi_2O_3 (fcc).

2. Experimental

Studies were performed on the systems $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3\text{--Dy}_2\text{O}_3$. Experimental details are described elsewhere [1, 2].

Neutron diffraction diagrams of $(\text{Bi}_2\text{O}_3)_{0.80}(\text{Er}_2\text{O}_3)_{0.20}$ were collected on the powder diffractometer at the HFR reactor at Petten. The measurements were performed on a rod with a length of 6 cm and a diameter of 1 cm, enclosed in a quartz ampoule [7]. The data were refined according the line profile method of Rietveld [8] and details will be published elsewhere [9].

3. Results and discussion

3.1. Optimization of the conductivity

The conditions leading to optimum conductivity of sintered oxides of the $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$ system were investigated by studying the systems $\text{Bi}_2\text{O}_3\text{--Er}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3\text{--Dy}_2\text{O}_3$ and combining these results with literature data for the following systems: $\text{Bi}_2\text{O}_3\text{--Y}_2\text{O}_3$ [3], $\text{Bi}_2\text{O}_3\text{--Gd}_2\text{O}_3$ [4], and $\text{Bi}_2\text{O}_3\text{--Yb}_2\text{O}_3$ [10].

A monophasic fcc structure was found for samples containing 17.5–45.5 mole% Er_2O_3 and 28.5–50.0 mole% Dy_2O_3 . Above and below this concentration range polyphasic regions appear.

These fcc phases showed high oxygen ion

conduction. The conductivity of sintered $\text{Bi}_2\text{O}_3\text{-Dy}_2\text{O}_3$ samples measured in air is given in fig. 1. At low temperatures the cubic phase for the sample containing 25 mole% Dy_2O_3 can exist only as a metastable state.

The ionic transference number was measured with a concentration cell, under the conditions of $P_{\text{O}_2} = 0.21$ atm and $P_{\text{O}_2}'' = 1.00$ atm. For the samples containing 17.5–30 mole% Er_2O_3 and 25–40 mole% Dy_2O_3 the ionic transference number is approximately one. At higher percentages of lanthanide, an electronic component is introduced at lower temperatures.

(a) *The influence of the ionic radius on the conductivity*

The logarithm of the conductivity of $(\text{Bi}_2\text{O}_3)_{0.65}(\text{Ln}_2\text{O}_3)_{0.35}$ increases linearly with the ionic radius. At 973 K the conductivity for $\text{Ln} = \text{Yb}^{3+}$ ($r_{\text{ion}} = 0.098$ nm) and $\text{Ln} = \text{Gd}^{3+}$ ($r_{\text{ion}} = 0.106$ nm) is $6.3 \Omega^{-1} \text{m}^{-1}$ and $10 \Omega^{-1} \text{m}^{-1}$ respectively. There are too few precise data to analyse the relationships between ionic radius and $\log \sigma_0$ and E_a further.

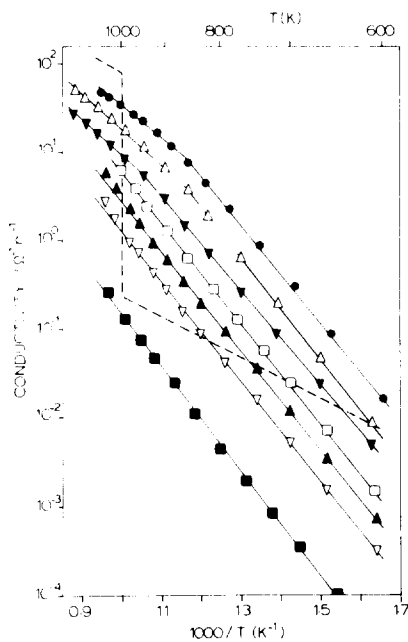


Fig. 1. Conductivity of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Dy}_2\text{O}_3)_x$ in air. \circ : $x = 0.25$ (fcc); \triangle : $x = 0.285$; \blacktriangledown : $x = 0.35$; \square : $x = 0.40$; \blacktriangle : $x = 0.45$; ∇ : $x = 0.50$; \blacksquare : $x = 0.60$. The broken line represents the conductivity of pure Bi_2O_3 as temperature is raised.

(b) *The influence of the lanthanide content on the conductivity*

As can be seen from fig. 1 the logarithm of the conductivity decreases with increasing lanthanide content. For all the systems investigated it appeared that the decrease of $\log \sigma$ was linear with the composition. This relationship will be

(c) *The influence of the ionic radius on the minimum concentration of lanthanide (X_{min}) necessary to stabilize the fcc phase*

It appears that there is a minimum for $r_{\text{ion}} = 0.100$ nm (Er^{3+} , $X_{\text{min}}(\text{Er}_2\text{O}_3) = 17.5$ mole%). Above and below this value, higher concentrations of lanthanide are necessary to stabilize the fcc phase. The shape of the curve can be qualitatively explained [2].

Summarizing these results, we can conclude that there are two contradictory tendencies: on the one hand, the ionic conductivity increases with increasing ionic radius; on the other X_{min} increases with increasing ionic radius and a high X value results in a low conductivity. The influence of the ionic radius on the conductivity, however, is smaller than the influence of the Ln_2O_3 content. Therefore the highest conductivity occurs at the lowest X_{min} , i.e. at $\text{Ln} = \text{Er}$ as shown in fig. 2. No data have so far been published for $\text{Ln} = \text{Tm}$, so it remains possible that the conductivity in the system $\text{Bi}_2\text{O}_3\text{-Tm}_2\text{O}_3$

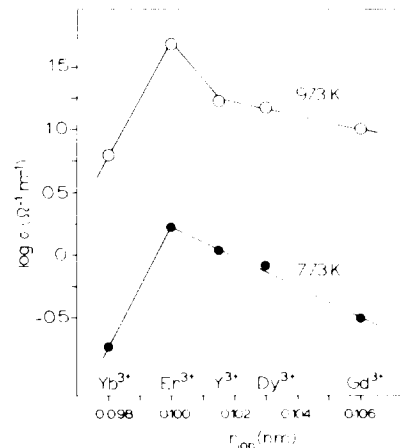


Fig. 2. The conductivity of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Ln}_2\text{O}_3)_x$ for $x = X_{\text{min}}$ versus the ionic radius of the Ln^{3+} ion at 737 K (closed circles) and 973 K (open circles).

is somewhat higher than in the system $\text{Bi}_2\text{O}_3\text{-Er}_2\text{O}_3$.

3.2. Conductivity mechanism

As shown in fig. 1 the samples containing 25.0–35.0 mole% Dy_2O_3 show a bend in the Arrhenius plot at a certain temperature T_x of ≈ 870 K. This bend is also reported for Bi_2O_3 stabilized with other lanthanides [1, 3–5]. From our work [1, 2] and published data [3, 4] we searched for relationships between the activation energy, $\log \sigma_0$ and the lanthanide content. For reasons of clarity the data are separately given for temperatures below 820 K and above 900 K. The results are given in figs. 3 and 4.

It appears that there are two different dependences, which can be related to different defect structures. Above 900 K for samples showing a bend in the Arrhenius plot the activation energy increases with increasing x whereas $\log \sigma_0$ is independent of x . The values of the activation energy and $\log \sigma_0$, extrapolated to $x = 0$, come very close to the values for $\delta\text{-Bi}_2\text{O}_3$. This suggests the existence of a high-temperature (disordered) oxygen lattice analog to pure $\delta\text{-Bi}_2\text{O}_3$. For samples showing no bend

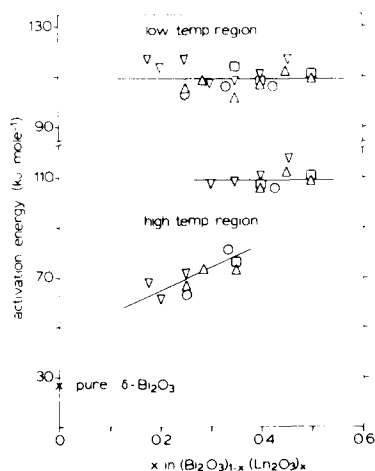


Fig. 3. The activation energy of the conductivity for the low-temperature region (<820 K) and for the high-temperature region (>900 K) as a function of the composition for several substituents. \circ : Ln = Y; \square : Ln = Gd; \triangle : Ln = Dy; ∇ : Ln = Er.

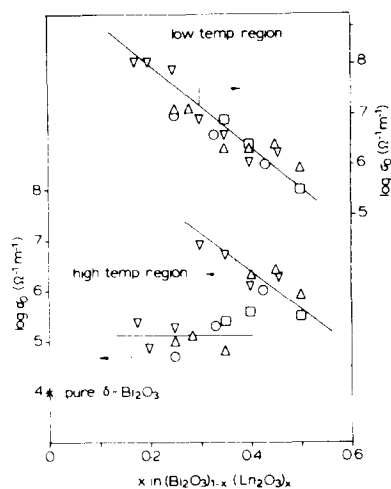


Fig. 4. The $\log \sigma_0$ of the conductivity for the low-temperature region (<820 K) and for the high-temperature region (>900 K) as a function of the composition for several substituents. \circ : Ln = Y; \square : Ln = Gd; \triangle : Ln = Dy; ∇ : Ln = Er.

in the Arrhenius plot, it appears that the activation energy is independent of x and that $\log \sigma_0$ decreases linearly with increasing x . The same holds below 820 K for samples showing a bend in the Arrhenius plot. These relations suggest that in this region the composition (and hence the lattice constant) has no significant influence on the thermal activated passage of oxygen through the lattice, whereas the composition has a strong influence on $\log \sigma_0$. It is therefore suggested that in this region the oxygen ions are partly ordered, and that the concentration of the mobile oxygen ions strongly decreases with increasing lanthanide content. To investigate possible ordering of oxygen ions, neutron diffraction studies were performed on stabilized bismuth sesquioxide.

3.3. Neutron diffraction study of $(\text{Bi}_2\text{O}_3)_{0.80}(\text{Er}_2\text{O}_3)_{0.20}$

Neutron diffraction studies were performed on $(\text{Bi}_2\text{O}_3)_{0.80}(\text{Er}_2\text{O}_3)_{0.20}$ in the temperature range 300–1100 K. At 870 K this sample shows a bend in the Arrhenius plot of the conductivity, the activation energy changes from 115 to 62 kJ mol^{-1} .

The neutron diffraction data were refined according to three models:

(a) Sillén model: fluorite lattice with ordered defects in the $\langle 111 \rangle$ direction. Space group: $\text{Pn}3\text{m}$.

(b) Gattow model: fluorite lattice with an average occupation of the anion sites (8c) of $\text{Fm}3\text{m}$ ($x\text{xx}$, $x = \frac{1}{4}$, site occupancy $\frac{3}{4}$).

(c) Willis model: fluorite lattice with an average occupation of the anion sites (32f) of $\text{Fm}3\text{m}$ ($x\text{xx}$, $x = \frac{1}{4} + \delta$, site occupancy $\frac{3}{16}$).

These models are extensively described by Harwig [7].

Table 1 shows the temperature factors (B) and the residual (χ^2) obtained for refinements of data at 300 K of the models described above. The residual for the Sillén model is not satisfactory, so we conclude that no long-range ordering of oxygen vacancies appears in the $\langle 111 \rangle$ direction. Using different temperature factors for the anions and the cations, satisfactory residuals were obtained for both the Gattow model and the Willis model. The difference in residual is too small to decide between these models. A very large temperature factor for oxygen was obtained. This may be an indication that there is a large (probably static) positional disorder in the oxygen lattice. This is supported by the flat shape of the residual versus the oxygen position as shown in fig. 5. At 1073 K an analogous relationship is obtained.

Below 870 K the temperature factors of the cations and anions are nearly temperature independent whereas above 870 K these temperature factors increase with rising temperature. At 870 K there is also a sudden increase in the lattice constant, accompanied by

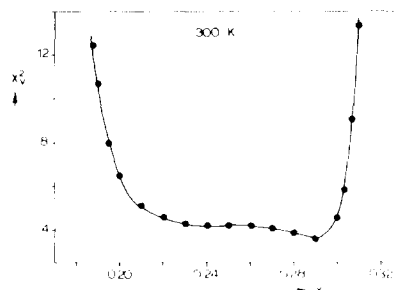


Fig. 5. The residual χ^2 versus the oxygen position x .

an increase in the expansion coefficient.

In the diffuse background, peaks were observed as shown in fig. 6. No peaks were observed for pure Bi_2O_3 (fcc). The intensity of these peaks decreased strongly for temperatures above 870 K. These peaks can be correlated with a short-range ordering process in the oxygen lattice under influence of the lanthanide.

The temperature T_x in the conductivity versus temperature plot coincides with the temperature where changes in the data of the neutron diffraction refinements were observed. The activation energy is determined by both the binding energy of the oxygen ions to the short-range ordered unit and the local strain components during migration from one cation tetrahedron to the next. At low temperatures the major contribution is due to the binding energy of the oxygen ions to the short-range ordered unit. At 870 K the short-range order is (partly) diminished as shown by neutron diffraction. As can be expected this is accompanied by an increase in the lattice constant. This results in a decrease in the activation

Table 1
Neutron diffraction data for $(\text{Bi}_2\text{O}_3)_{0.80}(\text{Er}_2\text{O}_3)_{0.20}$ at 300 K

Model	B_0	$B_{\text{Bi,Er}}$	χ^2
Sillén	2.9	2.9	342
	10.9	0.5	130
Gattow	5.6	5.6	240
	10.7	2.3	11
Willis	6.7	2.7	9

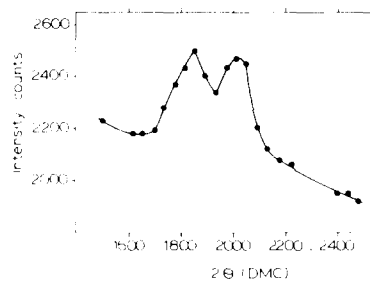


Fig. 6. A part of the diffuse background of $(\text{Bi}_2\text{O}_3)_{0.80}(\text{Er}_2\text{O}_3)_{0.20}$ at 773 K. The d values are 2.39 Å and 2.21 Å respectively.

energy. This suggests that the activation energy is here mainly determined by the local strain components during migration. Further neutron diffraction experiments are necessary to understand the conductivity of other compositions. It is suggested that at high lanthanide concentrations short-range order exists over the whole temperature range and so determines the (high) activation energy.

4. Conclusions

From the relationships found between the ionic radius, the conductivity and the minimum concentration of lanthanide necessary to stabilize the fcc phase it is concluded that the highest ionic conductivity will be found for Ln = Er or Tm.

From a study of relations between the activation energy, $\log \sigma_0$ and the composition it is concluded that two conductivity mechanisms play a role. This hypothesis is supported by neutron diffraction studies. At low temperatures short-range ordering determines the conductivity.

Acknowledgement

Dr. R.B. Helmholtz (Solid State Department of the Energy Centre the Netherlands) is thanked for cooperation in carrying out the neutron diffraction experiments. Financial assistance from Philips N.V. (Elcoma) is gratefully acknowledged.

References

- [1] M.J. Verkerk, K. Keizer and A.J. Burggraaf, *J. Appl. Electrochem.* 10 (1980) 81.
- [2] M.J. Verkerk and A.J. Burggraaf, *J. Electrochem. Soc.* 128 (1981) 75.
- [3] T. Takahashi, H. Iwahara and T. Arao, *J. Appl. Electrochem.* 5 (1975) 187.
- [4] T. Takahashi, T. Esaka and H. Iwahara, *J. Appl. Electrochem.* 5 (1975) 197.
- [5] H.T. Cahen, Thesis, State University of Utrecht (1980).
- [6] M.J. Verkerk and A.J. Burggraaf, *J. Appl. Electrochem.* 10 (1980) 677.
- [7] H.A. Harwig, *Z. Anorg. Allg. Chem.* 444 (1978) 151.
- [8] H.M. Rietveld, *J. Appl. Cryst.* 2 (1969) 65.
- [9] M.J. Verkerk, G.M.H. van de Velde, R.B. Helmholtz and A.J. Burggraaf, *J. Phys. Chem. Solids*, submitted for publication.
- [10] M.J. Verkerk, unpublished results.