HIGH OXYGEN ION CONDUCTION IN SINTERED OXIDES OF THE Bi$_2$O$_3$–Ln$_2$O$_3$ SYSTEM

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The conditions leading to optimum conductivity of the Bi$_2$O$_3$–Ln$_2$O$_3$ system were investigated. The highest conductivity was found for Ln = 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$_2$O$_3$ 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 δ-Bi$_2$O$_3$ can be achieved by stabilization of δ-Bi$_2$O$_3$ with lanthanides. At 900 K the equilibrium oxygen pressure of a stabilized Bi$_2$O$_3$ 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 Bi$_2$O$_3$–Ln$_2$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$_2$O$_3$ (fcc).

2. Experimental

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

Neutron diffraction diagrams of (Bi$_2$O$_3$)$_{0.80}$(Er$_2$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 Bi$_2$O$_3$–Ln$_2$O$_3$ system were investigated by studying the systems Bi$_2$O$_3$–Er$_2$O$_3$ and Bi$_2$O$_3$–Dy$_2$O$_3$ and combining these results with literature data for the following systems: Bi$_2$O$_3$–Y$_2$O$_3$ [3], Bi$_2$O$_3$–Gd$_2$O$_3$ [4], and Bi$_2$O$_3$–Yb$_2$O$_3$ [10].

A monophasic fcc structure was found for samples containing 17.5–45.5 mole% Er$_2$O$_3$ and 28.5–50.0 mole% Dy$_2$O$_3$. Above and below this concentration range polyphasic regions appear.

These fcc phases showed high oxygen ion...
conduction. The conductivity of sintered Bi$_2$O$_3$–Dy$_2$O$_3$ samples measured in air is given in fig. 1. At low temperatures the cubic phase for the sample containing 25 mole% Dy$_2$O$_3$ can exist only as a metastable state.

The ionic transference number was measured with a concentration cell, under the conditions of $P_{O_2} = 0.21$ atm and $P_{O_2}^\prime = 1.00$ atm. For the samples containing 17.5–30 mole% Er$_2$O$_3$ and 25–40 mole% Dy$_2$O$_3$ 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 (Bi$_2$O$_3$)$_{0.65}$(Ln$_2$O$_3$)$_{0.35}$ increases linearly with the ionic radius. At 973 K the conductivity for Ln = Yb$^{3+}$ ($r_{\text{ion}} = 0.098$ nm) and Ln = Gd$^{3+}$ ($r_{\text{ion}} = 0.106$ nm) is 6.3 $\Omega^{-1}$ m$^{-1}$ and 10 $\Omega^{-1}$ m$^{-1}$ respectively. There are too few precise data to analyse the relationships between ionic radius and log $\sigma_{\text{th}}$ and $E_a$ further.

(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 ($X_{\text{min}}$) necessary to stabilize the fcc phase

It appears that there is a minimum for $r_{\text{ion}} = 0.100$ nm (Er$^{3+}$, $X_{\text{min}}$(Er$_2$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 $X_{\text{min}}$ 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$_2$O$_3$ content. Therefore the highest conductivity occurs at the lowest $X_{\text{min}}$, i.e. at Ln = Er as shown in fig. 2. No data have so far been published for Ln = Tm, so it remains possible that the conductivity in the system Bi$_2$O$_3$–Tm$_2$O$_3$.
is somewhat higher than in the system Bi$_2$O$_3$–Er$_2$O$_3$.

3.2. Conductivity mechanism

As shown in fig. 1 the samples containing 25.0–35.0 mole% Dy$_2$O$_3$ show a bend in the Arrhenius plot at a certain temperature $T_c$ of $\approx$870 K. This bend is also reported for Bi$_2$O$_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 $\delta$-Bi$_2$O$_3$. This suggests the existence of a high-temperature (disordered) oxygen lattice analog to pure $\delta$-Bi$_2$O$_3$. For samples showing no bend 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 (Bi$_2$O$_3$)$_{0.80}$(Er$_2$O$_3$)$_{0.20}$

Neutron diffraction studies were performed on (Bi$_2$O$_3$)$_{0.80}$(Er$_2$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$^{-1}$. 

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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. O: Ln = Y; □: Ln = Gd; Δ: Ln = Dy; V: 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. O: Ln = Y; □: Ln = Gd; Δ: Ln = Dy; V: Ln = Er.
The neutron diffraction data were refined according to three models:

(a) Sillén model: fluorite lattice with ordered defects in the (111) direction. Space group: Pn3m.

(b) Gattow model: fluorite lattice with an average occupation of the anion sites (8c) of Fm3m (xxx, \(x = \frac{1}{4}\), site occupancy \(\frac{2}{3}\)).

(c) Willis model: fluorite lattice with an average occupation of the anion sites (32f) of Fm3m (xxx, \(x = \frac{1}{4} + \delta\), site occupancy \(\frac{6}{7}\)).

These models are extensively described by Harwig [7].

Table 1 shows the temperature factors (B) and the residual \(\chi^2\) 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 (111) 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 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\(_2\)O\(_3\) (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 \(T_s\) 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

\[\text{Fig. 5. The residual } \chi^2 \text{ versus the oxygen position } x.\]

\[\text{Fig. 6. A part of the diffuse background of } (\text{Bi}_2\text{O}_3)_{20}(\text{Er}_2\text{O}_3)_{30} \text{ at } 773 \text{ K. The } d \text{ values are } 2.39 \text{ Å and } 2.21 \text{ Å respectively.}\]
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.

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**References**