polarization and kinetic data arise mainly from the different cathodic reactions involved.

A model for thermal oxide growth at \( e \approx 1 \text{nm} \) in thickness is proposed, based on the kinetic and polarization data.

1. When oxidizing in steam, the reduction of the protons released is assisted by their surface conduction in the adsorbed water phase on the zirconia surface and the electron transport at the intermetallic sites. Therefore, the rest potential stays at low negative values and the oxidation proceeds at a fast rate comparable to that in the molten salts.

2. In dry air, the oxidation proceeds at a much slower rate than in steam and the molten salts. The electrical properties of the oxides grown in air, however, are similar to those of the oxides grown in the molten salts. Therefore, the low rates of oxidation in air are attributed to a highly negative rest potential on the alloy brought about by a high resistance for the surface conduction of electrons and the absence of a reduction step involving cationic species. The rate of oxidation, initially linear, is controlled by the reduction of oxygen at the surface; then the rate changes due to the buildup of an electronic space charge in the oxide and control by the combination of electron conductivity at the intermetallics and surface conduction.

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High Oxygen Ion Conduction in Sintered Oxides of the Bi$_2$O$_3$-Dy$_2$O$_3$ System

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ABSTRACT

The phase diagram of the Bi$_2$O$_3$-Dy$_2$O$_3$ system was investigated. A monophasic fcc structure was stabilized for samples containing 28.5-50.0 mole percent (m/o) Dy$_2$O$_3$. Above and below this concentration range polyphasic regions appear. The fcc phase showed high oxygen ion conduction. The ionic transference number is equal to one for specimens containing 28.5-49.0 m/o Dy$_2$O$_3$, whereas an electronic component is introduced at low temperatures for specimens containing 50.0 m/o Dy$_2$O$_3$. The conductivity of (Bi$_2$O$_3$)$_{0.715}$ (Dy$_2$O$_3$)$_{0.285}$ is 0.71 \( \Omega^{-1}\text{m}^{-1} \) and 14.4 \( \Omega^{-1}\text{m}^{-1} \) at 773 and 973 K, respectively. Relations were 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 in the system Bi$_2$O$_3$-Er$_2$O$_3$ or Bi$_2$O$_3$-Tm$_2$O$_3$. From a study of relations between the activation energy, log \( \sigma_a \) and the composition it is concluded that two conductivity mechanisms play a role.

Recently Harwig investigated the electrical and structural properties of Bi$_2$O$_3$ (1-5). At room temperature the monoclinic \( \alpha \)-phase is stable and the conductivity is predominantly electronic. On heating to 1002 K the oxide transforms to the face centered cubic (fcc) \( \delta \)-phase, which is stable up to the melting point at 1097 K. In the \( \delta \)-phase the electrical conductivity is about 100 \( \Omega^{-1}\text{m}^{-1} \) and varies little with temperature. The ionic transport number is equal to one (6). On cooling this highly conductive phase may be extended to 923 K, where it transforms into the tetragonal \( \beta \)-phase or to 912 K where it transforms into the body-centered cubic (bcc) \( \gamma \)-phase. These phase transformations are accompanied by sudden volume changes which cause deterioration of the mechanical properties of the material. The conductivity in the \( \beta \)- and \( \gamma \)-phase is mainly ionic and about three orders of magnitude lower than in the \( \delta \)-phase.

The temperature range at which this material can be used as a solid electrolyte can be extended by substituting Bi$_2$O$_3$. The region of highly ionic conductive \( \delta \)-phase can be extended to room temperature by intro-
duction of 17.5-45 m/o Er2O3 (7,8), 25-43 m/o Y2O3 (9), 35-55 m/o Gd2O3 (10), 25 m/o WO3 (11), 15-25 m/o Nb2O5 and 18-25 m/o Ta2O5 (12). The highest ionic conductivity is found in the system Bi2O3-Er2O3. The conductivity of (Bi2O3)0.50(Er2O3)0.50 is 2.3 and 37 \Omega^{-1} \text{cm}^{-1} at 773 and 973 K, respectively (7).

Oxygen ion conductors based on defect fluorite-type lattice, with a Guinier-Simon camera (heating rate: 5 K min\(^{-1}\)) were used. Small amounts of aluminum and silicon. The procedure is described elsewhere (7,22). The detection limits of these analyses are 0.005 weight percent (w/o) Al2O3 and 0.002 w/o Si.

Because of the relative ease of reduction at higher temperatures (6,13,14), the bismuth sesquioxide-based materials are not suitable for fuel cell applications. Their application will be limited to oxygen pumps [e.g., for oxygen-enrichment (15)] or electrolyte for “second generation” oxygen sensors [e.g., the device developed by Heyne (16, 17)]. The “second generation” oxygen sensor is used for automotive control and operates in the lean air/fuel ratio region, e.g., an oxygen-rich exhaust gas (1-10% O2). The sensor produces a feedback signal to keep the gas mixture fed to the motor oxygen rich. So all the fuel is burned and most pollutants can be removed catalytically (16,18,19).

The occurrence of the cubic phase (fcc) in the Bi2O3-Dy2O3 system is reported for 3Bi2O3-Dy2O3 by Datta and Meehan (20) and for Bi2O3-Dy2O3 by Nasanova et al. (21). The fcc phase in comparable binary compounds exhibits high oxygen ion conduction over a wide temperature range. Therefore, the authors have investigated the phase diagram and the conductivity of the Bi2O3-Dy2O3 system.

The investigations are a part of our efforts on a number of Bi2O3-Ln2O3 compositions. Phenomenological relations between the ionic radius of the lanthanide, the structure, and the conductivity are given. Some predictions about high ionic conductivity in stabilized Bi2O3 are made.

### Experimental

**Preparation and analysis of the specimens.**—Bi2O3 (Merck, very pure) and Dy2O3 (Serva, 99.9%) were thoroughly mixed and preheated at 1020-1120 K for 16 hr. finely ground and isostatically pressed at about 400 MPa, sintered in air for 45 hr, and cooled down (1/2 K min\(^{-1}\)) to room temperature. The sintering temperature was raised as the content of Dy2O3 was increased, as seen in Table I. Sintering and quenching were performed in platinum crucibles.

After the synthesis the composition of the samples was checked by x-ray fluorescence. The accuracy is 0.1% absolute. The specimens were analyzed for small amounts of aluminum and silicon. The procedure is described elsewhere (7,22). The detection limits of these analyses are 0.005 weight percent (w/o) Al and 0.001 w/o Si.

The crystal structures of the specimens were identified by a Philips PW 1790 diffractometer. Cu Kα radiation was used with a Ni filter. The lattice parameters were calculated from diffraction angles in the 60°-120° (20) region. obtained at a scanning speed of 1/4° min\(^{-1}\) using Pb(NO3)2 as the internal standard. High temperature x-ray experiments were performed with a Guinier-Simon camera (heating rate: 5 K hr\(^{-1}\)). The ceramic structures of polished and thermally etched samples were investigated with the scanning electron microscope (SEM) Type JEOL JSM U3. Differential thermal analysis (DTA) measurements were performed with a du Pont 990 Thermal Analyser, heating rate: 10 or 15 K min\(^{-1}\). The densities of the samples were measured at 298 K by the Archimedes method using mercury.

**Measurement of the ionic conductivity.**—The electrical conductivity was measured at a frequency of 10 kHz. The ionic transference number was measured by the emf of an oxygen gas concentration cell. Details of these measurements are described elsewhere (7).

### Results

**Samples prepared.**—The densities of the specimens after sintering were 92-94% of the theoretical density, see Table I. The average grain size of the samples is about 30 μm. The ceramic structure of a specimen is shown in Fig. 1. On this photograph it can be seen that the grain growth in this system is very fast even at temperatures of 1273 K. The grain boundaries move so fast that they become curved and pores are isolated within the grains. This implies that higher final densities are difficult to obtain without controlling grain growth.

The color of the specimens was yellow/orange for low percentages of Dy2O3 and dark brown for high percentages.

The difference between the calculated composition and the composition measured by x-ray fluorescence was 2.0% absolute or less. Concentrations of silicon and aluminum impurities are lower than 0.002 and 0.03 w/o, respectively.

**Density is given as a percentage of the theoretical density based on a perfect fluorite-type lattice.**

<table>
<thead>
<tr>
<th>Table I. Sintering temperature and density</th>
</tr>
</thead>
<tbody>
<tr>
<td>x in (Bi2O3)1-x(Dy2O3)x</td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>0.05-0.10</td>
</tr>
<tr>
<td>0.15-0.25</td>
</tr>
<tr>
<td>0.28-0.35</td>
</tr>
<tr>
<td>0.45-0.50</td>
</tr>
</tbody>
</table>

* Density is given as a percentage of the theoretical density.

**Fig. 1.** The ceramic microstructure of (Bi2O3)0.65(Dy2O3)0.35.
observed in the Bi$_2$O$_3$-Er$_2$O$_3$ system (7). Possibly the existence of the fcc phase for $3\text{Bi}_2\text{O}_3\cdot\text{Dy}_2\text{O}_3$ one tetragonal compound exists. It is suggested that at lower temperatures the solid solution exists over a narrower range of composition and ultimately only one tetragonal compound exists. It is suggested that this is the case in the Bi$_2$O$_3$-Y$_2$O$_3$ system (20).

The high temperature structure of the sample containing 10-25 m/o Dy$_2$O$_3$ is cubic (fcc). This can be concluded from the quenching experiments and was checked by HTG. The low temperature structure is rhombohedral, as can be seen from the samples cooled down by 1/2 K min$^{-1}$ as well as from the annealing experiments. The annealing experiments indicate that the rhombohedral solid solution is found from about 15 m/o Dy$_2$O$_3$ to 25 m/o Dy$_2$O$_3$. After annealing for 2000 hr at 880 K the structure of the specimen containing 25 m/o Dy$_2$O$_3$ was $\approx$ 95% rhombohedral. Table III shows the transition temperature of the rhombohedral structure to the cubic structure measured by DTA.

The equilibrium monophasic fcc structure was observed at low temperatures for samples containing 28.5-50.0 m/o Dy$_2$O$_3$. These results do not agree with the observations of Datta and Meehan (20) who reported the existence of the fcc phase for $3\text{Bi}_2\text{O}_3\cdot\text{Dy}_2\text{O}_3$ at low temperatures. It is very likely that these authors reported the nonequilibrium high temperature structure. Possibly contamination by the porcelain or silica crucibles used for the synthesis of the materials may play a role. The observations of the fcc phase for Bi$_2$O$_3$-Dy$_2$O$_3$ by Nasonova et al. (21) is confirmed.

As shown in Fig. 2 we see that in the whole range of the stabilized fcc phase (28.5-50 m/o Dy$_2$O$_3$) and in the range where the high temperature fcc phase can be retained by quenching (10-25 m/o Dy$_2$O$_3$) the lattice constant decreases linearly with an increasing Dy$_2$O$_3$ content, i.e., Vegard's rule holds.

The specimen containing 60 m/o Dy$_2$O$_3$ shows an fcc phase and an unknown phase. Attempts to determine the composition of the two phases with the EDAX unit of the SEM failed because the size of the separate phases was too small compared to that of the analyzed area (0.5-1 $\mu$m$^2$). The deviation of the lattice constant of the fcc phase from the cubic sample

The theoretical densities can be calculated from the measured lattice constants assuming several defect models and can be compared with the observed densities. These defect models are extensively described and discussed in Ref. (7) and will not be repeated here. It appears that the system Bi$_2$O$_3$-Dy$_2$O$_3$ shows the same features as reported for Bi$_2$O$_3$-Er$_2$O$_3$ (7). So we conclude that all cations occupy their normal sites in the fluorite structure and that there are two vacancies in a unit cell, i.e., $\text{Bi}_2\text{O}_3\cdot\text{Dy}_2\text{O}_3$.

Conductivity of the sintered specimens.—The conductivity of the sintered Bi$_2$O$_3$-Dy$_2$O$_3$ specimens measured in air is shown in Fig. 3 and 4. In Fig. 4 the conductivity of pure Bi$_2$O$_3$ [after Takahashi et al. (6)] is given as a reference material. Table IV summarizes the values of the activation energies $E_a$ and the preexponential terms $\sigma_0$ for the Arrhenius plots of the conductivity, while the derivation is given in the 90% reliability interval.

Table II. Survey of the structural information of the Bi$_2$O$_3$-Dy$_2$O$_3$ system

<table>
<thead>
<tr>
<th>$x$ in (Bi$_2$O$<em>3$)$</em>{1-x}$(Dy$_2$O$_3$)$_x$</th>
<th>&quot;Quenched&quot; at sintering temperature</th>
<th>Cooled down by 1/2 K min$^{-1}$</th>
<th>Annealing temperature (K)</th>
<th>Annealed for 350 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>$\beta^*$</td>
<td>$\beta$ + $\gamma$ + $\delta$</td>
<td>823</td>
<td>$\beta$ + $\gamma$ + $\delta$</td>
</tr>
<tr>
<td>0.10</td>
<td>$\gamma$</td>
<td>$\gamma$ + $\delta$</td>
<td>823</td>
<td>$\gamma$ + $\delta$</td>
</tr>
<tr>
<td>0.15</td>
<td>$\delta$</td>
<td>$\delta$ + $\epsilon$</td>
<td>903</td>
<td>$\delta$</td>
</tr>
<tr>
<td>0.20</td>
<td>$\delta$</td>
<td>$\delta$ + $\epsilon$</td>
<td>973</td>
<td>$\delta$</td>
</tr>
<tr>
<td>0.25</td>
<td>$\delta$</td>
<td>$\delta$ + $\epsilon$</td>
<td>973</td>
<td>$\delta$</td>
</tr>
<tr>
<td>0.28-0.50</td>
<td>$\delta$</td>
<td>$\delta$ + $\epsilon$</td>
<td>973</td>
<td>$\delta$</td>
</tr>
<tr>
<td>0.60</td>
<td>$\delta$</td>
<td>$\delta$ + $\epsilon$</td>
<td>973</td>
<td>$\delta$</td>
</tr>
</tbody>
</table>

* The $\beta$ phase has a tetragonal structure.
** In this table $x$ denotes the unknown structure.
† The underlined structures appear in minor concentrations.

Table III. Transition temperatures measured by DTA in the heating-up direction

<table>
<thead>
<tr>
<th>$x$ in (Bi$_2$O$<em>3$)$</em>{1-x}$(Dy$_2$O$_3$)$_x$</th>
<th>Transition</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>$\beta$</td>
<td>912</td>
</tr>
<tr>
<td>0.10</td>
<td>$\gamma$</td>
<td>846</td>
</tr>
<tr>
<td>0.15</td>
<td>$\delta$</td>
<td>946</td>
</tr>
<tr>
<td>0.20</td>
<td>$\delta$</td>
<td>989</td>
</tr>
<tr>
<td>0.23†</td>
<td>$\epsilon$</td>
<td>1018</td>
</tr>
</tbody>
</table>

* Measured on samples cooled down by 1/2 K min$^{-1}$ from sintering temperature.
† Measured on the annealed sample (2000 hr at 880 K).

Fig. 2. Lattice constant of the fcc phase of the specimens cooled from the sintering temperature to room temperature by 1/2 K min$^{-1}$. (For $x = 0.1-0.2$ the specimens were quenched.)
there is a change in the activation energy at about 870 K, this is discussed below.

The structure and the dimensions of the lattices of these phases are very different and the influence on the conductivity is striking. The volume of the rhombohedral and cubic unit cells is 0.123 and 0.166 nm$^3$, respectively. The cubic lattice is “blown up” compared with the rhombohedral one. Therefore a flat potential profile along the transport path between oxygen ion lattice sites can be expected and rapid transport can occur in the cubic lattice, as suggested for other systems by Huggins (23).

Figure 4 gives the Arrhenius plots of the conductivity of the cubic specimens containing 0.25-0.60 m/o Dy$_2$O$_3$. The samples containing 0.25-0.35 m/o Dy$_2$O$_3$ show a knee in the Arrhenius plot at about 870-950 K. The changes in the activation energies and the pre-exponential terms are given in Table IV. Present authors (7) correlated this knee to a change in the lattice constant, probably caused by changes in the ordering of oxygen in the lattice. The increase of the lattice constant for (Bi$_2$O$_3$)$_{0.50}$(Er$_2$O$_3$)$_{0.50}$ was confirmed by the Simon camera and is in the order of 1.5%. However, for the samples containing Dy$_2$O$_3$ no increase in the lattice constant could be measured with HTG. We conclude that the change in activation energy and the change in log $\sigma_0$ is caused by a minor change in the structure which is not always accompanied by a measurable change in the unit cell volume.

The best oxygen ionic conductor in this system is found in the material with the composition (Bi$_2$O$_3$)$_{0.75}$(Dy$_2$O$_3$)$_{0.25}$. The conductivity at 773 and 973 K is 0.71 and 14.4 $\Omega$-m$^{-1}$, respectively. This is about three times lower than the conductivity of (Bi$_2$O$_3$)$_{0.80}$(Er$_2$O$_3$)$_{0.20}$ (7) and more than ten times higher than the conductivity of (ZrO$_2$)$_{0.195}$(Y$_2$O$_3$)$_{0.805}$ at the same temperatures.

The ionic transference number.—The ionic transference number was measured with an oxygen gas concentration cell under the condition of $P'_O_2 = 0.21$ atm and $P''O_2 = 1.00$ atm. The ratio of the measured emf to the theoretical emf is given in Table V. For (Bi$_2$O$_3$)$_{1-x}$(Dy$_2$O$_3$)$_x$ with $x = 0.25-0.40$ the ionic transference number is approximately one, therefore the conductivity in the range 1-100% O$_2$ can be almost wholly attributed to oxygen ions [this work, (27), (31)]. It may be remembered that the deviation
the ionic transference number measured by oxygen concentration cells is about 5%. Additional experiments are necessary to determine the (small) contribution of the electronic conductivity. The sample containing 80 m/o Dy2O3 had an electronic component at low temperatures (T < 900 K). For the sample containing 60 m/o Dy2O3 an electronic component was measured for all temperatures. Because the ionic transference number for the monophasic fcc samples coexisting with the second phase is approximately one, the electronic conductivity has to be ascribed to the second phase. In this temperature range and at these oxygen partial pressures pure Dy2O3 is an electronic conductor (24). Possibly the unknown phase is Dy2O3 rich.

**Discussion**

The results of this study were combined with literature data of the following systems: Bi2O3-Er2O3 (7, 8), Bi2O3-Y2O3 (9), Bi2O3-Gd2O3 (10), and Bi2O3-Yb2O3 (25). Our attention is directed to two subjects, first, the optimization of the ionic conductivity in sintered oxides of the Bi2O3-Ln2O3 system and, second, some considerations concerning the defect structure.

The optimization of the conductivity.—The conditions leading to an optimal conductivity of sintered oxides of the Bi2O3-Ln2O3 system were investigated concerning several aspects. These are, first, the influence of the ionic radius on the conductivity, second, the influence of the composition on the conductivity, and third, the influence of the ionic radius on the minimum substituent concentration necessary to stabilize the fcc phase.

Figure 5 gives the conductivity of bismuth sesquioxide stabilized by several lantanides as a function of the ionic radius of the substituent. The ionic radii are based on r(VO2+) = 0.140 nm, coordination number VIII, as given by Shannon and Prewitt (26). The conductivity increases slightly with increasing ionic radius. No precise data about the lattice constants for some of the compositions are known. However, there is a linear relation between the ionic radius of the substituent and the lattice constant, as shown by Cahen (27), and thus there is a linear relation between the conductivity and the lattice constant. There is too little precise data known up till now to analyze this relation further in terms of relationships between the lattice constant and log ao respectively Eo.

We propose that it may be ascribed to a change in Eo. Assuming the same defect structure for all substituents at x = 0.35 the amount of vacancies is constant, so log a0 will also be constant. Increasing the ionic radius of the substituent will cause an increase in the lattice constant. This may cause a decrease in the contributions of the local strain components during the passage of oxygen ions through the lattice, which leads to a decrease in the activation energy. This explanation agrees with the observation that the slope of the log σ vs. rion relation at 773 K is larger than that at 973 K. This hypothesis is confirmed in a related system. Kubo and Obayashi (26) showed that in Ce1-xLn2O3-x/2 for x = 0.30 the activation energy decreases with increasing ionic radius of the lanthanide.

In Fig. 6 the oxygen ion conductivity in the Bi2O3-Dy2O3 system is plotted against the Dy2O3 content at different temperatures. The conductivity of (Bi2O3)0.8(Er2O3)0.20 (7) is given as a reference. In the fcc solid solution phase field the conductivity decreases linearly with the composition. For x = 0.60 there is a negative deviation from this linear relation. This is due to the second phase. The deviation at x = 0.25 is caused by a structural phase transformation. The conductivity of the metastable fcc phase at x = 0.25 satisfies this linear relation as shown in Fig. 6. It should be noted that a linear relation between conductivity and concentration holds at temperatures above and below the observed knee in the Arrhenious plot. A linear relation in the fcc solid solution phase field is also found for Bi2O3 stabilized with Er2O3 (7), Y2O3 (9), and Gd2O3 (10).

From the Fig. 5 and 6 it is clear that the highest ionic conductivity will be found for large ions and low substituent percentages. As will be shown, these are contradictory requirements. Attention should be paid to the influence of the ionic radius of the Ln3+ ion on the minimum substituent concentration (xmin) necessary to stabilize the fcc structure at room temperature. The correlation between the ionic radius and xmin is given in Fig. 7. It should be noted that the minimum concentrations given in (9, 10) for Gd2O3 and Y2O3 may be too low. Present work and (7) show that high temperature structures may be easily retained at low temperatures. So the cooling procedures applied in (9, 10) to determine the phase boundary of the fcc structure may not be sufficient to produce the "equilibrium" phase boundary. Figure 7 shows that there is a minimum in this curve at rion. = 0.100 nm (Er3+). In literature there are no data about for Ln = Tm3+ (rion = 0.099 nm). So it is possible that xmin for Tm3+ is somewhat lower than for Er3+.
The shape of the curve may be qualitatively explained in the following way. We assume that stabilization of the (very open) high temperature structure occurs at a certain contraction of this structure by the substituent. If the difference between the ionic radii of the \( Ln^{3+} \) ion and the \( Bi^{3+} \) ion is large, this will result in a large distortion in the host lattice and a small amount of substituent is necessary for supplying the energy required to stabilize the fcc phase, i.e., for \( Bi^{3+} \). Reversely, a small difference between the ionic radii needs a large amount of substituent to supply the energy to stabilize the fcc phase, i.e., for \( Gd^{3+} \). For too large differences between the ionic radii of the \( Ln^{3+} \) ion and the \( Bi^{3+} \) ion the fcc phase becomes disfavored. At this stage we do not understand the stabilization of the fcc phase at higher concentration of \( Yb^{3+} \), i.e., a substituent with a relatively large difference in ionic radius with respect to \( Bi^{3+} \).

From Fig. 5 we can conclude that the fcc structure will also be stabilized at low temperatures for \( Ln = Tm \) (\( r_{ion} = 0.099 \) nm), \( Ln = Ho \) (\( r_{ion} = 0.102 \) nm), \( Ln = Tb \) (\( r_{ion} = 0.104 \) nm), and possibly for \( Ln = Sm \) (\( r_{ion} = 0.102 \) nm). The \( x_{min} \) values for these substituents are predicted in this figure.

This discussion allows us to make some predictions about the possibility of the ionic conductivity of \( Bi_{2}O_{3} \) stabilized by lanthanides. There are two contradictory tendencies. First, the ionic conductivity increases with increasing ionic radius (Fig. 5). Second, \( x_{min} \) increases with increasing ionic radius (Fig. 7) and a high \( x_{min} \) value results in a low conductivity (Fig. 6). However, the influence of the ionic radius on the conductivity is smaller than the influence of the \( Ln_{2}O_{3} \) content. Therefore the optimization of the conductivity is only possible by lowering \( x_{min} \). Figure 7 shows that there is a minimum in the \( x_{min} \) vs. \( r_{ion} \) plot at \( 0.088 \) nm. The ions \( Er^{3+} \) (\( r_{ion} = 0.100 \) nm) and \( Tm^{3+} \) (\( r_{ion} = 0.099 \) nm) fall within this range. The highest conductivity occurs at the lowest \( x_{min} \). The ions \( Er^{3+} \) and \( Tm^{3+} \) are able to stabilize the fcc phase stabilized by \( Bi_{2}O_{3} \) or \( Tb_{2}O_{3} \).

If the conductivity above the knee could be stabilized at low temperature, a further optimization of the conductivity could be achieved. As shown below, the knee is correlated with an ordering process in the oxygen lattice. Therefore it is not very likely that the high temperature conductivity can be stabilized at lower temperatures.

**Defect structure.**—As pointed out before the knee in the Arrhenius plot cannot simply be ascribed to a change in the lattice constant, but has to be ascribed to a change in the defect structure. At about the same temperature a knee in the Arrhenius plot is reported for \( Bi_{2}O_{3} \) stabilized with \( Er_{2}O_{3} \) (7), \( Y_{2}O_{3} \) (9), and \( Gd_{2}O_{3} \) (10), for yttria-stabilized zirconia (29, 30) and for lanthanide-doped ceria (28).

From this work and the results mentioned in literature (7, 9, 10) we searched for relations between the activation energy, \( log \sigma_{o} \) 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 Fig. 9 and 10. It appears that there are two different dependences, which can be related to different defect structures.

Above 900 K for the samples showing a knee in the Arrhenius plot the activation energy increases with increasing \( x \), whereas \( log \sigma_{o} \) is independent of \( x \). The values of the activation energy and \( log \sigma_{o} \) for lanthane content. This hypothesis is supported by neutron diffraction studies at room temperature by the present authors on \( Bi_{2}O_{3} \) (9), \( Er_{2}O_{3} \) (7), which show a peak in the diffuse background, which can be correlated with a short distance ordering of oxygen ions. Further neutron diffraction studies are now being performed and will be correlated with a detailed description of the conductivity mechanism.

**Conclusions**

High oxygen ion conductivity is found in the system \( Bi_{2}O_{3}-Dy_{2}O_{3} \). The fcc phase can be stabilized by 28.5-50.0 m/o \( Dy_{2}O_{3} \) for the samples containing 28.5-40.0
The influence of the ionic radius on the conductivity is smaller than the influence of the lanthanide content. Therefore it is concluded that the highest ionic conductivity based on Bi$_2$O$_5$ will be found in the systems Bi$_2$O$_5$-Er$_2$O$_3$ or Bi$_2$O$_5$-Tm$_2$O$_5$. The knee in the Arrhenius plot of the conductivity of several specimens is ascribed to a charge in the defect structure.

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Dr. K. Keizer is thanked for performing some preliminary experiments in this system. We would like to express our appreciation to Mrs. A. van Pelt, Mr. J. Boeysma, and Mr. Th. van Dam for their experimental assistance. Financial assistance from Philips N.V. (Elcoma) is gratefully acknowledged.

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**REFERENCES**


**Fig. 9.** The activation energy of the conductivity for the low temperature region (<320 K) and for the high temperature region (>900 K) as a function of the composition for several substituents. ○, Ln = Y; □, Ln = Gd; △, Ln = Dy; ▽, Ln = Er.

**Fig. 10.** The log $\sigma_0$ of the conductivity for the low temperature region (<320 K) and for the high temperature region (>900 K) as a function of the composition for several substituents. ○, Ln = Y; □, Ln = Gd; △, Ln = Dy; ▽, Ln = Er.

m/o Dy$_2$O$_3$ the ionic transference number is one over the whole temperature range investigated, whereas for the sample containing 50.0 m/o Dy$_2$O$_3$ an electronic component is introduced at low temperatures. The conductivity of the most desirable composition in this system, i.e., (Bi$_2$O$_5$)$_{0.75}$(Dy$_2$O$_3$)$_{0.25}$, is about three times lower than the conductivity of the best oxygen ion conductor reported for Bi$_2$O$_5$-based solid solutions.

It is concluded that the lowest percentage of lanthanide necessary to stabilize the fcc phase is found for Er$_2$O$_3$ or Tm$_2$O$_3$. 
Diffusion-Limited Charge Transport at Platinum Electrodes on Doped CeO$_2$

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ABSTRACT

We have measured the d-c and a-c properties of platinum paste electrodes on samples of the solid electrolyte (CeO$_2$)$_{0.9}$(Gd$_2$O$_3$)$_{0.1}$ in the temperature range 700°-900°C and the oxygen pressure range 1 ~ P$_{O_2}$ ~ 10$^{-4}$ atm. The d-c measurements showed that the current through the system saturated at a value proportional to the oxygen pressure and that the cathode (the electrode where oxygen enters) limits the current. We explain the limitation by a gas diffusion mechanism, which adds a small term to the dynamic resistance of the sample. The dynamic resistance is mainly determined by the resistivity of the electrolyte together with the current constriction at the triple line gas-electrolyte-electrode. A-C measurements gave impedance plots with the shape of a quarter circle, pointing to a diffusion process. We propose as model that part of the oxygen molecules arriving at the triple line is ionized directly and enters the electrolyte, and a second part diffuses as atoms along the interface electrolyte-electrode before being ionized. This model explains the observed quarter circle as well as the impedances measured for $\omega = 0$ and for $\omega = \infty$.

It is well known that electrode impedance plays an important role in the overall impedance of high temperature fuel cells. A large number of papers treat the subject phenomenologically but only a few try to understand the subject in microscopic detail. Some authors measured d-c properties and proposed a detailed model (1-3), other measured also a-c properties but did not analyze the results microscopically (4-7).

In the present paper we report on d-c and a-c properties of platinum electrodes on gadolinia-doped ceria, combined with scanning electron microscope studies of these electrodes. We then present a detailed model for the processes involved.

Very recently two papers by Wang and Nowick (8, 9) reported on a-c and d-c measurements on the same system. We believe that the differences between the results of their work and ours is due to the structure of the electrodes and we shall come back to this in the discussion.

Sample and Electrode Preparation

The starting material for the electrolyte was prepared by coprecipitation of oxalates of cerium and gadolinium and calcination at 1000°C to obtain (CeO$_2$)$_{0.9}$(Gd$_2$O$_3$)$_{0.1}$. The powder was then pressed at 2000 bar ($2 \times 10^3$ N/m$^2$) and sintered at 1700°C for 3 hr.

The shape after sintering was a round cylinder 40 mm long and 11 mm across. Pellet-shaped samples about 1 mm thick were cut with a diamond saw from this cylinder. Some additional samples were prepared directly as pellets and sintered under similar conditions. Platinum electrodes were prepared by spreading a thin layer of platinum paste (Engelhard 6082), heating to 900°C at 100°C/hr, and cooling to room temperature in 1 hr. Scanning electron microscope (SEM) pictures confirm that the heating rate is crucial for the electrode resistance: if the rate is too fast (less than a few hours to 900°C) the platinum tends to form separate islands. This was found to increase the impedance of the sample. Figure 1 shows an SEM picture of a Pt-paste electrode heated slowly; it is seen that the platinum grains are connected and do not form separate islands.

The platinum covered surface $S_{Pt}$ equals about 70% of the visual gross electrode area $S_E$, which is 0.64 cm$^2$. The cross section of the sample, $S_o$, is 1.13 cm$^2$. The typical width of the interconnected platinum islands in Fig. 1 is 2 $\mu$m.

We observed also that the surface condition of the sample influences strongly the two-point resistance of the sample. For electrodes prepared on the surface of sintered pellets (the SEM picture of such a surface is shown in Fig. 2) the two-point resistance was a few hundred ohms at 800°C, much higher than the 2.2$\Omega$ calculated from the bulk conductivity with the assumption of ideal electrodes (see below). If the surface of the sample was roughened with sandpaper, the...