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TRANSPORT PROPERTIES OF Bi$_6$Mo$_2$O$_{15}$

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The Seebeck coefficient $\alpha$ and the conductivity of $O^{2-}$ conducting Bi$_6$Mo$_2$O$_{15}$ has been measured as function of temperature and oxygen pressure. The heat of transport $u$ is much smaller than the activation energy for $O^{2-}$ conduction. A model is presented which accounts for results of the electrical conductivity and thermopower measurements.

The material shows a phase transformation at high temperature and is instable with respect to evaporation of MoO$_3$.

1. INTRODUCTION

The system bismuth oxide-molybdenum oxide has attracted much attention. One reason for this attention is the high catalytic activity for the partial oxidation of olefins found in some of these compounds. In this oxidation reaction oxygen transfer in the bismuth molybdate plays an important role.

The second reason for the interest in bismuth molybdates is related to the very high ionic conductivity of bismuth oxide. Such a high conductivity might be useful for applications in oxygen sensors, fuel cells and such. Some work has been performed for instance on MoO$_3$ doped Bi$_2$O$_3$.

However, a number of aspects have been ignored or insufficiently investigated in previous studies. Therefore we have undertaken a study of the defect chemistry in the Bi$_2$O$_3$-MoO$_3$ system. In this paper we report on the electrical transport properties of the compound Bi$_6$Mo$_2$O$_{15}$. Earlier work has shown this compound to be a pure oxygen ion conductor in the temperature range 500-800°C. No attention was paid so far to the polymorphism or to the influence of the evaporation of volatile MoO$_3$ at elevated temperatures.

2. EXPERIMENTAL

2.1. Preparation of the samples

Bismuth nitrate (Merck P.A. (1860)) was decomposed into bismuth oxide, and ammonium heptamolybdate (Reidel P.A. (31402)) was decomposed into molybdenum oxide. Bi$_6$Mo$_2$O$_{15}$ was obtained by a solid state reaction from Bi$_2$O$_3$ and MoO$_3$. By sintering at 800°C disk-shaped samples were produced with 80-90% of the theoretical density. After polishing, the surfaces were painted with platinum (Leitplatin 308A Demetron) or sputtered with gold. Firing of the electrodes was performed at the highest measuring temperature. Samples for transport-number measurement were also made by hot pressing and had densities up to 95% of the theoretical density.

2.2. Measurements of the electrical conductivity and thermopower.

The samples were spring-loaded in an alumina conductivity cell. 2-Probe AC-conductivity measurements were performed with a Solartron 1174 frequency response analyser in the frequency range 1MHz-1kHz. The signal applied across the sample was usually less than 100mV rms. For DC-measurements a Keithley 610 C solid state electrometer (input impedance 10$^{14}$ Ohm) was used. Seebeck-measurements were performed in an alumina cell with two platinum-wired resistance...
heating elements at both electrodes, which made it possible to keep the average temperature constant within one degree. At low temperatures the measurement range was limited by the increased pick-up of electrical noise from the heating elements and the furnace or by the irreversibility of the electrodes towards gas exchange. The temperature gradient across the sample was kept below 10°C. Measurements of the transport number were performed in a special quartz cell, in which two different oxygen pressures could be controlled separately at two sides of the sample. Details of the cell were published elsewhere. The oxygen pressure was measured using a calcia stabilized zirconia cell, operating at 625°C. Measurements were performed in the temperature range 400-850°C, with different O\textsubscript{2}-N\textsubscript{2}, Ar(1%O\textsubscript{2})-N\textsubscript{2} and N\textsubscript{2}-Ar(1%O\textsubscript{2}) mixtures in the oxygen partial pressure range 10ppm-1 atm O\textsubscript{2}. A Brooks instrument (4250) gas mixing system was used for the control of the oxygen partial pressure and the gases were supplied at a rate of 200 cm\textsuperscript{3}/min. The compositions of the samples after conductivity measurements at high temperatures were measured by means of EPMA with the use of well-characterised standards of Bi\textsubscript{2}MoO\textsubscript{4}. Concentrations of Bi and Mo were determined by measuring the intensities of L and M lines for Mo and Bi and the oxygen content in the material was analysed by difference. The accuracy of measurement was estimated at ± 3% in the bismuth: molybdenum metal ratio, caused by the fact that the best accuracy of the metal concentration was 0.5%.

3. EXPERIMENTAL RESULTS

3.1. X-ray diffraction results

The XRD patterns of the samples were in agreement with literature data\textsuperscript{9} presented for Bi\textsubscript{6}Mo\textsubscript{2}O\textsubscript{15}. However, we calculated from data, given by Miyazawa for the quantitative analysis of the grown crystals, that the actual composition was (2.64 ± 0.14)Bi\textsubscript{2}O\textsubscript{3},2MoO\textsubscript{3} instead of Bi\textsubscript{6}Mo\textsubscript{2}O\textsubscript{15}. According to Egashira\textsuperscript{4}, the compound Bi\textsubscript{6}Mo\textsubscript{2}O\textsubscript{15} has two modifications i.e. a low temperature form Bi\textsubscript{6}Mo\textsubscript{2}O\textsubscript{15} (L.T.) and a high temperature form Bi\textsubscript{6}Mo\textsubscript{2}O\textsubscript{15} (H.T.). Our data are in agreement with their Bi\textsubscript{6}Mo\textsubscript{2}O\textsubscript{15} (H.T.) modification and we calculated cell parameters for this monoclinic compound: \(a = 24.705\) \(\text{Å}\), \(b = 5.8037\) \(\text{Å}\), \(c = 23.5023\) \(\text{Å}\) and \(\beta = 103.05^\circ\). The calculated density was 7.67 g/cm\textsuperscript{3}. We also analysed our Bi\textsubscript{6}Mo\textsubscript{2}O\textsubscript{15} compound with EPMA and found that the composition was (3.0 ± 0.1) Bi\textsubscript{2}O\textsubscript{3},2MoO\textsubscript{3}, in agreement with the starting material which contained 60.0 ± 0.1 mol%Bi\textsubscript{2}O\textsubscript{3} and 40.0 ± 0.1 MoO\textsubscript{3}. According to Kohlmueller and Badaud\textsuperscript{2} there exists a solid solution of xBi\textsubscript{2}O\textsubscript{3},2MoO\textsubscript{3} with 2.44≤x≤3.26, in agreement with Erman\textsuperscript{1}, who found a solid solution with 2.6≤x≤3.0 which he called the c-phase. So it might be concluded that the material, made by Miyazawa\textsuperscript{9}, has a composition corresponding to the solid solubility limit of the c-phase on the MoO\textsubscript{3} rich side.


The ionic transport number \(t_i\) was measured in the temperature range 480°C-800°C for a sample with a density of 6.68 g/cm\textsuperscript{3} under an oxygen pressure \(P(\text{O}_2) = 10^{-2}\) atm at one side and \(P(\text{O}_2) = 1\) atm at the other side. The transport number \(t_i = 1.00 ± 0.02\) over the whole temperature range. The same experiments with a sample with a density of 6.06 g/cm\textsuperscript{3} under an oxygen pressure of 0.21 atm at one side and 1.0 atm at the other side showed \(t_i = 0.96 ± 0.02\). The difference is probably caused by leakage through the sample due to a high degree of open porosity in the less dense sample (total porosity 21%). From these measurements it was concluded that this material is an oxygen ionic conductor over the whole temperature range, at least at
higher oxygen pressure, in agreement with Taka- hashi. Measurements at temperatures lower than 480°C showed that it took a long time (> 15 min.) before the E.M.F. became constant. It was also noticed that under these conditions spurious voltages under the same oxygen pressures at both sides of the samples were measured, which could not be attributed to temperature gradients over the sample. This was attributed to the fact that an equilibrium situation was attained very slowly below 480°C. The kinetics of the oxygen gas exchange reaction at the solid-electrolyte surface are very slow in this region.

3.3. Conductivity Measurements.

For the determination of the conductivity, frequency dependent measurements of the resistance of the sample were performed at different temperatures and oxygen pressures. A typical example of the complex impedance diagram is given in Fig. 1. Both the shape of these diagrams and the impedance values change with oxygen partial pressure and temperature.

Measurements as function of P(O2) showed that the high frequency intercept did not show any pressure dependence. From this fact, in combination with the measured value of the transport number, it was concluded that this point represented the bulk ionic resistance of the sample and that the low frequency part of the diagram is associated with electrode effects. To explain this, we have analysed the impedance plots, assuming an equivalent circuit which could describe the physicochemical processes occurring in the solid and at the electrodes. The best fit was obtained for the equivalent circuit shown in fig. 2, which consists of two parallel RQ branches connected in series with the bulk ionic resistance R. In this circuit, the Q element represents the constant phase angle (CPA) element which has an impedance $Z_{\text{CPA}} = Q(j\omega)^{-\alpha}$ with $0 < \alpha < 1$. The two RQ-branches are associated with gas-solid exchange reactions at anode and cathode. The anode and cathode resistances are both thermally activated, whereas the values Q and $\alpha$ hardly change with temperature and appear to be the same for anode and cathode. The total conductivity of the sample was calculated from the impedance plots and is due to electrode resistance effects and bulk

FIG. 1: Impedance plots for BigMo2015 at different temperatures.

FIG. 2: Electrical circuit which gives the best results for experimental data of Fig. 1. $Q_1$ and $Q_2$ are constant phase angle elements. $R_1$ = bulk resistance, $R_2$ = electrode resistances.
FIG. 3: DC-conductivity of Bi$_6$Mo$_2$O$_{15}$ at 798°C (o), 686°C (△), 594°C (+) and 523°C (d) as function of the oxygen partial pressure.

resistance effects. It can be seen from figs. 1 and 3 that electrode effects strongly decrease with temperature and increasing oxygen partial pressure. In fig. 4 we plotted the oxygen ionic conductivity, represented by the AC conductivity and the total conductivity, represented by the DC conductivity as a function of the reciprocal temperature for several heating and cooling cycles. The ionic conductivity has a rather low activation energy of $E_{AC} = 0.55 \pm 0.05$ eV, and the total conductivity has an activation energy of $E_t = 2.1 \pm 0.1$ eV in the low temperature region ($T < 700^\circ$C), where it is mainly determined by electrode effects. Above 700°C the DC conductivity becomes equal to the AC conductivity because the electrode blocking effects can be neglected compared to the ionic conductivity. The behaviour of the DC-conductivity is probably caused by adsorption and diffusion on the solid electrolyte and is not connected with the adsorption and diffusion on the electrode material for several reasons: First, if the same measurements with the same type of electrode material on bismuth molybdates with different compositions e.g. Bi$_2$Mo$_3$O$_{12}$, Bi$_2$Mo$_2$O$_9$ and Bi$_2$MoO$_6$ are performed these effects are not observed and the activation energy of the DC-conductivity has a much smaller value. Second, the use of Pt or Au-electrodes shows that the DC behaviour, except minor variations, is basically the same. Third, for Bi$_2$O$_3$-based materials, doped with Er$_2$O$_3$ the
behaviour of the electrode resistance also was
governed by adsorption and diffusion on the
solid electrolyte.

Another phenomenon observed is, that where
the ionic conductivity is virtually independent
of the oxygen pressure the DC-conductivity is
not. This is shown in fig. 3 for Pt-electrodes.
The DC-conductivity increases very much with de-
creasing oxygen pressure, indicating that the
cathodic reaction is rate-limiting under low-
oxen pressure conditions.

3.4. Thermopower-experimental

The Seebeckcoefficient \( \alpha \) of Bi\(_6\)Mo\(_2\)O\(_{15}\) was
measured in the temperature range 430-820\(^\circ\)C
for three different oxygen pressures. The re-
sults are shown in fig. 5 , for \( P(0_2) =
10^{-5}, 10^{-2} \) and 1 atm. It can be seen that the
experimental data are almost independent of the
temperature, except the data at the lowest

4. THEORY OF THERMOPower MEASUREMENTS

The thermopower \( \alpha \) is defined as

\[
\alpha = \frac{1}{\Delta T} \left[ \frac{E(T,T+\Delta T)}{\Delta T} \right]
\]

for a thermocell

\[
P(0_2), \text{Pt}\|\text{Bi}_2\text{O}_3\|\text{Pt,Pb}_2.
\]

In this definition the
sign of the dominant charge carrier is given

\[
\text{Pb}_2\text{O}_2, \text{Pt}\|\text{Bi}_2\text{O}_3\|\text{Pt,Pb}_2.
\]

\[
\text{Pb}_2\text{O}_2, \text{Pt}\|\text{Bi}_2\text{O}_3\|\text{Pt,Pb}_2.
\]
by the sign of $\alpha$. If we assume that $\tau_\infty = 1$
i.e. no chemical diffusion, the temperature gradient over the sample will cause a potential
difference, given by

$$a(T) = F^{-1} \left( -\frac{1}{\tau_\infty} \tilde{s}_{02^-} + \tilde{s}_{e,pt} + \frac{1}{\tau} \tilde{s}_{O_2} \right)$$  \hspace{1cm} (1)

Here, $F$ is the Faraday constant, $\tilde{s}_{02^-}$ the
transported entropy of oxygen ions, $\tilde{s}_{e,pt}$ the
transported entropy of electrons in the platinum
leads and electrodes and $\tilde{s}_{O_2}$ the partial
entropy of oxygen molecules. We have $\tilde{s}_{02^-} =
\tilde{s}_{02^-}^0 - R \ln \rho_{O_2}$ and $\tilde{s}_{O_2} = \tilde{s}_{02^-} + \tilde{s}_{O_2^-} / T$ where
$\tilde{s}_{02^-}^0$ is the standard entropy of oxygen gas,
$\tilde{s}_{O_2^-}$ is the heat of transport. By combining
these expressions we find

$$a(T) = F^{-1} \left( -\frac{1}{\tau} \tilde{s}_{02^-} - \frac{1}{\tau} \tilde{s}_{O_2^-} / T + \frac{1}{\tau} \tilde{s}_{e,pt} + i \frac{1}{\tau} \tilde{s}_{O_2^-} -
\frac{i}{\tau} R \ln \rho_{O_2} \right)$$  \hspace{1cm} (2)

which may be written as $a(T) = a^0(T) - 49.6$
$10^{-6} \log p_{O_2}$ (Volts). As $\tilde{s}_{O_2^-}$-values cannot
be found directly, they have to be estimated
from the entropy of the oxides itself. The en-
tropy of the mixed oxide is assumed to be about
that of a simple mixture of 60 m/o Bi$_2$O$_3$ and
40 m/o MoO$_3$ according to a method first de-
scribed by Fischer:

$$\tilde{s}_{02^-} \text{ (mixed oxide)} = (1-x)\tilde{s}_{02^-} \text{ (Bi$_2$O$_3$)} +
x \tilde{s}_{02^-} \text{ (MoO$_3$)}$$  \hspace{1cm} (3)

We calculated the transported entropy of oxygen
ions for the binary oxides according to a pro-
cedure described by Pitzer, taking into ac-
count the ratio of cationic and anionic masses

$$\tilde{s}_{02^-} \text{ (Bi$_2$O$_3$)} = \frac{1}{5} S^0 \text{ (Bi$_2$O$_3$)} - \frac{3}{5} R \ln (m_{Bi}^{+} / m_{O_2^-})$$  \hspace{1cm} (4)

$$\tilde{s}_{02^-} \text{ (MoO$_3$)} = \frac{1}{8} S^0 \text{ (MoO$_3$)} - \frac{3}{8} R \ln (m_{Mo}^{+} / m_{O_2^-})$$  \hspace{1cm} (5)

Numerical values of $S^0 \text{ (a-Bi$_2$O$_3$)}$, $S^0 \text{ (MoO$_3$)}$, and
$S^0 \text{ (O$_2$)}$ can be found in tabulations and numerical
values of $\tilde{s}_{e,pt}$ were found in the work
of Moore and Graves. A small problem arises
in choosing the polymorph of Bi$_2$O$_3$ as basis for
our compound. According to Takahashi the
structure of Bi$_6$Mo$_2$O$_{15}$ is derived from $\beta$-Bi$_2$O$_3$.
Therefore, the transition entropy for the $\alpha \rightarrow \beta$
transition was calculated from literature
data, and the same value was adopted for the
virtual transition to a $\gamma$-phase structure from
the monoclinic $\alpha$-phase structure.

Under the assumption that the temperature
dependence of the partial entropy term of
oxygen ions, and the standard entropy term of
oxygen gas cancel each other, a plot of the
Seebeck coefficient vs reciprocal temperature,
will allow an estimation of the heat of trans-
port, especially when experimental data are
compared with calculated data. The validity of
equation (2) can be checked separately by plot-
ing the Seebeck coefficient vs log $p_{O_2}$.

In fig. 7 we plotted the calculated values,
based on equation (2) with experimental data,
using tabulated values for $\alpha$-Bi$_2$O$_3$. If correc-
tions for the $\alpha \rightarrow \beta$ or $\alpha \rightarrow \gamma$ transitions are made,
the experimental and calculated data shift
7.5 $\mu$/K more towards each other. For the $\alpha \rightarrow \beta$
transition this correction would be about 32
$\mu$/K. From this calculation the heat of

$\text{FIG. 7:}$ The experimental and calculated Seebeck
coefficient without the heat of transport term
$Q / 2T$, which is plotted as the difference of
experimental and calculated data.
transport was estimated to have a very small value of \( Q = 0.05 \pm 0.05 \text{ eV} \) i.e. a value similar to other oxygen ionic conductors as given in table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>( Q(\text{eV}) )</th>
<th>( E_a(\text{eV}) )</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta-\text{Bi}_2\text{O}_3 )</td>
<td>0.13-0.19</td>
<td>0.3</td>
<td>16</td>
</tr>
<tr>
<td>((\text{Bi}_2\text{O}<em>3)</em>{1-x}(\text{RE}_2\text{O}_3)_x )</td>
<td>0.18</td>
<td>1.15</td>
<td>16</td>
</tr>
<tr>
<td>((\text{ZrO}<em>2)</em>{0.88}(\text{CaO})_{0.12} )</td>
<td>&lt;0.01</td>
<td>0.8</td>
<td>11</td>
</tr>
<tr>
<td>((\text{ZrO}<em>2)</em>{0.91}(\text{Y}_2\text{O}<em>3)</em>{0.09} )</td>
<td>&lt;0.055</td>
<td>1.5</td>
<td>11</td>
</tr>
<tr>
<td>( \text{Bi}_6\text{Mo}<em>2\text{O}</em>{15} )</td>
<td>0.05±0.05</td>
<td>0.55</td>
<td>this work</td>
</tr>
</tbody>
</table>

4.1. Combination of conduction and thermopower

There are two main models to describe the movement of ions in a solid conductor under a thermal gradient.

In the "free ion model" the existence of an energy gap in the ionic density of states is postulated\(^{18}\). Conduction occurs via the excitation of ions from localized states to a "continuous" state above the energy gap \( E_g(T) \). The value of \( E_g \) can be obtained from measurements of the temperature dependence of the ionic conductivity

\[
E_a = \frac{\Delta\text{ln} \sigma}{\Delta(T/K)} = E_g.
\]

This theory implies that the heat of transport \( Q = E_g \) if \( E_g \gg kT \) and it is obvious that this model is not capable in explaining the results. The second model to explain the difference in \( Q \) and \( E_a \), is based on the extended lattice theory of Girvin\(^{19}\). In this model we assume a potential well of depth \( W + \lambda \chi \), consisting of several vibrational states. \( W \) describes a static barrier height, determined by the positions of the cage ions and \( \lambda \chi \) describes a barrier term due to displacements in the positions of cage ions when they are vibrating. The low vibrational states are strongly localized, and hopping of an ion from one well to another can only occur after excitation to a high vibrational state, that can couple with phonons in the background lattice. This polaron coupling can be described with a dynamical barrier height, which is equal to half the polaron binding energy \( E_b/2 \). Neglecting correlations, one finds that the static and dynamic barriers simply add in their effect on the conductivity so that the activation energy is given by \( E_a = W + E_b/2 + \lambda \chi \). As the dynamic barrier does not contribute to the heat of transport, this results in a heat of transport \( Q = W + \lambda \chi \) for sufficiently high temperatures. With this model, we calculated a heat of transport of 0.05 eV \( \pm 0.05 \) eV and a high value of the polaron binding energy of 1.0 \( \pm 0.1 \) eV (\( E_a \approx 0.55 \) eV) for \( \text{Bi}_6\text{Mo}_2\text{O}_{15} \). This is a much higher value than the value for \( \delta-\text{Bi}_2\text{O}_3 \) (\( W \approx 2kT = E_b \)). Anion-cation coupling plays only a modest role in \( \delta-\text{Bi}_2\text{O}_3 \), probably caused by the high polarizability of the \( \text{Bi}^{3+} \)-ion, which has a 6s\(^2\) lone pair. In \( \text{Bi}_6\text{Mo}_2\text{O}_{15} \) part of \( \text{Bi}^{3+} \)-ions is replaced by \( \text{Mo}^{6+} \)-ions as compared to \( \delta-\text{Bi}_2\text{O}_3 \). The \( \text{Mo}^{6+} \)-ion has a closed shell structure and a much lower polarizability, then the \( \text{Bi}^{3+} \)-ion. This leads apparently to a much stronger anion-cation coupling, resulting in a high value of the polaron binding energy.

The same discrepancy between heat of transport and activation energy was observed for CSZ and YSZ\(^{11}\). Apparently polaron coupling is even stronger in these materials as they have higher activation energies. This is due to the less polarizable metal sublattice.

4.2. Stability of \( \text{Bi}_6\text{Mo}_2\text{O}_{15} \)

Finally we investigated the stability of this material. As shown in fig. 8, there is a hysteresis effect in the conductivity of this material in the 700-800\(^\circ\)C region. Above 800\(^\circ\)C, the activation energy of the conductivity is somewhat
The A.C. conductivity as function of the reciprocal temperature. The material shows hysteresis upon heating (●) and cooling (●) cycles. The arrows show the temperature region in which the slow phase transition takes place.

lower (0.36 eV) than the activation energy in the low temperature regions (0.60 eV). However, the ionic transport number remains unity and this effect was not reflected in a different Seebeck coefficient. We attribute this to a slow reversible transition to a high temperature phase based on $\delta$-Bi$_2$O$_3$, for two reasons. Firstly, the activation energy of 0.36 eV is very close to the value of 0.3 eV found for $\delta$-Bi$_2$O$_3$. Secondly, the high temperature diffraction pattern found in quenching experiments at 800-900°C is different from the low temperature diffraction pattern. Similar behaviour was found for Bi$_2$O$_3$ doped with different oxides and pure Bi$_2$O$_3$.

Additionally, a second effect was noticed during conductivity experiments, which were performed upon heating and cooling cycles over the period of a month. As shown in fig. 4, there is a continuous decrease of the conductivity with time for several heating and cooling cycles. After a month, the sample showed a weight decrease of about 5%. We therefore analysed the sample afterwards using EPMA and found that it contained two phases with compositions (3.0 ± 0.1)Bi$_2$O$_3$, 2MoO$_3$ and (5.0 ± 0.2)Bi$_2$O$_3$,2MoO$_3$. From these findings it can be concluded that the material is instable with respect to decomposition. This is caused by the evaporation of the highly volatile MoO$_3$: 5Bi$_6$Mo$_2$O$_{15}$ (s) → 3Bi$_{10}$Mo$_2$O$_{21}$ (s) + 4MoO$_3$ (g). The composition Bi$_{10}$Mo$_2$O$_{21}$ is very close to the solid solution limit of Takahashi's tetragonal phase and in agreement with his observations that a two phase mixture between Bi$_6$Mo$_2$O$_{15}$ and Bi$_{10}$Mo$_2$O$_{21}$ was seen.

CONCLUSIONS

- There are two modifications of Bi$_6$Mo$_2$O$_{15}$: a low temperature, and a high temperature form. Both are pure oxygen ionic conductors, but the conductivity of the low temperature form has a higher activation energy then the conductivity of the high temperature form. The transformation between both forms occurs in temperature region 700-800°C and is very slow, but reversible.
- At low temperatures, electrode effects become dominating - more pronounced at low oxygen pressures - and equilibrium is attained very slowly.
- The estimated heat of transport is very low as in other oxygen ion conductors like $\delta$-Bi$_2$O$_3$, CSZ and YSZ.
- The ionic polaron binding energy is about 1.0 eV.
- The material is not stable over a long period, due to evaporation of MoO$_3$. Therefore, application in high temperature devices does not seem appropriate for this material.

REFERENCES