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Phase transitions and electrical properties of Bi_2O_3 up to 2.5 GPa

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ABSTRACT

The effect of pressure between 0.5 and 2.5 GPa on the phase transitions and electrical conductivity of Bi_2O_3 has been studied by the use of electrical impedance spectroscopy. By analyzing the Arrhenius plots gained from the electrical conductivity measurements in the temperature range of the α–δ phase transition, the pressure dependence of the critical temperature (T_c) and activation energy were determined.

The measurements demonstrated that the pressure effect between 0.5 and 2.5 GPa has a significant effect on the α–δ phase transition temperature in Bi_2O_3, and the increase of T_c for the α–δ phase transformation is more than 60 °C compared to previous research with DTA [E.M. Levin, R.S. Roth, Polymorphism of Bismuth Sesquioxide. I. Pure Bi_2O_3, Journal of Research of the National Bureau of Standards – A. Physics and Chemistry 68A (2) (1964) 189–195]. The activation energies of electric conductivity in α–δ phases seem not to be affected by raising the pressure.

During cooling, the δ–α transformation occurred approximately at the temperature corresponding to T_c monitored during the heating cycle. Neither a δ–β, a δ–γ phase transformation nor a hysteresis effect has been found under pressure, which is in contrast with normal pressure studies that used DTA, electrical conductivity measurements and XRD [E.M. Levin, R.S. Roth, Polymorphism of Bismuth Sesquioxide. I. Pure Bi_2O_3, Journal of Research of the National Bureau of Standards – A. Physics and Chemistry 68A (2) (1964) 189–195; H.A. Harwig, A.G. Gerards, Electrical Properties of the α-, β-, γ- and δ-Phases of Bismuth Sesquioxide, Journal of Solid State Chemistry 26 (1978) 265–274].

0. Introduction

Previous studies of phase transitions in bismuth oxide have shown that Bi_2O_3 exists as a stable monoclinic (space group $P2_1/c$) α-phase under normal pressure at room temperature up to c. 730 °C [1,2]. During further heating this monoclinic phase inverses into a fast ion conductive fcc δ-phase with the transformational volume increase 7%. This cubic phase is stable up to the melting point at c. 825 °C. The δ-phase belongs to a defect CaF_2-type structure (space group $Fm\bar{3}m$) and has an about 25% oxygen-defective lattice [3–5]. On cooling, the δ-phase transforms into a tetragonal β-phase (space group $P\bar{4}2_1c$) or a γ-phase (sillenite type structure) between 630 and 650 °C depending on experimental conditions. At about 550 °C a reverse transformation to α-phase occurs. If the sample is not heated to higher than 748 °C, it transforms from δ-phase to α-phase directly at about 700 °C [1].

The purpose of this study is to investigate the effect of high pressure on the electrical properties and the phase transition temperatures T_c of Bi_2O_3. A special aspect to be covered by these experiments is to check if it is possible to keep the fast oxygen ion conductive high-temperature δ-phase at room temperature by applying a hydrostatic pressure.

1. Description of experiments

1.1. Bi_2O_3 samples

The Bi_2O_3 powder on metal basis was obtained from Alfa Aesar with purity 99.9995% and grain size powder −20 mesh. Before experiments the powder was stored dry in an exicator. Prior to an experimental run samples were kept in a drier for several hours. Then, powder samples sintered in the piston-cylinder press at temperatures not higher than 500 °C and desired pressure 0.5–2.5 GPa over 48 h.

The samples of Bi_2O_3 sintered in the piston were located in a coaxial capacitor with calibrated geometric factor, and were examined with low-frequency impedance spectroscopy. The press calibration and the electrical conductivity cell are described elsewhere [6]. The impedance spectroscopy measurements consisted of measurements of the real and imaginary impedance of samples at varying pressures and temperatures. By analyzing Arrhenius plots of the temperature dependence of the impedance data, T_c and activation energies of electrical conductivity can be determined. This analysis has been done for fixed pressures of 0.5, 1, 1.5, 2 and 2.5 GPa, each with manually controlled temperature.

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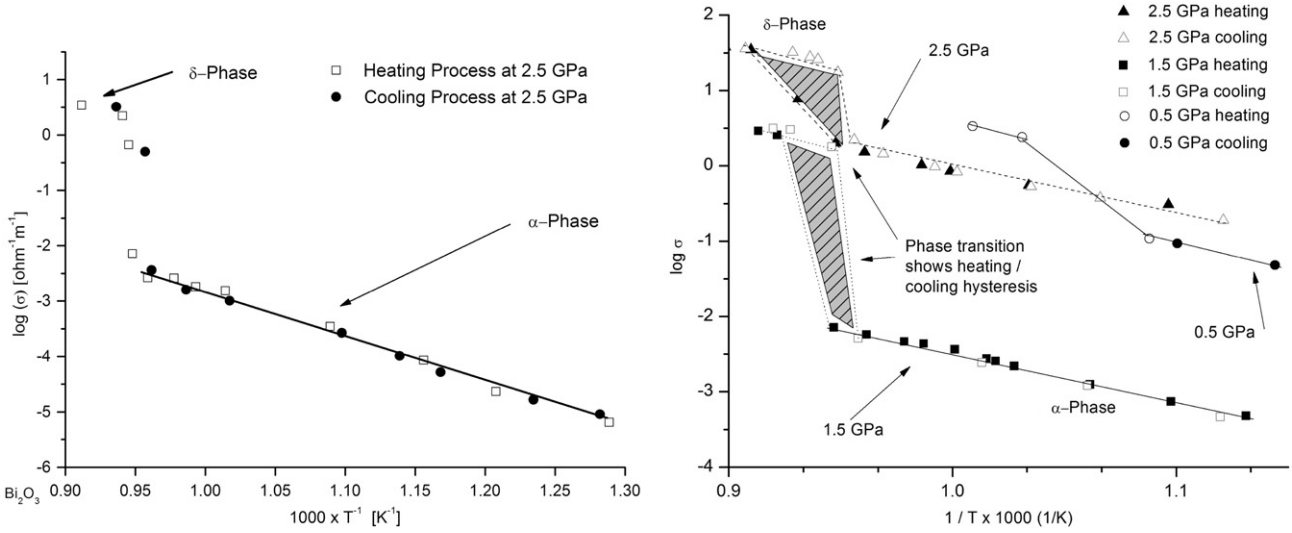

Fig. 1. (Left panel) Plot of electric conductivity measurements in Bi_2O_3 at 2.5 GPa. At the α–δ phase transition a sudden rise in conductivity occurs. Only two phases can be determined by impedance spectroscopy under high pressures. (Right panel) Between heating and cooling processes nearly no hysteresis of the phase transition is observed.

1.2. Piston-cylinder

The apparatus used is a conventional piston-cylinder press produced by Danfoss™, Denmark. The high-pressure cell consisted of a CaF_2 pressure transmitting sleeve, graphite heater, MgO insulating sleeve, outer electrode of 4.0 × 3.9 mm Pt tube, inner electrode of 2.1–2.0 mm Pt tube, and 1.9 mm Al_2O_3 thermocouple capillary. For each sample a geometric factor of the cylindrical capacitor was calculated with the formula

$$G = 2\pi \frac{L}{\ln\left(\frac{D}{d}\right)},$$

where L stands for the length of the coaxial cylinder, D is the outer electrode diameter and d is the inner electrode diameter. Values of G in experimental setups varied between 6 and 7.2 cm. The pressure was set to 0.5 to 2.5 GPa in 0.5 GPa steps. A servo-motor provided a constant pressure (±0.05 MPa) and the gauge monitored the position of the compressing piston inside the high-pressure autoclave.

The highest temperature to which the sample was heated during most of the experimental runs was c. 810 °C for 0.5 GPa and up to 912 °C for 2.5 GPa. The heating cycle followed a slow cooling up to room temperature. The radial temperature gradient was estimated in independent experiments to be about within 1°/mm, and the vertical temperature gradient 2°/mm.

1.3. Impedance spectroscopy

The electric impedance was measured with a 0.5–2 V sine signal of a Solartron® 1260 phase gain analyzer. The AC short connection of the experimental setup was 0.4 Ω. To reduce the external electrical noise such as from the servo-motor driving the piston, the automatic control of pressure was switched off during electrical measurements. The impedance spectra were collected in the frequency range 0.1 Hz–100 kHz during heating and cooling cycles of Bi_2O_3 samples with a temperature step 5°–10° and at fixed pressure.

2. Results

The low-frequency impedance was measured and analyzed using Argand plots. To calculate the bulk AC resistance of samples the standard fitting procedure of the measured data to a two-term Cole–Cole function has been used [6]. From the bulk resistance data the bulk electrical conductivity has been calculated. The results of the bulk electrical conductivity were plotted as $\log[\sigma \cdot T]$ vs. $1/T$ in order to determine the activation energy of electrical conductivity (see Fig. 1), where the conductivity σ [$ohm^{-1} \cdot m^{-1}$] is the reciprocal value of the measured bulk impedance multiplied by the geometric factor G of the capacitor. The Arrhenius plots of the bulk electrical conductivity demonstrate a sudden change of slope at temperature corresponding to T_c.

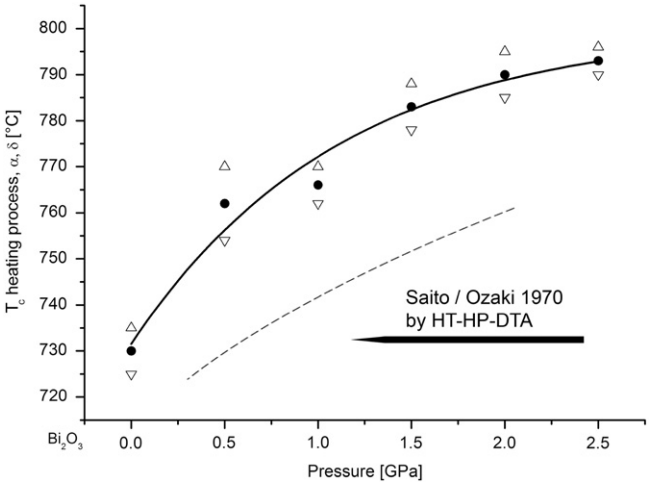

Fig. 2. The P–T_c dependence of Bi_2O_3 for the α–δ phase transition. Triangles mark the maximum error caused by the steps in which temperature was increased between each conductivity measurement. The value which is indicated for normal pressure is from [3–5]. The fitting curve is sigmoidal type, $y = A_2 + (A_1 - A_2)/(1 + \exp((x - x_0)/dx))$ with $A_1 = -933.95$, $A_2 = 799.84$, $x_0 = -3.4425$ and $dx = 1.077$.R^2 is 0.973. For comparison the DTA determinations of T_c from [9] are shown.

Results of the activation energy and T_c determinations are listed in Table 1. The diagram for the temperature dependence of the electric conductivity is shown in Fig. 1. The pressure dependence of T_c is shown in Fig. 2.

The experiments show a significant increase of T_c of the phase transition α-Bi_2O_3 to δ-Bi_2O_3 under pressure compared to T_c determined for normal pressure [1,2,7]. While under normal pressure a large hysteresis in the phase transition temperature occurs between the heating–cooling cycles, this can hardly be seen during the high-pressure experiments.

Table 1
Summary of experimental results

P, GPa	T_c, °C, α, δ	T_c, °C, δ, α	$W_{A,}$ eV, α	$W_{A,}$ eV, δ
0/normal pressure	730 ± 5 [1]	700 [1]	1.4 [4]	
0.5	762 ± 8		1.6 ± 0.1	
1.0	766 ± 4	767 ± 10	1.4 ± 0.1	
1.5	783 ± 5	780 ± 5	1.4 ± 0.1	0.35 ± 0.1
2.0	790 ± 5	790 ± 10	1.3 ± 0.1	
2.5	793 ± 3	795 ± 5	1.4 ± 0.1	0.3 ± 0.1

The phase transition temperature T_c increases with increasing pressure. The pressure dependence of the activation energy of electrical conductivity seems not to be significant within the given range of pressures.

At T_c the electrical resistivity of the sample decreased greatly during the heating cycle and increased again at that point during the cooling process. The previously reported values for activation energy of Bi_2O_3 measured under room pressure are rather scattered. In the given experiment the activation energy of electrical conductivity in the α-phase Wa was determined to be between 1.3 eV and 1.6 eV at all given pressures, which is similar to what has been shown by Rao et al. at normal pressure. [4] The value of 0.64 eV presented by Monnereau et al. [7] for normal pressure has been measured on the β-phase of Bi_2O_3 in the field of stability of the α-phase. The activation energy of the self-diffusion of Bi in the α-phase of Bi_2O_3 is 0.9 eV and is not affected by the presence of impurities of different size cations [8]. So, it seems reasonable to expect also a negligible change of activation energy of the electric conductivity of the α-phase in the pressure range between room pressure and 2.5 GPa.

The pressure dependence of the α–δ phase transition temperature is positive but non-linear. A certain non-linearity could also be already deducted from the results of Saito and Ozaki [9], though their results seem to give too low temperatures for the α–δ phase transition, which leads to a lower value for T_c at room pressure when their high-pressure data are extrapolated to 0.1 MPa. The results of the present study fit well to a consistent curve with T_c results found by other authors at normal pressure.

With the given method no phase transitions to the β-phase or γ-phase as observed under normal pressure conditions with DTA, XRD or conductivity measurements during the cooling process [1,2,7] could be noted in any of the high-pressure experiments. These metastable phases seem not to occur under high pressures. Bi_2O_3 samples before and after the experiment were not distinguishable by microscopic and XRD analyses. XRD analysis of the samples after high-pressure experiments has shown no traces of δ-, β-, or γ-phases.

The melting point was not reached during any of the experiments. It seems to be drastically increased as the sample at 2.5 GPa was heated to 912 °C, which is very well above the melting point of Bi_2O_3 under normal pressure, ~820 °C.

3. Conclusions

(1) High-pressure impedance spectroscopy proved to be a valid method to identify phase inversions in Bi_2O_3 and allows one to distinguish α-phase and δ-phase stability fields. β-phase and γ-phase could not be identified at high pressures; they seem not to be stable under the high pressures.
(2) Pressure increases the α–δ T_c of Bi_2O_3 significantly and non-linearly. The melting point is increased as well. The effect of pressure on the activation energy of the electrical conductivity is less than ~0.05 eV/GPa.
(3) Stabilization of δ-phase down to room temperature was not possible by the use of hydrostatic pressures.

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