Temperature dependence of $\text{Bi}_2\text{O}_3$ structural parameters close to the $\alpha$-$\delta$ phase transition

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RESEARCH ARTICLE

Temperature dependence of Bi₂O₃ structural parameters close to the α–δ phase transition

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This article presents the results of in situ X-ray powder diffraction, Raman spectroscopy, and electrical impedance spectroscopy of the α-phase of Bi₂O₃, at 0.1 MPa in the temperature range below and above the α–δ-phase transition. This work demonstrated subtle nonlinear temperature variations of the cell parameters, of the hard-mode Raman shift, and of the activation energy of electrical conductivity in the temperature range about 100–120 °C below the α–δ phase transition temperature \( T_{Tr} \approx 725^\circ C \) in Bi₂O₃. At \( T < 600^\circ C \), the linear variation of the inverse dielectric susceptibility \( (\chi^{-1}) \) correlates well with the hard mode frequency shift \( \Delta(\omega^2) \) of Raman \( A_{1g} \) mode as \( \Delta(\chi^{-1})/\Delta(\omega^2) \approx 5.5 \times 10^{-7} \, \text{cm}^2 \). A structural model describing the mechanism of \( O^2^- \) anion distribution and electric dipole disordering in the vicinity of \( T_{Tr} \) is discussed.

Keywords: Bi₂O₃; anionic conductor; Raman shift; phase transition; cell parameters

1. Introduction

Bi₂O₃ has been studied intensively over the last decade due to an ongoing search for a superionic conducting electrolyte material which can be used in a fuel cell, in which a chemical energy may be directly converted into an electrical one. In the case of Bi₂O₃, the δ-phase which is stable only at high temperatures exhibits an extraordinarily high anionic conductivity \( \sim 100 \, \text{S m}^{-1} \) [1]. This anionic conductor is recognized as a possible solidstate electrolyte for the use in high-temperature oxygen pumps and different gas sensors [1,2].

As it was shown in previous experimental works, Bi₂O₃ exists in a stable monoclinic α-phase under normal conditions up to approximately 730°C [3–5]. At high temperatures, Bi₂O₃ turns into a fast ion conductive fcc δ-phase and melts at approximately 825°C. The δ-phase possesses an oxygen-defective lattice and belongs to the defective CaF₂-type structure [6,7]. During the cooling process, the δ-phase transforms into tetragonal β- or cubic γ-phases between 630°C and 650°C depending on the experimental conditions. At about 550°C, it usually transforms back into α-phase. If the sample is not heated over 748°C, it will revert back into α-phase directly after a hysteresis at about 700°C [3].

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The high-temperature cubic modification of Bi₂O₃ represents a classic oxygen ion conductor based on the fluorite defective structure with a presumably 25% of oxygen vacancy content. The high-conductive δ-phase is stable only within 730–825°C at normal pressure, which is not favorable for the application of Bi₂O₃ as a solid electrolyte in fuel cells [1,2]. There were numerous attempts to stabilize the high-temperature conductive phase by doping the structure with various cations, for example, with rare-earth metals [1,2,8], with the combination of rare-earth cations and Re [9], or by electrodepositing this phase as a thin film on ceramic or metallic substrates [10–13]. The additional surface tension exerted in Bi₂O₃ film seems to stabilize the δ-phase at room temperature, but measurements of the electric conductivity revealed a chaotic character of the charge carrier transport in this case [14].

Most of the previous experiments were conducted under normal pressure conditions in order to explore the physical properties of Bi₂O₃, i.e., structure, phase transitions, and electrical conductivity [3–5,15,16]. Only a few high-pressure measurements were performed on Bi₂O₃, which revealed a significant pressure dependence of the α–δ phase transition temperatures \( T_{Tr} \) [17,18]. The temperature range below \( T_{Tr} \) is also very interesting. Some authors observed a metastable hexagonal A-phase, which can be synthesized at a pressure of 6 GPa and a temperature of 880°C [19]. At pressure \( P > 30 \) GPa, the α-phase experienced a pressure-induced amorphization [20].

The purpose of this study is twofold: first, to verify the temperature range of α–δ-phase transitions with \textit{in-situ} Raman spectroscopy, powder diffractometry (HT-XRD), calibrated differential thermo analysis (DTA), and impedance spectroscopy (IS). Second, to check how the behavior of Bi₂O₃ deviates from the well-known temperature dependence of spontaneous strains, Raman shift, and electrical conductivity from a typical first-order phase transition in the temperature range close to the α–δ inversion.

2. Description of experimental setups

2.1. \( \text{Bi}_2\text{O}_3 \) samples

The \( \text{Bi}_2\text{O}_3 \) powder on metal basis was obtained from Alfa Aesar\textsuperscript{®}. The indicated purity is 99.9995%, and the grain size is −20 meshes. Between experiments the powder was stored dry in a desiccator. Prior to use in experiments, the powder was kept for 24 h in an oven at 120°C.

Twenty grams of \( \text{Bi}_2\text{O}_3 \) powder was melted in a quartz crucible at 1000°C for 2 h and cooled down slowly at 1°C min\(^{-1}\) to 700°C, held for 5 h and subsequently cooled down to room temperature over 12 h. The contact zone between the quartz container and melted \( \text{Bi}_2\text{O}_3 \) showed the traces of chemical reaction. Only the central part of the crucible containing a noncontaminated sample of α-Bi₂O₃ was cut out and used in further experiments. The X-ray diffraction analysis of the melted product indicated the presence of only the α-phase of Bi₂O₃. Small crystalline pieces 1 mm × 1 mm × 1 mm of α-Bi₂O₃ were used as a starting material for Raman-shift measurements. Some of the crystalline material was ground to powder, which was used for the high-temperature X-ray diffraction, IS, and DTA experiments.

2.2. Structural analysis of \( \text{Bi}_2\text{O}_3 \) by powder diffractometry

The analysis was performed using a Siemens Kristalloflex 810 powder diffractometer with Cu-K\( \alpha \) X-ray radiation (\( \lambda = 0.154 \) nm). The apparatus and heating stage were calibrated
thoroughly during previous works, providing a thermal stability of ±2°C at the hottest spot. The Bi₂O₃ powder was fixed on the Pt sample holder with a drop of water to prevent the powder from sliding off the holder during measurements. The heating process was controlled by a stabilized heater (RE 2400, Edmund Bühler, Tübingen). The measurement data were automatically stored in a PC. A second experimental setup was performed using a Siemens D5000 powder diffractometer to confirm the first data set using a wider range of 2θ angles with a smaller angle step. The setup was θ–θ type with nickel-filtered Cu-Kα X-ray radiation (40 kV/30 mA) and a scintillation counter. A water-cooled HTK heating stage (Anton Paar, Graz) with Pt sample holder and Pt/Pt–Rh thermocouple was employed. In this setup 2θ range was 15–75° changed with 0.05° step-size. In the range of temperatures 600–730°C, the diffractograms of α-Bi₂O₃ has been taken with the temperature step ~10°C.

2.3. Polarized Raman spectroscopy in Bi₂O₃

The Raman-shift measurements were conducted using 80 mW Nd: YAG-laser with a wavelength of λ = 473 nm combined with an Acton SP-2356 spectrometer. The optical resolution of the Raman-shift measurements is 1.5 cm⁻¹. Polarization of the light source was used to eliminate the strong effect of the thermal background radiation during measurements at high temperatures. A Slutsky-type heating stage with quartz glass windows was used for Raman-shift measurements. The design of the heating stage is described elsewhere [21]. The heating element was a cylindrical loop of Pt-foil 0.2 mm in thickness. The outer diameter of the heater is 2.5 mm; the length of the cylindrical heater is 5 mm. The sample was fixed at the centre of the loop with clips made of Pt-foil with an attached S-type thermocouple. The temperature was controlled within ±1.5°C. Thermal equilibration time was less than 1 min and can be neglected in comparison with the measurement time of approximately 45 min. per spectrum. The casting of the heating stage was cooled using running water; the inner space of the stage was purged with pure air to avoid a reduction of the sample at high temperatures.

2.4. Calibrated DTA measurements in Bi₂O₃

To confirm the known phase transitions in synthesized Bi₂O₃ samples, a control measurement of the sample was conducted under ambient pressure conditions in closed platinum cylinders using a conventional Netzsch STA 409 thermal analyzer, calibrated DTA type. The heating rate of 10°C min⁻¹ is in the same order of magnitude as the heating rate during the other experiments.

2.5. Electrical conductivity of Bi₂O₃ at 0.1 MPa

Details of IS measurements at high pressures can be obtained from [22]. The electric impedance was measured with a 0.5–2 V sine signal of a Solartron® 1260 Phase-Gain-Analyzer in a DANFOSS, Denmark, piston-cylinder-press. For measurements of electrical resistance >100 MΩ, a special dielectric interface (BDC Novocontrol®) has been used. During the experiment at 0.1 MPa, the press was unloaded; the pressure exerted on the sample was normal pressure. One of the electrode wires was the S-type thermocouple connected to the inner electrode. The AC short connection of the setup was measured to be 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 at temperatures above 700°C during electrical impedance measurements [22].

3. Experimental results

3.1. Powder diffraction

At the \( \alpha-\delta \) phase transition, a strong change of the cell parameters occurs. As the monoclinic \( \alpha \)-phase with its many diffraction planes transforms into the face-centered cubic \( \delta \)-phase, many reflections vanish at about 725°C and a few new ones arise. HTXRD data are displayed in Figure 1. The traces of the \( \alpha \)-phase seem to be present above 730°C. The scatter of cell parameters in the temperature range \( 600^\circ C < T < T_{Tr} \) is probably a result of the coexistence of \( \alpha \)- and \( \delta \)-phases.

From the collected data the cell parameters of \( \alpha \)-phase of Bi\(_2\)O\(_3\) were obtained using the software "Powder Cell V2.4" [23]. The collected results were compared with the ICSD Files #2374 (\( \alpha \)-phase) and #2375 (\( \delta \)-phase) whose content was measured in [24]. Additionally, for the HT-XRD data measured in the second setup, the Rietveld refinement

![Graphical representation of HT-diffractograms](image)

Figure 1. Powder HT-diffractograms of Bi\(_2\)O\(_3\) around the \( \alpha-\delta \) phase transition temperature during the heating process. HT-XRD measured at Siemens Kristalloflex 810 (a) and at Siemens D5000 (b).
method has been applied (software Topas/DASH) to fit the cell parameter data to the mixture of two phases. The difference in the calculated cell parameters with “Powder Cell” and Rietveld refinement is minor. The values for α-Bi₂O₃ were computed from the measurement results retrieved at 20°C and are displayed in Table 1. The results gained during the two experimental runs on two differing diffractometers provide similar results that agree well with the previously published data. The cell parameter data above 620–650°C have a large scatter and their temperature dependence deviates significantly from low-temperature results (Figure 2).

The data of the present work are compared with the results given by Ivanov et al. [15], Orlov et al. [16], and Yashima et al. [26], and they demonstrate a good general consistency providing that Orlov et al. found rather large cell parameters by X-ray powder diffractometry in comparison to others. The measurements of angle β leads to an inverse trend compared to the data given by Orlov et al. The decreasing angle β as a function of temperature corresponds to a change from 113° to 90° at α-δ phase transition. This temperature trend of cell parameters has also been confirmed by other authors from neutron diffraction measurements [26].

In the present study, a subtle change of the cell parameters is observed which occurs in the temperature range 50–150°C below T_{Tr}. This might be surprising, but the comparison with the results of other experimental methods support the evidence that, in the above-mentioned temperature range, below the phase transition from α- to δ-phase the material deviates from its linear temperature behavior. For the variation of the angle β, which is mostly responsible for a shear strain in the cell, the deviation starts even at 150°C below T_{Tr}, for a, b, and c it is about 75°C (Figure 2). Using neutron scattering, Yashima et al. [26] also have found a small scatter of cell parameters between two points which are closest to T_{Tr}. The authors did not pay attention to the behavior of cell parameters in this temperature range.

Data given by Klinkova et al. [31] are also included in the cell parameter diagrams. The samples of α-Bi₂O₃ were annealed at different temperatures and the authors have found only very small differences in cell parameters after cooling to room temperature. The results of [31] demonstrated that the enlargement of cell parameters in α-Bi₂O₃ is a thermally controlled process and is fully reversible during heating–cooling cycles below T_{Tr}.

Table 1. Result of present study and comparison with several previous publications on cell parameters of α-Bi₂O₃ with different methods at room temperature and normal pressure.

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β</th>
<th>Study, method</th>
</tr>
</thead>
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<tr>
<td>5.8465</td>
<td>8.165</td>
<td>7.5062</td>
<td>113.00</td>
<td>Present study</td>
</tr>
<tr>
<td>5.9590</td>
<td>8.3180</td>
<td>7.5800</td>
<td>112.820</td>
<td>[25]</td>
</tr>
<tr>
<td>5.8458</td>
<td>8.1656</td>
<td>7.5077</td>
<td>112.969</td>
<td>[26]</td>
</tr>
<tr>
<td>5.8444</td>
<td>8.1574</td>
<td>7.5032</td>
<td>112.97</td>
<td>[15]</td>
</tr>
<tr>
<td>5.85</td>
<td>8.16</td>
<td>7.51</td>
<td>112.977</td>
<td>[27]</td>
</tr>
<tr>
<td>5.8504</td>
<td>8.1708</td>
<td>7.5136</td>
<td>112.98</td>
<td>[16]</td>
</tr>
<tr>
<td>5.8496</td>
<td>8.1673</td>
<td>7.5102</td>
<td>112.979</td>
<td>[28]</td>
</tr>
<tr>
<td>5.8496</td>
<td>8.1648</td>
<td>7.5101</td>
<td>112.977</td>
<td>[21]</td>
</tr>
<tr>
<td>5.8486</td>
<td>8.1661</td>
<td>7.5097</td>
<td>113.00</td>
<td>[29]</td>
</tr>
<tr>
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<td>8.14</td>
<td>7.48</td>
<td>112.93</td>
<td>[30]</td>
</tr>
<tr>
<td>5.8574</td>
<td>8.1771</td>
<td>7.5131</td>
<td>112.960</td>
<td>Average of studies above</td>
</tr>
</tbody>
</table>

Note: Present XRD-study does not differ from average values of all listed works by more than about 0.2%.
Figure 3 shows the temperature variations of the measured Raman spectrum. With the rise in temperature, the amplitude of Raman shift in the Bi₂O₃ sample degrades strongly. At temperatures above the α–ß phase transition, nearly no Raman spectrum can be recorded. The Raman shift at 539 cm⁻¹ shows the strongest temperature dependence under the given conditions (hard mode), which is why it was chosen for detailed temperature-dependent analysis during the present work. This peak corresponds to the A₂₇-mode which was previously calculated at 529 cm⁻¹ and experimentally found at 536 cm⁻¹ by Denisov et al. [32] who performed a much more extensive study of Bi₂O₃ Raman spectra, which was not the aim of this study.

3.2. Raman spectroscopy

Figure 2. Temperature dependency of cell parameters a, b, c, β and the volume of the α-Bi₂O₃ unit cell. (*) Data by Klinkova et al. (2007) are not in-situ measurements. They have been measured after annealing at a given temperature.
In Figures 4 and 5 the temperature dependence of the Ag-mode peak parameters of 539 cm$^{-1}$ mode are plotted: intensity and frequency shift. There are noticeable changes in the temperature range below $T_{Tr}$, which can be observed, in the intensity and in the Raman-shift graphs as a function of temperature. Above 650$^\circ$C the normalized intensity deviates from the smooth curve, corresponding to the $\alpha$-phase at low temperatures. The temperature-dependent Raman-shift of the Ag-mode, which is 539 cm$^{-1}$ at 20$^\circ$C, shows a sharp kink in the temperature dependence above 600$^\circ$C. The temperature dependence of the peak intensity at $T < 600^\circ$C is proportional to $\sim(T_{Tr} - T)^\beta$ with $\beta < 1$, and at 600$^\circ$C $< T < T_{Tr}$ depends linearly on temperature (Figure 4). According to the Landau theory of phase transitions, if the polynomial expansion of the free energy of the order parameter $Q$ has the coefficients at even-order terms as follows $1/2 \cdot a \cdot (T - T_c)$, $1/4 \cdot B$, and $1/6 \cdot c$, then for the first-order phase transition the temperature dependence of $Q^2$ is as follows:

$$Q^2 = \frac{-B + \sqrt{B^2 + 4a \cdot c \cdot (T_{Tr} - T)}}{2c},$$

(1)

where $T_c = T_{Tr} - 3 \cdot B^2/(16 \cdot a \cdot c)$ [33]. The intensity of the hard mode is proportional to the square of the order parameter $I \sim Q^2$ [34]. Thus, the intensity in the temperature range $T < T_{Tr}$ is roughly proportional to $I \sim (T_{Tr} - T)^{1/2}$, according to Equation (1). This is confirmed in Figure 4 at $T < 600^\circ$C. At 600$^\circ$C $< T < T_{Tr}$, the normalized intensity is a linear function of $(T_{Tr} - T)$. So again, a deviation of the material properties from a
first-order transition behavior can be detected above 600°C, which is significantly below the phase transition temperature $T_{Tr} \sim 725°C$ (Figure 4). The shape of the curve at $T < 600°C$ implies $T_c \sim 600°C$.

The Raman-shift frequency of a hard mode across the phase transition depends on the order parameter $Q$ as follows [34]:

$$\Delta(o)^2 \propto \Delta\omega \propto a \cdot (T_c - T) \cdot Q^2 + B \cdot Q^4.$$  \hspace{1cm} (2)

In Figure 5, the square of Raman frequency shift for $A_g$ mode is plotted as a function of temperatures. The observed behavior is almost linear at $T < 650°C$, and at $650°C < T < T_{Tr}$, the slope of the temperature dependence $\Delta(o)$ versus $T$ becomes smaller. The linearity $\Delta(o) \sim (T_{Tr} - T)$ would imply a slightly first-order phase transition with rather large negative constant $B$ in Equation (2) [35].

3.3. **Calibrated DTA**

The results of calibrated DTA measurements in Bi$_2$O$_3$ are shown in Figure 6. Only the known transitions detected by Levin and Roth [3] from the $\alpha$- to $\delta$-phase ($727 \pm 2°C$), melting point ($822 \pm 3°C$), from the $\delta$- to $\beta$-phase ($639 \pm 2°C$), and the $\beta$--$\alpha$-phase ($563 \pm 2°C$) can be identified due to their strong endo- or exothermic characters.
This proves that there is no first-order phase transition taking place in the 600–720°C temperature range during the heating process, but the presence of order–disorder or displacive phase transitions cannot be excluded. The peak at the phase transition is unexpectedly wide. The relaxation point of the corresponding DTA peak is slightly below 750°C.

3.4. Impedance spectroscopy

Figure 7 demonstrates the results of 0.1 MPa electrical conductivity measurements during the heating and cooling process. The activation energy of electrical conductivity in the α-phase in the extrinsic region (T < 370°C) is about 0.86 eV and is equal to the activation energy of vacancy migration. In the intrinsic conductivity region 610°C > T > 370°C, the activation energy is 1.58 eV. Thus, the calculated activation energy of vacancy formation is ~1.44 eV, e.g., [22]. Above 610°C, the activation energy of conductivity decreases to 1.02 eV. Below the phase transition temperature at 680–710°C, the activation energy is even less than 0.65 eV. During the heating cycle α and δ phases can be identified, and the phase transition occurs at ca.723–726°C. In the temperature range 100–120°C, below the T_{Tr} the activation energy of the electric conductivity in α-phase decreases to 0.9–1.0 eV.

4. Discussion

Although the physical properties of Bi$_2$O$_3$ have been within the scope of numerous review papers [36,37], there is still no unanimous view on the phase relations of Bi$_2$O$_3$ at high temperatures. Sometimes authors discovered unexpected behavior of the high-temperature α- and δ-phases. As discussed earlier by Orlov et al. [16], the α-Bi$_2$O$_3$ polymorph exhibits temperature-dependent anomalies which seem not to be directly connected to the
well-explored phase transitions in this material. The magnetic properties of the \( \alpha \)-phase turn out to be very unusual – the electric polarization can be induced by an external magnetic field. This phenomenon has been explained as an antiferroelectric ordering in \( \alpha \)-Bi\(_2\)O\(_3\). The high-temperature \( \delta \)-phase is characterized by a disordered structure of oxygen sites. The temperature at which the oxide ions in the \( \delta \)-phase are completely disordered is higher than \( T_{Tr} \) [38]. Depero and Sangaletti [39] have shown that the structural (static) disorder in \( \delta \)-Bi\(_2\)O\(_3\) can be structurally derived from the \( \alpha \)-phase. As a consequence of the growing degree of oxygen site disorder with increasing temperature, the oxygen sublattice exhibits a liquid-like behavior which promotes higher oxygen ion diffusion only when a certain degree of the structural disorder is achieved, mimicking a process which is analogous to a pre-melting phenomenon. Here we may only speculate that the start, or a small degree, of the oxide ion disorder begins at temperatures below \( T_{Tr} \) and results in the above-mentioned features of deviation from the linear temperature dependence of the Raman shift, the observable fluctuation of the cell parameters in the \( \alpha \)-phase below \( T_{Tr} \), and in a lower activation energy of electrical conductivity in the temperature range 100°C below the \( \alpha \)-\( \delta \)-phase transition. Pressure extends the temperature range of the \( \delta \)-phase disorder [18].

Using the measured cell parameters of \( \alpha \)- and \( \delta \)-phases (Figure 2), the spontaneous strains have been calculated according to [40] and plotted in Figure 8.

\[
\begin{align*}
\varepsilon_{11} & = \frac{a_\alpha}{a_\delta} - 1 \\
\varepsilon_{22} & = \frac{b_\alpha}{b_\delta} - 1 \\
\varepsilon_{33} & = \frac{c_\alpha}{c_\delta} \cdot \sin \beta^{\alpha} - 1 \\
\varepsilon_{13} & = \frac{1}{2} \cdot \left[ \frac{c_\alpha \cdot \cos \beta^{\alpha}}{c_\delta} \right].
\end{align*}
\]
The subscript represents the phase, $\beta^*$ is the reciprocal angle of $\beta$, and other components of spontaneous strain tensor are 0 [40]. In Equation (3) the $\delta$-phase has been chosen as the reference state: $a_{\delta} = b_{\delta} = c_{\delta} = 5.65$ Å. The volume strain for a monoclinic–cubic phase transition is $\varepsilon_V = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}$. The results of spontaneous strain calculations are presented in Figure 8. The small continuous temperature variation of spontaneous strains as a function of temperature at $T < 600^\circ$C disappears in the temperature range ca. 70°C below the $T_{Tr}$. These variations of the spontaneous strains near the phase transition temperature are typical for a first-order phase transition with a large difference between $T_c$ and $T_{Tr}$ and a large negative coefficient $B$ in the fourth-order term of the Landau expansion of the free energy of the order parameter $Q$ [33]. Comparison of spontaneous strain obtained in this work with the calculated data from the cell parameters [26] shows a slight deviation from the linear trend close to $T_{Tr}$. The low-temperature results of [26] are in agreement with the present data. The significant drop of spontaneous strains and of the order parameter $Q$ at $T_{Tr}$ explains a noticeable latent heat of this phase transition which is proportional to the product $B \cdot T_{Tr}$ (Figure 6).

From the electrical impedance measurements carried out at 0.1 MPa in the frequency range from 10$^5$ to 0.1 Hz, the dielectric susceptibility $\chi$ has been calculated as a function of frequency and temperature as follows:

$$\chi(\omega, T) = \frac{C(\omega, T)}{\varepsilon_0 \cdot G_f} - 1,$$

where $C$ is the measured capacitance as a function of frequency and temperature, $\varepsilon_0$ is the dielectric vacuum constant, and $G_f$ is the geometric factor of the cylindrical capacitor used as a measuring cell (ca. 0.05 m). The frequency scans of $\chi(\omega)$ at each temperature for $\alpha$ and $\delta$ phases have been fitted to the Cole–Cole relaxation function and the low frequency or static susceptibility $\chi(0)$ has been estimated:

$$\chi(\omega) = \chi(\infty) + \frac{\chi(0) - \chi(\infty)}{1 + (i \cdot \omega \cdot \tau)^n},$$

Figure 8. Spontaneous strains in $\alpha$-Bi$_2$O$_3$. Spontaneous strains are close to a constant over a wide range of temperatures. The small variation with temperature starts at about 680°C. This can be seen as well in the neutron diffraction data of [26]. At $T_{Tr}$, the main drop of the spontaneous strains and order parameter occurs (see insert of the graph). Here $\varepsilon_{13}$ has been plotted as a positive value for scaling reasons.
where $\chi(\infty)$ is the dielectric susceptibility at high frequency, $\tau$ is the dielectric relaxation time of the sample, and $n < 1$ is the Cole–Cole exponent. In the $\delta$-phase, $\chi(0)^{-1}$ is about 0 in comparison with that in $\alpha$-phase. The results of calculations $\Delta(\chi^{-1}) = \chi(0)^{-1}_\alpha - \chi(0)^{-1}_\delta$ are presented in Figure 9 as a function of temperature. Between the hard mode frequency shift and the change in inverse dielectric susceptibility there is a relation [34,41]:

$$\Delta \chi^{-1} \propto \Delta(\omega^2) = R \cdot |\omega^2_\alpha - \omega^2_\delta|,$$

where $R$ is the constant having the dimension of the moment of inertia to electrostatic binding energy, $\omega_\alpha$ and $\omega_\delta$ are the Raman-shift frequencies in $\alpha$- and $\delta$-phases, respectively [41]. Figure 9 demonstrates a good correlation between $\Delta \chi^{-1}$ and $\Delta(\omega^2)$ as a function of temperature in $\alpha$-phase up to 600°C. In the inset of Figure 9 the constant $R$ is shown, which drops almost to 0 at $T > 600^\circ$C. At $T < 600^\circ$C, the proportionality constant is $R \approx 5.5 \times 10^{-7}$ cm$^2$. The proportionality constant $R$ is a measure for the moment of inertia of dipoles induced by a change of the binding energy due to the rearrangement during a phase transition. The decrease of this constant at $T > 600^\circ$C means a sudden decrease of cooperative antiferroelectric ordering of dipoles starting from 100°C to 120°C below $T_{Tr}$ [41]. Skorodumova et al. [14] explained the random electrical conductivity mechanisms in $\delta$-Bi$_2$O$_3$, which was stabilized at room temperature by electrical deposition on the solid substrate, due to the time-dependent ordering of oxygen vacancies at low temperatures which result in a nonstable electrical conductivity of $\delta$-phase film. The present work shows that during heating ca. 100°C below the $\alpha$–$\delta$-phase transition, substantial disordering of electric dipoles in $\alpha$-Bi$_2$O$_3$ takes place which affects the optical and electrical properties and might, in addition, have an effect on the cell parameters of the sample. The explanation of this phenomenon lies in the heavily defective structure of the $\delta$-phase of Bi$_2$O$_3$. Based on the results of neutron scattering [42] and on the static cell simulations [38], it was proposed that the charge transfer in the $\delta$-phase occurs via the formation of oxygen pair vacancies preferably in the $\langle111\rangle$ direction. The formation of $\langle111\rangle$ vacancy strings provides a possible diffusion path where O$^{2-}$ can move through a face of the surrounding Bi tetrahedron to the octahedral cavity and then re-enter a neighboring anion site [38]. Due to the arrangement of vacant oxygen sites in a $\langle111\rangle$ configuration around Bi atoms, the Bi coordination sphere is slightly distorted due to the $\langle111\rangle$ lattice anion displacements.
These displacements are almost of a shear type. The thermal activation of the shear displacements within the $\alpha$-phase is the main precursor of the $\alpha$–$\delta$-phase transition, which takes place below $T_{Tr}$. The formation of (111) vacancy pairs may reduce the activation energy of the electrical conductivity in $\alpha$-phase of Bi$_2$O$_3$ from 1.6–1.4 eV to ca.0.9–1.0 eV [18], which is close to the activation energy of Bi self-diffusion in $\alpha$-phase [32]. The activation energy of vacancy formation in the temperature range 100°C close to $T_{Tr}$ decreases from 1.44 to 0.3 eV.

Conclusions

1. The temperature dependence of cell parameters, spontaneous strains, and Raman-peak of $A_g$-mode demonstrates a continuous nonlinear variation within a temperature range of ca. 70–100°C below the $\alpha$–$\delta$-phase transition temperature in Bi$_2$O$_3$.

2. The IS electrical conductivity measurements at 0.1 MPa indicate lower values of the activation energy in the $\alpha$-phase in the same temperature range. The activation energy of vacancy formation decreases from 1.44 eV at $T < 610°C$ to 0.3 eV at $610°C < T < T_{Tr}$.

3. The temperature behavior of $\alpha$-phase below $\alpha$–$\delta$ phase transition may be explained by a start of the disordering tendency of vacant oxygen sites and their displacement relative to Bi atoms, i.e., pre-melting of the oxygen sublattice in the structure of $\alpha$-Bi$_2$O$_3$ below $T_{Tr}$.

4. The ratio of $\Delta K^{-1}/\Delta(\omega^2)$ drops from $1.5 \times 10^{-7}$ cm$^2$ to 0 at $T \sim 600°C$, indicating a sudden decrease of dipole cooperative antiferroelectric ordering 100–120° below $\alpha$–$\delta$ phase transition.

5. The $\alpha$–$\delta$ phase transition might not be fully completed at 727°C, but rather continues gradually up to approximately 750°C.

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