Structural phase transitions in ionic conductor Bi$_2$O$_3$ by temperature dependent XPD and XAS

Yingcai Zhu, Pengfei An, Meijuan Yu, Augusto Marcelli, Yong Liu, Tiandou Hu, and Wei Xu

1Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, China
2INFN – Laboratori Nazionali di Frascati, Via E. Fermi 40, 00044 Frascati, Rome, Italy
3AVIC, Beijing Institute of Aeronautical Materials, Beijing 100095, China.

These two authors contributed equally

E-mail: yumj@mail.ihep.ac.cn and xuw@mail.ihep.ac.cn

Abstract. The superionic behavior of cubic δ-phase Bi$_2$O$_3$, a metastable phase at high temperature, is of great interests from both scientific and technological perspectives. With the highest ionic conductivity among all known compounds, the δ-phase Bi$_2$O$_3$ possesses promising applications in solid-oxide fuel cells. Previous investigations pointed out the α to δ-phase transition occurs during the heating process, as supported by the X-ray and Neutron diffraction experiments. Through in situ measurements of the long-range order structure and the local structure by X-ray powder diffraction and X-ray absorption spectroscopy, we investigated the evolution of the structures under different temperatures. Both techniques provided ample evidence that the existence of meta-stable β-phase are crucial for forming the defective fluorite cubic δ phase. Our finding suggested that the phase transition from tetragonal β-phase to δ-phase is an influencing factor for the generation of the oxygen-ion pathways.

1. Introduction

The demand of energy is triggering large investments in energy related researches spanning from physics, chemistry, materials sciences to biology. The main goal of these researches is essentially that to resolve bottleneck issues regarding storage, conversion and transport of energy. Among the promising candidates for energy storage applications, the solid-oxide fuel cells (SOFCs) possess unique merits such as high efficiency, great stability, low cost and a low environmental impact. However, the mechanical/physical compatibility of components hamper the performance of SOFCs because these structural phase transitions occur at high temperature. Investigation of the structural phase transitions involving SOFCs components is mandatory, being a real critical issue that focus interests from both a fundamental and a technological perspective.
The ionic conductor Bi$_2$O$_3$ is a promising electrolyte for SOFC because it exhibits an extraordinary high ionic conductivity at high temperature. Actually, at high temperature, Bi$_2$O$_3$ exhibits a complicated phase transition diagram involving four polymorphs (Fig. S1).[1] By heating up the material from room temperature to 700°C, Bi$_2$O$_3$ experience a monoclinic $\alpha$-phase to cubic $\delta$-phase transition, whereas several other phases (tetragonal $\beta$-phase or bcc $\gamma$-phase) appear as the material is cooled down to low temperature.[1] The ionic conductivity in the high temperature cubic phase is four orders of magnitude larger than that at room temperature in the monoclinic phase,[2] pointing out a structural origin for this ionic conductivity. The cubic $\delta$-phase exhibits a defective fluorite structure with 25% of oxygen sites empty. Intriguingly, theoretical studies pointed out that the ionic conduction mechanism is closely related with 3D configurations of oxygen vacancies.[3] Configurations (Figure. S1) derived as (100), (110) and (111), respectively, are probably correlated to the lone electron pairs (LEP) of Bi$^{3+}$ ions.[4] Moreover, due to the “soft” cation lattice, ionic diffusions are supported by the formation of transport paths associated to oxygen vacancies.[5] Furthermore, as previously showed the atomic disorder is ubiquitous at high temperature while the average symmetry is cubic. In spite of the available experimental data, a detailed understanding of the phase transition path from the $\alpha$- to $\delta$-phase while heating and cooling, which may explain the principles of the SOFC degradation in Bi$_2$O$_3$ is lacking. Furthermore, the understanding of nonequilibrium phenomena such as the temperature-dependent phase transitions is of fundamental significance in condensed matter physics. It is well known that X-ray powder diffraction and X-ray absorption spectroscopy are complementary techniques in resolving the average long-range ordered atomic structure as well as the average local atomic structure. Owing to the unique element and site selectivity, the X-ray Absorption spectroscopy probes the local geometric and electronic structure of the system.[6] Previously, the temperature dependent structural phase transitions in Bi$_2$O$_3$ were investigated by X-ray diffraction,[1] neutron diffraction[7] and Raman spectroscopy,[8] revealing the $\alpha$- to $\delta$-phase transition. Recently, the short-range order structure were investigated by analyzing the diffuse scattering part of neutron total scattering data.[9] Interestingly, the short range ion-ion correlation[9] in disordered $\delta$ phase Bi$_2$O$_3$ are different from that deduced from the long-range order structure.[6-8]

In this article, we investigate the phase transformation path of Bi$_2$O$_3$ polymorphs during a cycle of heating and cooling by resolving the variations in local structure as well as the evolution of the average long-range ordered structure. By employing the in situ X-ray powder diffraction and the in situ X-ray absorption spectroscopy, the structural phase transition can be deciphered readily. Our findings suggest the formation of $\beta$-phase nanoclusters on the track of phase transition from $\alpha$- to $\delta$-phase, implying the meta-stable $\beta$-phase is crucial for in forming the defective fluorite superionic state in disordered cubic $\delta$ phase.

2. Experimental and calculation method

Temperature dependent X-ray Absorption Fine structure Spectroscopy (T-XAFS) experiments were performed at the 1W2B endstation of the Beijing Synchrotron Radiation Facility. Bi$_2$O$_3$ pellets were housed in a home-made furnace.[10] The samples were heated from RT to 750°C then cooled down to RT. The heating rate was about 10°C/min from room temperature to 750°C when performing the QXAFS; the cooling rate was controlled as 10°C/min from 750°C to 500°C; then the sample was left to naturally cooling down to room temperature within 10 minutes. During the heating process, we collected QXAFS spectra in the transmission mode; while fine scan XAFS spectra were measured at separate temperature.

The temperature dependent X-ray powder diffraction (T-XPD) experiments were performed at the 4B9A endstation of the Beijing Synchrotron Radiation Facility. The Bi$_2$O$_3$ powder were brushed upon a Pt heater in the commercial furnace. The XPD experiments were performed in both quick and fine scan mode while heating from RT to 800°C. The heating rate for XPD was set the same as for XAFS.

XAFS spectra are normalized after subtracting the atomic absorption background using the Demeter and IFEFFIT package.[11] Fourier Transforms of $k^2$ weighted EXAFS $\chi(k)$ were performed with a Hanning type window over the $k$ range of 2 to 13 Å$^{-1}$. To perform a consistent fitting for all
temperatures, the k range was fixed to [2.2, 10.5] Å⁻¹ and the fitted R range lied in [1, 4] Å. The simulation of near-edge region of the X-ray Absorption Spectra (XAS) were carried out using the full multiple scattering (FMS) theory as implemented in FEFF9.6 code.[12] The muffin-tin potential and Hedin-Lundqvist exchange-correlation potential were adopted to calculate the atomic potential in self-consistent field (SCF). To achieve good convergence, in our calculations the cluster radius for SCF potential and full multiple scattering is 5 and 8 Å, respectively.

3. Results and Discussions

The temperature dependent X-ray powder diffraction profiles (Fig.1(a) and Fig.S4) can be used to determine the phase qualitatively. As shown in Fig.1(a), the XPD profiles of Bi₂O₃ from room temperature to 800 °C clearly show phase transformation during the heating process. The room temperature phase can be purely indexed to the monoclinic \( \alpha \)-phase ( PDF#41-1449). The relative intensity ratio between the (002) and (120) plane are slightly different from the PDF card, indicating preference of certain orientations in the powder samples in which the particle orientations are anisotropic. The peaks at high angles above 60° remain for all measured temperature, which is systematic background not related with the sample. After heating up to 400 °C, the intensity of (002) peak decreases but the \( \alpha \)-phase is still maintained. Above 600°C, the peak at 28° becomes more pronounced indicating the emergence of \( \beta \)-phase. Therefore, a mixture of \( \alpha \) and \( \beta \) is shown in temperatures above 600°C. Both \( \delta \)-and \( \alpha \)-phase show a strong line at 26°; so we may resort to the line at 54° to identify the \( \delta \)-phase. The (002) peak disappears at 800°C, indicating that the corresponding preferred orientation was broken due to large temperature-induced disordering occurring at high temperature. The peak at 54° emerges in 800°C that is likely related to the \( \delta \)-phase. Hence it is concluded that phase stable temperature window for \( \alpha \)- and \( \beta \)-phase is 400 to 600°C and 600°C to 700°C, respectively. On the other hand, since the Bi₂O₃ melts quickly about 830°C, the phase stable window for \( \delta \)-phase is quite narrow (from 800 to 830°C). Meanwhile, we observed that the phase transition is not sharp since the mixed \( \alpha \), \( \beta \)-, and \( \delta \)-phase are indexed even at 800°C.

![Figure 1.](image)

**Figure 1.** (a) Temperature dependent X-ray Powder diffraction and the PDF cards corresponding to Bi₂O₃ polymorphs; (b) T-XAS versus the theoretical calculations of all Bi₂O₃ polymorphs.

Next, we focus on the temperature induced local structure transition. As shown in Fig.1(b), the XANES spectra at Bi \( L_3 \)-edge not only reflect the electronic transition from Bi 2p core electrons to Bi 5d empty states but also the multiple scattering of the photon excited electrons by coordinate atoms.
Owing to the lack of empty d shells and longer core-hole width (~5.98 eV), the spectra at Bi $L_3$-edge are flat and seemingly featureless. The feature becomes more broadened at high temperature due to thermal atomic disordering. To identify the phase, we performed theoretical simulations of the XANES spectra by employing Full Multiple Scattering Theory. Firstly, comparison of the experimental XANES spectra of Bi$_2$O$_3$ and theoretical XANES spectra based on different atomic models suggest that the mixture phase appears at high temperatures above 600 °C. Different configurations of oxygen vacancies are adopted to simulate the defective fluorite cubic $\delta$-phase. However, the theoretical spectra deviate from the experimental spectra, suggesting that $\delta$-phase does not exist even at 750°C. Furthermore, the EXAFS fitting (Figure.S3, and Table. S1) of the phases using $\alpha$-and $\beta$-phase models suggested that the mixture of both phases at high temperatures above 600 °C while heating. The $\beta$-phase is stabilized while cooling down to 500°C. As shown in Fig.1(a), there is evidence for $\delta$-phase at 800°C from XPD. But we cannot identify $\delta$-phase from XAFS.

4. Conclusions
The in situ X-ray powder diffraction and in situ X-ray absorption spectroscopy were employed to investigate the polymorphs of Bi$_2$O$_3$ under temperature. Upon heating from room temperature to 400°C, Bi$_2$O$_3$ are well crystallized in $\alpha$-phase; while mixed $\alpha$-and $\beta$-phase are identified above 400°C. The $\delta$-phase exists in very narrow window (800°C-830°C). Unlike the previous reports for sharp phase transition from $\alpha$- to $\delta$-phase,[1] our XAFS and XPD data indicate a sluggish phase transition from $\alpha$- to $\delta$-phase mediated by $\beta$-phase. The formation of $\beta$-phase in heating process participate in the formation of oxygen indicates an alternative thermodynamic pathways form forming vacancies as required for $\delta$-phase. Upon cooling down to 500°C, the intermediate tetragonal $\beta$-phase formed in heating process can be stabilized.

Moreover, the soft oxygen sub-lattice and the 6$s^2$ lone electron pairs of Bi$^{3+}$ plays an essential role in the temperature induced phase transitions owing to the highly modulated potential energy surface.[13] The formation of $\beta$-phase prior to the $\delta$-phase may induce drastic variations of the potential energy surface; hence, the phase transition from $\alpha$ to $\delta$ can be either hampered or facilitated depending on the thermodynamic pathways, remaining an open question for further investigations. The findings provide an insight to the understanding of superionic conductivity in Bi$_2$O$_3$ at high temperature as applied in solid-oxide fuel cells.

Acknowledgments
The authors acknowledge the financial support from the NSF of China under Grant No. 11205186, No. U1532128, and No. 11105172. W. X acknowledge the financial support from the INFN-IHEP collaborative framework. This work is dedicated to the late Prof. Dr. Ziyu Wu.

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