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New ϵ-Bi_2O_3 Metastable Polymorph

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The new metastable ϵ-Bi_2O_3 polymorph has been prepared by hydrothermal treatment and structurally characterized. It shows strong relationships with the room temperature α form and the metastable β form through rearrangements of [Bi_2O_3] columns formed by edge-sharing OBi_4 tetrahedra. Its fully ordered crystal structure yields an ionic insulating character. It irreversibly transforms at 400 °C to the α form. The chemical analysis indicates its undoped bismuth oxide nature, then leading to the fifth characterized Bi_2O_3 polymorph to date.

State of the Art. Bismuth sesquioxide has been the subject of a number of studies concerning its polymorphism and the formation of stable and metastable competing forms.[1] Indeed, the room-temperature stable monoclinic α form transforms upon heating at $T = 729$ °C to the cubic δ form stable up to the melting point at 824 °C. Upon cooling, two metastable phases may occur depending on the applied thermal treatment, i.e., the tetragonal β phase near 650 °C and the body-centered-cubic γ phase near 640 °C. The former systematically transforms to the α form near 300 °C, whereas the latter can persist until room temperature upon slow cooling.[2] Several nonstoichiometric phases are also reported in the literature under particular conditions (thin films), but one should note the recent characterization of the metastable triclinic form, the so-called ω-Bi_2O_3, appearing at 800 °C on a BeO substrate.[3] Only its X-ray diffraction (XRD) pattern indexation has been reported so far. Another exciting aspect of this complex phase diagram is the high O^{2-} ionic conductivity of the δ phase that results from the combination of the high polarizability of Bi^{3+} ($6s^2$ active lone pair, LP) and its anionic defective-fluorite structure.[4] Indeed, several structural models have been proposed for the δ form by Sillén,[1a] Gattow and Schröder,[1c] and Willis,[5] but more recent neutron diffraction experiments by Battle et al. and Yashima and Ishimura[6] indicate a regular face-centered-cubic (fcc) sublattice for Bi^{3+}, space group $Fm\bar{3}m$, while two sets of partially vacant oxide positions coexist. In addition to these series of polymorphs, we have developed herein hydrothermal protocols to synthesize a new low-temperature, ϵ-Bi_2O_3 form. We report its elemental analysis, crystal structure, thermal stability, and structural relationship with the other forms. Considering the flexible Bi^{3+} oxygen coordination sphere, the relationship to the fluorite lattice is essential to the descriptive aspect of Bi_2O_3 forms and has been applied. However, the oxygen sublattice is essential to the descriptive aspect, and an original concept based on OBi_x polyhedra has been used to understand structural relationships between the antagonist forms.

Preparation and Crystal Structure. Single crystals of ϵ-Bi_2O_3 have been obtained from the hydrothermal treatment of $Bi(NO_3)_3 \cdot 5H_2O$, MnO_2, $MnSO_4 \cdot H_2O$, and $(NH_4)_2HPO_4$ with different ratios, in a highly concentrated KOH solution. ϵ-Bi_2O_3 has been successfully obtained for a Bi/Mn/P ratio included in the 1:3−6:1 range. Note that only the Mn^{2+}/Mn^{4+} ratio adjusted to $Mn^{+2.66}$ leads to the title compound. During our attempts to obtain pure material by suppression of Mn and/or P, it has been observed that deviations from these conditions failed. A small amount of thin transparent needles as long as 3 mm can be morphologically distinguished and isolated from the obtained mixture (Figure 1). They are accompanied by α-Bi_2O_3 single crystals in a polycrystalline mixture of various phases. The details of the synthesis and the identification of the reaction products are

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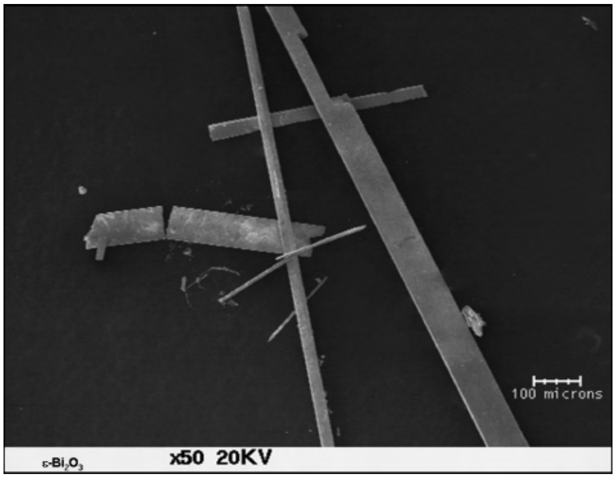

Figure 1. Scanning electron microscopy photograph of ϵ-Bi_2O_3 single crystals.

given in the Supporting Information. The small amount of sorted pure material limits the further characterizations and neither elemental analysis nor redox titration has been possible. However, the energy-dispersive spectrometry (EDS) analysis of a single crystal shows O and Bi only. Thus, a possible stabilization of the ϵ form by Mn or another doping agent cannot be totally excluded but would involve centesimal concentrations. At this stage, the chemical formation process for ϵ-Bi_2O_3 is not well understood, but the mineralizing role of P and Mn is likely efficient.

The single-crystal XRD investigation indicates the crystal structure data: orthorhombic system, $a = 4.9555(1)$ Å, $b = 5.5854(2)$ Å, $c = 12.7299$ (3) Å, space group *Pbnb*, formula Bi_2O_3, $Z = 4$, $R_F = 3.12\%$, $wR_F = 7.84\%$. Three independent atoms occupy the unit cell with full occupancy as follows: Bi 8e, $x = 0.03511(3)$, $y = 0.31723(2)$, $z = 0.01203(5)$; O1 8e, $x = 0.3758(7)$, $y = 0.1662(5)$, $z = 0.4413(2)$; O3 4c, $x = {}^1/_4$, $y = 0.5051(7)$, $z = {}^1/_4$. The crystal, refinement, and structural data are given in the Supporting Information.

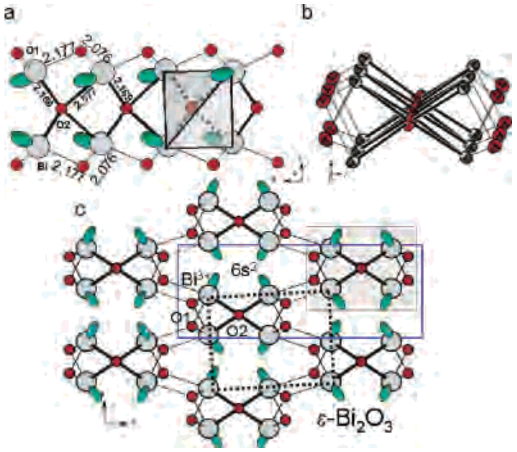

Figure 2. ϵ-Bi_2O_3: (a) tetrahedral columns growing along *b*; (b) perspective view of the columns (50% probability thermal ellipsoids); (c) arrangement of [Bi_2O_3] columns and LPs. The dotted connections show intercolumnar bonds. The dotted lattice shows the correspondence with the fcc Bi^{3+} lattice of fluorite phases.

Table 1. Bi−O Distances (Å) and Bi Bond Valence Sums for Several Bi_2O_3 Forms

bond type	orthorhombic ϵ-Bi_2O_3		monoclinic α-Bi_2O_3	tetragonal β-Bi_2O_3
intracolumn Bi−O1; S_{ij}	2.076(3); 1.04	Bia	2.198; 0.75	2.530; 0.30
	2.177(3); 0.79	Bib	2.137; 0.88 2.213; 0.72 2.200; 0.74	2.087; 1.10
tetrahedral intracolumn Bi−O2; S_{ij}	2.169(2); 0.807	Bia	2.119; 0.92	2.094; 0.99
	2.577(3); 0.268	Bib	2.525; 0.30 2.277; 0.60 2.798; 0.15	2.736; 0.17
intercolumn Bi−O1; S_{ij}	2.489(3); 0.340	Bia	2.428; 0.40	2.176; 0.79
		Bib	2.563; 0.28 2.627; 0.23	
$\sum S_{ij} =$	3.24	Bia Bib	3.09 2.89	3.36

We recently developed structural models based on edge-sharing of $O(Bi,M)_4$ tetrahedra available for a number of Bi−O-related systems and especially well suited in the Bi_2O_3−MO−P_2O_5 phase diagrams.[7] Thus, structural species from infinite chains, one tetrahedron wide, up to larger ribbons *n* tetrahedra wide are systematically evidenced, a useful descriptive tool in the case of disorder. The edge sharing of $O(Bi,M)_4$ generally leads to the existence of an intrinsic crystallographic axis approximately equal to 5.5 Å, along which infinite species are growing (Figure 2a). The projection along *b* (=5.58 Å) of ϵ-Bi_2O_3 is shown in Figure 2b. With regard to the cationic surroundings, O1 is at the center of almost planar OBi_3 triangles whereas O2 is surrounded by a strongly distorted Bi_4 tetrahedron, i.e., O2−Bi (Å), 2 × 2.169(2) and 2 × 2.577(3); Bi−O2−Bi (deg), from 94.8(1) to 124.47(4). They are bordered by O1 ions, each involved in two short Bi−O1 bonds, 2.076(3) and 2.177(3) Å, so forming isolated [Bi_2O_3] columns highlighted in gray in Figure 2a. The cohesion is effected by intercolumn bonds Bi−O1 of 2.489(3) Å in length. For the three independent atoms, thermal ellipsoids show strongly isotropic displacements. The arrangement of [Bi_2O_3] columns is such that the fluorite-like fcc lattice is almost conserved for Bi^{3+} cations but elongated along the *c* axis, as is pictured by the dotted line showing the δ-Bi_2O_3 cubic unit cell correspondence.

Structural Relationship. The Bi−O bonds for α-, β-, and ϵ-Bi_2O_3 are reported in Table 1. In the monoclinic α-Bi_2O_3, the fcc Bi^{3+} lattice is roughly conserved but strongly distorted (Figure 3a). However, the Bi_2O_3 columns grow along *a* (=5.849 Å) with similar intrinsic characteristics. Of course, because of $P2_1/c$ symmetry, two sets of columns are rotated from each other by ~44° and their rectangular bases are not aligned anymore. Finally, the same Bi_2O_3 columns grow along the *c* axis (=5.63 Å) in the tetragonal β-Bi_2O_3 but are turned from each other by 90° because of the 4-fold axis (Figure 3b). This descriptive model may appear more or less virtual because some intracolumn bonds are longer than intercolumn Bi−O separations, but it at least highlights rather

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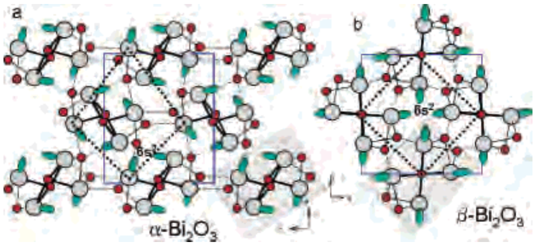

Figure 3. Arrangement of [Bi_2O_3] columns and LPs in (a) α-Bi_2O_3 and (b) β-Bi_2O_3.

well the structural relationship between the three concerned forms. Furthermore, the $6s^2$ LP localization gives additional clues of its validity, as detailed below.

Under the influence of the local electric field E, the LP is displaced by the distance d deduced by the relation $qd = \alpha E$, where q is 2− (LP charge) and α the Bi^{3+} polarizability (=6.12 Å^3).[8] It has been localized using the program *HYBRIDE* through the self-consistent calculation of the (x, y, z) local field using Ewald's method.[9] It yields LP coordinates given in the Supporting Information for α-, β-, and ϵ-Bi_2O_3 with $d(6s^2\ Bi) = 1.39$ Å for our compound using ionic models (3+ for Bi^{3+} and 2− for O^{2-}). The LP's pictured in Figures 2 and 3 point externally to the Bi_2O_3 columns, in good agreement with the compact electrostatic cohesion of the columns in terms of individual entities. The low calculated density, d = 8.784, compared to other $\alpha-\beta-\gamma-\delta-\omega$ polymorphs (9.146−9.372) involves a greater volume of the intercolumnar space pictured by the strong stereoactive character of the $6s^2$ LP. This feature certainly agrees with the self-building aspect of the [Bi_2O_3] columnar units.

According to the progressive reorientation of the columns between α-, β-, and ϵ-Bi_2O_3, the latter may appear as a low-temperature form of the bismuth sesquioxide. This classification is comforted by the low-temperature synthesis process (T = 240 °C). The valence bond (VB) sums have been calculated from Brese and O′Keeffe data[10] for the Bi^{3+} cations in the three compared Bi_2O_3 forms (Table 1). Compared to α-Bi_2O_3 used as a reference for the VB parameter estimation (mean $\sum s_{ij} = 3.0$ for Bia and Bib), Bi^{3+} appears overbonded in ϵ- and β-Bi_2O_3. Assorted crystal data with VB calculations strongly suggest the sole presence of Bi^{3+} in the 8e site, whereas the presence of oxidizing Mn^{4+} during the synthesis questions the possible Bi^{5+} presence. As detailed in the Supporting Information, the unique contribution on the Bi 4f doublet observed from the X-ray photoelectron spectroscopy (XPS) analysis of ϵ-Bi_2O_3 single crystals reinforces the Bi_2O_3 stoichiometry at least at the outer surface (binding energies for $4f_{7/2-5/2}$: 159.2−164.6 eV).

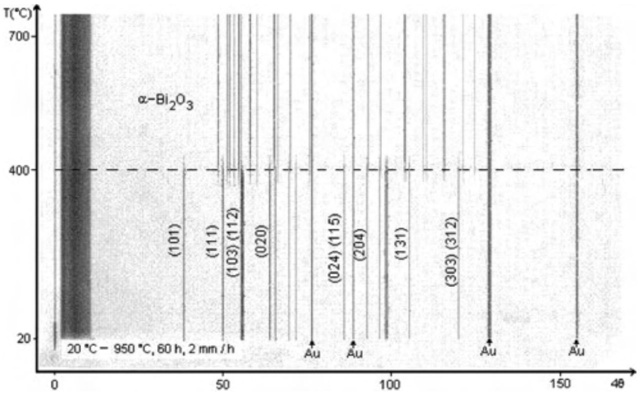

Figure 4. High-temperature XRD pattern for ϵ-Bi_2O_3.

Thermal Behavior. The lattice parameters versus temperature have been refined every 30 °C upon heating using a single-crystal, high-temperature Nonius support. The three parameters a, b, and c monotonically slightly increase versus the temperature. The crystal lattice shows a low volumic thermal expansion estimated to 0.6% per °C from the 400 °C data. At 430 °C, the crystal collapses. Single crystals have been crushed for a powder XRD analysis. High-temperature diffraction powder data have been collected using a Guinier−Lenné diffraction system. This is shown in Figure 4. At 400 °C, the ϵ to α transition occurs. Afterward, α-Bi_2O_3 follows its normal behavior.

The transition is irreversible upon cooling, in agreement with a metastable state. It comforts the Bi_2O_3 exact stoichiometry because the presence of doping elements would likely yield the γ-type sillenite form stabilized by chemical substitution, e.g., $Bi_{12}GeO_{20}$.[11] Finally, as expected from its ordered crystal structure, ϵ-Bi_2O_3 is an ionic insulator. It was checked by impedance spectroscopy. The sample was a selected single crystal with gold paste contacts at both sides of the needle axis (=b). No exploitable impedance diagram has been collected upon the applied heating/cooling cycle from room temperature up to 600 °C.

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Supporting Information Available: Experimental preparation, EDS and XPS analysis, powder XRD pattern, and crystallographic data for ϵ-Bi_2O_3 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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