Supplementary materials for : **The new ϵ -Bi₂O₃ metastable polymorph**

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Synthesis : Synthesis were performed under autogenous pressure in 23 mL Parr Instruments Teflon-lined vessels. A Teflon liner was charged with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, MnO_2 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ according to the different Bi:Mn:P ratios reported table S1. A strongly concentrated KOH solution (KOH:H₂O ratio = 18/25) was added to the mixture as reported in the Table S1. The liner was capped, placed into a steel hydrothermal bomb and tightened. Reactors were then put into an oven during 72 hours at 240°C. Only the most representative preparations are reported, but, in general, all the reactions lead to powder compounds accompanied, in some cases, by single crystals of $\alpha\text{-Bi}_2\text{O}_3$ only or, or a mixture of $\alpha\text{-Bi}_2\text{O}_3$ and the new $\epsilon\text{-Bi}_2\text{O}_3$. Products were washed with hot water dried in air and analysed. As announced in the manuscript, $\epsilon\text{-Bi}_2\text{O}_3$ is obtained in needle shaped single crystals dispersed in the powder. Transparent crystals were identified as the title compound and isolated from transparent-yellow crystals of $\alpha\text{-Bi}_2\text{O}_3$. Only small amount of pure material can be sorted. Powders were identified by powder XRD using the PDF Database. Modifications of our experimental conditions to increase the quantity of $\epsilon\text{-Bi}_2\text{O}_3$ failed as soon as the Maganese mean valence deviates from +2.66. The simultaneous presence of Bi, P and Mn appears necessary to grow the concerned single crystals. This mechanism is not yet understood.

Table S1 : obtained compounds vs initial mixture for experiments realized under pressure at 240°C during 72 h in a KOH/H₂O (180/250) solution

Reactants	Bi:Mn:P ratio	Compound obtained	
		Powder	Single crystal
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	1 : 0 : 0	$\alpha\text{-Bi}_2\text{O}_3$	-
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2	6 : 1 (Mn^{+4}) : 0	$\alpha\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$	-
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $(\text{NH}_4)_2\text{HPO}_4$	6 : 1 (Mn^{+4}) : 0.4	$\alpha\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$	-
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 0 : 0.33	$\alpha\text{-Bi}_2\text{O}_3$	-
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 6 ($\text{Mn}^{+2.66}$) : 1	$\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ "KBi ₆ O ₉ I"	$\alpha\text{-Bi}_2\text{O}_3$ $\epsilon\text{-Bi}_2\text{O}_3$
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 3 ($\text{Mn}^{+2.66}$) : 1	$\alpha\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ KBiO ₂	$\alpha\text{-Bi}_2\text{O}_3$ $\epsilon\text{-Bi}_2\text{O}_3$
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 3 ($\text{Mn}^{+2.5}$) : 0.5	$\alpha\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$	-
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 2 (Mn^{+3}) : 1	$\alpha\text{-Bi}_2\text{O}_3$ $\beta\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$	$\alpha\text{-Bi}_2\text{O}_3$
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$	1 : 2 (Mn^{+3}) : 0	-	-
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 1.5 ($\text{Mn}^{+2.66}$) : 1	$\alpha\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$	-
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 1.5 (Mn^{+3}) : 0.5	$\alpha\text{-Bi}_2\text{O}_3$ $\epsilon\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ "KBi ₆ O ₉ I"	$\alpha\text{-Bi}_2\text{O}_3$
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ MnO_2 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{HPO}_4$	1 : 1.5 ($\text{Mn}^{+2.66}$) : 0.25	$\alpha\text{-Bi}_2\text{O}_3$ $\beta\text{-Bi}_2\text{O}_3$ $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$	$\alpha\text{-Bi}_2\text{O}_3$

Table S2 : Data collection and refinement parameters for ϵ -Bi₂O₃

Crystal data	
Crystal symmetry	orthorhombic
Space group	Pbnb
Unit cell (Å)	a = 4.9555(1)Å b = 5.5854(2)Å c = 12.7299(3)Å
Formula, Z	Bi ₂ O ₃ , 4
Calculated density (g/cm ³)	8.784
Mw (g/mol), μ (mm ⁻¹) for MoK α	465.95, 99.5
Volume (Å ³)	352.34(2)
Data collection	
Diffractometer	Bruker X 8
Radiation MoK α (Å)	0.71073
Refinement parameters	
Scan mode	ω -scan/ φ -scan
Recorded angular range θ (°)	4.41 – 51.82
Recording reciprocal space	$-10 \leq h \leq 5$, $-4 \leq k \leq 11$, $-24 \leq l \leq 28$
Number of measured reflections	5451
Number of ind. Reflexions, total	1818
Number of ind. Reflections, $I > 2\sigma(I)$	1371
Crystal morphology (distance in mm to the crystal centre)	$0\ 0\ 1, 0\ 0\ \bar{1}$: 0.015
	$1\ 0\ 1, \bar{1}\ 0\ \bar{1}$: 0.0235
	$\bar{1}\ 0\ 1, 1\ 0\ \bar{1}$: 0.0245
	$0\ 1\ 0, 0\ \bar{1}\ 0$: 0.165
Transmission factor range (Tmin / Tmax (%))	0.9 / 14.4
R merging factor (%)	6.66
Refinement parameters	
Weighting scheme	$1/[\sigma^2 \cdot F_o^2 + (0.0394 \cdot P)^2]$, $P = (F_o^2 + 2F_c^2)/3$
Refinement Software	SHELXL 97
Number of refined parameters	25
Goof = S (goodness of fit)	0.976
R _F [F>4F], wR _I (%)	3.12, 7.84
R _F (all) (%)	4.34
Max / Min $\Delta\rho$ e/Å ³ (0.77 Å from Bi)	4.517 / -4.722

Table S3 : Refined atomic coordinates and atomic displacement parameters for the average structure ϵ -Bi₂O₃

<i>Atom</i>	<i>Site, occ.</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq} (Å²)</i>
Bi	8e, 1	0.03511(3)	0.31723(2)	0.373416(10)	0.01203(5)
O1	8e ,1	0.3758(7)	0.1662(5)	0.4413(2)	0.0139(5)
O2	4c, 1	0.2500	0.5051(7)	0.2500	0.0174(8)

Table S4 : Anisotropic Displacement Parameters (Å²) for ϵ -Bi₂O₃

<i>Atom</i>	<i>U₁₁</i>	<i>U₂₂</i>	<i>U₃₃</i>	<i>U₁₂</i>	<i>U₁₃</i>	<i>U₂₃</i>
Bi	0.01208	0.01083	0.01317	-0.00090	-0.00216	0.00067
O1	0.01560	0.01069	0.01549	0.00401	-0.00386	-0.00257
O2	0.03127	0.00795	0.01290	0.00000	0.00742	0.00000

Table S5 : Selected Distances (Å) and Angles (°) in ϵ -Bi₂O₃

<i>Distance</i>		<i>O-Bi-O Angles</i>	
Bi-O1	2.076(3)	O(1)-Bi-O(1)	91.93(10)
Bi-O1	2.177(3)	O(1)-Bi-O(1)	83.03(7)
Bi-O1	2.489(3)	O(1)-Bi-O(1)	69.81(12)
Bi-O2	2.169(2)	O(1)-Bi-O(2)	69.07(8)
Bi-O2	2.577(3)	O(1)-Bi-O(2)	95.67(10)
		O(1)-Bi-O(2)	137.21(10)
		O(1)-Bi-O(2)	139.80(10)
		O(2)-Bi-O(1)	75.81(12)
		O(2)-Bi-O(1)	145.51(11)
		O(2)-Bi-O(2)	71.51(3)
		<i>Bi-O-Bi Angles</i>	
		Bi-O(1)-Bi	110.19(12)
		Bi-O(1)-Bi	111.31(13)
		Bi-O(1)-Bi	129.59(14)
		Bi-O(2)-Bi	94.86(14)
		Bi-O(2)-Bi	95.08(3)
		Bi-O(2)-Bi	122.13(19)
		Bi-O(2)-Bi	124.47(4)

Table S6 : Lone pair localization for the three compared Bi₂O₃ forms.

<i>Compound</i>	<i>notation</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>d</i>
ϵ -Bi ₂ O ₃	6s ²	-0.1713	0.15460	0.3502	1.3991
β -Bi ₂ O ₃	6s ²	-0.0038	0.1743	0.1380	0.9105
α -Bi ₂ O ₃	6s ² (Bia)	0.4527	0.2405	0.5839	1.9233
	6s ² (Bib)	0.1685	0.1617	0.7185	1.3962

EDS analysis : it was performed on a JEOL JSM-5300 scanning microscope equipped with an IMIX system of Princeton Gamma Technology, at 15kV. Three different points at the crystal surface have been scanned as shown on the figure S1. It clearly shows no Mn presence on the clean area while, small amount of manganese is detected on the impurities clusters present which contaminate the surface. This result comforts the Bi-O only chemical nature of the investigated single crystals.

Figure S1 : Energy dispersive spectroscopy realized on several crystals revealing the presence of only Bismuth and Oxygen. Measurements were performed on a JEOL JSM-5300 scanning microscope equipped with an IMIX system of Princeton Gamma Technology, at 15kV.

X-ray Photoelectron Spectroscopy (XPS) : A VG ESCALAB 220XL spectrophotometer was used at a pressure $< 10^{-7}$ Pa with Al $K\alpha$ (1486.6 eV) radiation for excitation and an analyzer pass energy of 40 eV. The 4f level was used to detect Bismuth. The sample consists in a pavement of ϵ - Bi_2O_3 single crystals deposited on graphite tape. The 4f ($5/2$ - $7/2$) doublet shows a single bismuth contribution evidenced by nice symmetrical peaks, fig. S2. The binding energies agree with the ones reported for α - Bi_2O_3 ($4f_{7/2}$: 158.6-161.5 eV in the literature). This result is consistent with the Bi^{3+} only nature of the single crystals surface (penetration length ~ 10 nm).

Figure S2 : XPS Bi-4f spectrum for ϵ - Bi_2O_3 single crystals

Powder XRD : ϵ - Bi_2O_3 single crystals have been isolated and crushed. The small amount of obtained powder has been deposited on a Si- oriented sample holder. The XRD pattern , using a Bruker-D8 diffractometer (λ Cu- α radiation) is shown on the figure S3. The intensities have been estimated by a pattern matching process, table S7.

Figure S3 : Indexed XRD powder pattern for ϵ - Bi_2O_3

Table S7 : XRD indexed lines with their relative intensities

h k l	2 Θ (°)	I (a.u.)	h k l	2 Θ (°)	I (a.u.)
0 0 2	13.909	8.9	1 1 6	49.486	296.1
1 0 1	19.216	233.0	2 2 1	49.701	76.4
1 1 1	25.015	132.3	2 2 2	51.334	0.2
1 0 3	27.669	59.8	1 2 5	51.976	3.2
1 1 2	27.846	751.7	1 3 1	53.025	89.0
0 0 4	28.029	661.6	1 0 7	53.671	13.0
0 2 0	32.045	51.6	2 2 3	53.976	56.4
1 1 3	32.054	53.9	2 1 5	54.189	22.8
0 2 1	32.828	61.9	0 2 6	54.286	1.3
0 2 2	35.084	5.7	1 3 2	54.586	16.8
2 0 0	36.248	675.3	3 0 1	56.136	133.8
1 2 0	36.941	4.5	1 1 7	56.335	29.5
1 1 4	37.228	8.0	1 3 3	57.124	49.5
1 2 1	37.635	3.1	2 0 6	57.141	30.6
0 2 3	38.587	32.8	2 2 4	57.533	68.4
2 0 2	39.000	1.8	1 2 6	57.632	4.0
1 2 2	39.652	2.0	0 0 8	57.937	439.3
1 0 5	39.794	3.7	3 1 1	58.726	40.0
2 1 1	40.443	45.4	2 1 6	59.703	21.8
2 1 2	42.349	48.3	3 0 3	60.094	132.3
0 0 6	42.600	2.4	3 1 2	60.189	239.4
1 2 3	42.838	8.9	1 3 4	60.560	3.1
0 2 4	43.084	68.8	0 2 7	60.762	27.9
1 1 5	43.091	57.3	2 2 5	61.911	52.1
2 1 3	45.380	81.7	3 1 3	62.581	22.4
2 0 4	46.435	456.9	2 3 1	62.850	1.1
1 2 4	47.003	13.6	1 1 8	63.617	2.0
0 2 5	48.366	51.7	1 2 7	63.892	0.6
2 2 0	49.148	67.2	2 3 2	64.258	26.3
2 1 4	49.376	18.9	1 3 5	64.816	41.2