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Note

NOTE

Phase composition of Bi₂O₃ specimens doped with Ti, Zr and Hf

DEJAN POLETI^{1*#}, LJILJANA KARANOVIĆ², MIODRAG ZDUJIĆ^{3#}
and ČEDOMIR JOVALEKIĆ⁴

¹Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia, ²Laboratory of Crystallography, Faculty of Mining and Geology, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia, ³Institute of Technical Sciences of the Serbian Academy of Science and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia and ⁴Institute for Multidisciplinary Research, Kneza Višeslava 1a, 11000 Belgrade, Serbia

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Abstract: Powder mixtures of α -Bi₂O₃ containing 2, 5 and 10 mol % of TiO₂, ZrO₂ or HfO₂ were homogenized, heated at 820 °C for 24 h and quenched in air. The X-ray powder diffraction technique was used to characterize the prepared samples. In all cases, metastable Bi₂O₃ polymorphs, γ -Bi₂O₃ or β -Bi₂O₃, were found as single or major phases. The addition of Ti⁴⁺ stabilizes the γ -Bi₂O₃ polymorph, while both Zr⁴⁺ and Hf⁴⁺ stabilize the β -Bi₂O₃ polymorph. In the samples with 2 and 5 mol % of TiO₂ the presence of even two γ -Bi₂O₃ phases (the Bi₁₂TiO₂₀ compound and a very low Ti-doped γ -Bi₂O₃) was established. Similarly, in the sample with 2 mol % of HfO₂, two β -Bi₂O₃ phases were found. The phase composition of the prepared samples, the values of the unit cell parameters and the appearance of two polymorphs with identical crystal structure but different unit cell parameters are discussed and compared with known data.

Keywords: bismuth(III) oxide; dopants; 4th group elements; X-ray powder diffraction; phase composition; unit cell parameters.

INTRODUCTION

Due to the great diversity of the polymorphic modifications and many useful physical properties, pure or doped bismuth(III) oxide, Bi₂O₃, is permanently in the focus of scientific interest. In addition to four well-known polymorphs: α -, β -, γ - and δ -Bi₂O₃,^{1–4} three new Bi₂O₃ polymorphs were described recently.^{5,6} There is general agreement that only the α -Bi₂O₃ form is stable at room tempe-

* Corresponding author. E-mail: dejan@tmf.bg.ac.rs

Serbian Chemical Society member.

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perature.^{2,7,8} However, various metastable or high-temperature polymorphs, such as β -, γ - and δ -Bi₂O₃, can be readily stabilized by addition of proper dopants, which can be cations of any charge, usually added as the corresponding oxides.^{4,6,7,9–11} Some bismuth(III) oxides of this kind, such as γ -Bi₂O₃, have valuable optical (photorefractive, photoluminescent, photoconductive) properties,¹² some other, such as β - and δ -Bi₂O₃, belong to the group of high oxide ion conductors.^{13,14}

Although the Bi₂O₃–TiO₂ system should be considered as well-characterized since detailed phase diagrams are known,¹⁵ in a previous study⁹ the quite unusual co-existence of two Ti-doped γ -Bi₂O₃ phases was observed in the Bi₂O₃-rich region. At the same time, Bi₂O₃–MO₂ systems, where M = Zr or Hf, are not so well known and the data are often contradictory, both for the Bi₂O₃-rich^{7,10,11,16} and MO₂-rich^{17,18} region. For these reasons, a systematic crystallographic study of Bi₂O₃ samples low-doped (2, 5 and 10 mole %) with Ti, Zr and Hf as 4th group elements is described herein.

EXPERIMENTAL

Four commercial powders: Bi₂O₃ (> 99 % purity), TiO₂ (99.8 %), ZrO₂ (> 99 %) and HfO₂ (> 98.5 %) were used in this study. By means of the X-ray powder diffraction technique (XRPD), Bi₂O₃ and TiO₂ were identified as being in the α -Bi₂O₃ (bismite) and rutile form, respectively; ZrO₂ was mostly present as the baddeleyite modification, but contained about 5 mass % of the high-temperature tetragonal polymorph (JCPDS card No. 42-1164), whereas HfO₂ was in the monoclinic, analogous to baddeleyite, modification (JCPDS Card No. 34-0104) with about 1.5 mass % of ZrO₂ as an impurity.

Powder mixtures of α -Bi₂O₃ containing 2, 5 and 10 mole % of TiO₂, ZrO₂ or HfO₂ were dry homogenized in an agate mortar, pressed into tablets ($d = 8$ mm, $h \approx 1.5$ mm) under a pressure of 50 MPa, calcined in Pt-crucibles at 820 °C for 24 h and air-quenched to room temperature.

After regrinding, XRPD data of the prepared samples were collected on a Philips PW1710 diffractometer equipped with a graphite monochromator (Cu-K α radiation, $\lambda = 1.5418$ Å) in the 2θ range 10–90° (step-length: 0.02° 2θ , scan time: 1 s). The program PowderCell¹⁹ was used for a semi-quantitative phase analysis. The unit cell parameters were calculated by the least-squares method using the program LSUCRIPC.²⁰

RESULTS AND DISCUSSION

The results are summarized in Table I and can be commented as follows.

Bi₂O₃–TiO₂ system. The definite composition of the body-centered cubic γ -Bi₂O₃ phase in this system is Bi₁₂TiO₂₀ (14.3 mol % TiO₂),³ which was confirmed several times by crystal structure determination.⁹ As briefly mentioned in the Introduction, if the quantity of TiO₂ was reduced to 7.7 mol %, a mixture of two phases, both with the γ -Bi₂O₃ structure, was previously obtained.⁹ The same feature was observed in this study (Fig. S1 of the Supplementary material to this note), but the results showed that the actual range of the two-phase region extends toward very low TiO₂ content. Thus, a quantity of only 2 mol % (0.35 mass %)

was sufficient to obtain mixed-phase specimens. One unit cell parameter (a_{Ti} , Table I) is in agreement with the literature data for the unit cell parameter of the Bi₁₂TiO₂₀ phase ($a \approx 10.18 - 10.19 \text{ \AA}$), while the other (a_{ss} , Table I) corresponds to the unit cell parameter of undoped γ -Bi₂O₃ ($a \approx 10.26 \text{ \AA}$).⁹ As expected, with increasing Ti-content, the amount of the Bi₁₂TiO₂₀ phase increased, showing the significance of the initial mixture stoichiometry. The co-existence of two phases with a γ -Bi₂O₃ structure was also noticed and discussed by Guha *et al.*²¹ in the Bi₂O₃-rich region of the Bi₂O₃-ZnO₂ system. After comprehensive research, they concluded that one phase was Bi₃₈ZnO₅₈ (equivalent to Bi₁₂TiO₂₀), whereas the second phase was described as a γ -Bi₂O₃ solid solution with no more than 2.2 mol % of ZnO. Very likely, an analogous solid solution exists in the Bi₂O₃-TiO₂ system, although this was not predicted in the phase diagram. Preliminary results of EDS analysis also revealed traces of Ti in the present γ -Bi₂O₃ solid solution.

TABLE I. Phase composition of the investigated samples and calculated unit cell parameters of the Bi₂O₃ phases

Dopant	Amount of dopant, mol %	Phase composition and mass ratio of present phases, %	Unit cell parameters of Bi ₂ O ₃ phases, \AA , and unit cell volume of β -Bi ₂ O ₃ phase, $V / \text{\AA}^3$
TiO ₂	2	Mixture of two γ -Bi ₂ O ₃ phases, Bi ₁₂ TiO ₂₀ : γ -Bi ₂ O ₃ (ss) = 24:76	$a_{\text{Ti}} = 10.186(1)$, $a_{\text{ss}} = 10.2627(6)$
	5	Bi ₁₂ TiO ₂₀ : γ -Bi ₂ O ₃ (ss) = 75:25	$a_{\text{Ti}} = 10.1877(7)$, $a_{\text{ss}} = 10.263(2)$
	10	Mixture of Bi ₁₂ TiO ₂₀ and Bi ₄ Ti ₃ O ₁₂ , Bi ₁₂ TiO ₂₀ :Bi ₄ Ti ₃ O ₁₂ = 90:10	$a_{\text{Ti}} = 10.1790(9)$
ZrO ₂	2	Single β -Bi ₂ O ₃ phase	$a_{\beta} = 7.731(1)$, $c_{\beta} = 5.629(2)$, $V = 336.4$
	5	Single β -Bi ₂ O ₃ phase	$a_{\beta} = 7.714(2)$, $c_{\beta} = 5.632(3)$, $V = 335.1$
	10	Single β -Bi ₂ O ₃ phase	$a_{\beta} = 7.722(1)$, $c_{\beta} = 5.637(2)$, $V = 336.1$
HfO ₂	2	Mixture of two β -Bi ₂ O ₃ phases, β_1 -Bi ₂ O ₃ : β_2 -Bi ₂ O ₃ = 84:16	$a_{\beta_1} = 7.716(3)$, $c_{\beta_1} = 5.636(4)$ $V = 335.5$, $a_{\beta_2} = 7.726(4)$ $c_{\beta_2} = 5.768(5)$, $V = 344.2$
	5	Mixture of β -Bi ₂ O ₃ and δ -Bi ₂ O ₃ with traces (< 5 mass %) of δ -Bi ₂ O ₃ ^a	$a_{\beta} = 7.735(2)$, $c_{\beta} = 5.654(2)$, $V = 338.3$
	10	Mixture of β -Bi ₂ O ₃ , δ -Bi ₂ O ₃ and HfO ₂ , β -Bi ₂ O ₃ : δ -Bi ₂ O ₃ :HfO ₂ = 86:10:4	$a_{\beta} = 7.744(2)$, $c_{\beta} = 5.649(3)$, $V = 338.8$, $a_{\delta} = 5.568(4)$

^aDue to the low content, it was not possible to calculate the precise lattice constant of the δ -Bi₂O₃ phase

The appearance of Bi₄Ti₃O₁₂ in the sample with 10 mol % of TiO₂ was also surprising because under similar conditions Bi₈TiO₁₄, but not Bi₄Ti₃O₁₂, may arise according to the phase diagram.¹⁵

Bi₂O₃–ZrO₂ system. As seen from Table I and Fig. S2 of the Supplementary material, in the Bi₂O₃–ZrO₂ system containing ≤ 10 mol % of ZrO₂, single-phase β -Bi₂O₃ specimens that can be described as solid solutions with the general formula Bi_{2–x}Zr_xO_{3+x/2} were obtained in all cases. Therefore, stabilization by Zr⁴⁺ is the simplest way to obtain a tetragonal β -Bi₂O₃ phase at room temperature. While the values of the *c*-axis were nearly constant (Table I), the values of the *a*-axes and unit cell volume pass through minimum at about $x = 0.05$. When compared with the unit cell volume of undoped β -Bi₂O₃,²² the unit cell volumes of the Zr-doped β -Bi₂O₃ were smaller due to the smaller radius of Zr⁴⁺ with respect to Bi³⁺.²³ This also confirmed the presence of Zr⁴⁺ in the prepared solid solutions. These results are in general agreement with data published by Abrahams and co-workers,¹⁰ but their samples with $x < 0.05$ were not single-phase and contained α -Bi₂O₃ as a secondary phase. A plausible explanation for such discrepancy could be different heat treatments applied.

Bi₂O₃–HfO₂ system. Apparently, Hf⁴⁺ also tend to stabilize β -Bi₂O₃, since this phase predominated in all samples (Table I, Fig. S3 of the Supplementary material). With one exception, the unit cells of Bi_{2–x}Hf_xO_{3+x/2} were larger than the unit cells of the corresponding Bi_{2–x}Zr_xO_{3+x/2} solid solutions and undoped β -Bi₂O₃, implying a larger effective ionic radius of Hf⁴⁺ in the Bi₂O₃ host lattice. In comparison to the Bi₂O₃–ZrO₂ system, the main difference is that single-phase samples were not obtained, while in samples with higher Hf-contents, cubic δ -Bi₂O₃ appeared as a minor phase. In fact, trace amounts of HfO₂ were also observed in the sample doped with 10 mol % of HfO₂, suggesting that thermodynamic equilibrium was not achieved. However, due to the long annealing time applied, this should be related to the upper limits of solubility of Zr⁴⁺ and Hf⁴⁺ in the corresponding solid solutions with β -Bi₂O₃ structure. According to Sorokina and Sleight, the solubility of Hf⁴⁺ is smaller than that of Zr⁴⁺ and the limiting formulae are Bi_{1.84}Zr_{0.16}O_{3.08} and Bi_{1.94}Hf_{0.06}O_{3.03}.¹¹ Similarly, Ayala and López-García¹⁷ found that the maximum concentration of Hf⁴⁺ ions in Bi_{2–x}Hf_xO_{3+x/2} solid solution was only about 5 mol %. An increased tendency of Hf⁴⁺ to stabilize the cubic δ -Bi₂O₃ phase, as described in previous papers,^{24,25} could also have some influence. The unit cell parameter of the δ -phase in the sample doped with 10 mol % of HfO₂ was higher than the values reported (5.266–5.459 Å) for the corresponding δ -phases containing Hf⁴⁺,¹¹ but lower than the values (5.655–5.665 Å) for undoped δ -Bi₂O₃.^{2,26}

The most interesting result of this study was the appearance of two β -Bi₂O₃ phases in the sample with 2 mol % of HfO₂. To the best of our knowledge, this has never been reported before and shows that there are some analogies between γ - and β -Bi₂O₃, *i.e.*, that the coexistence of two crystallographically identical phases with different unit cell parameters in very low-doped samples can be expected. Unit cell parameters of major, β_1 -Bi₂O₃ phase (Table I) are close to the

literature values¹⁷ and JCPDS Card No. 43-0207 but the obtained very high unit cell parameters of the minor β -Bi₂O₃ phase are difficult to explain. The proper rationalization of this system requires additional studies and will be the issue of our future work.

In conclusion, the described differences between Bi₂O₃ samples doped with Ti and doped with Zr or Hf can be judged as expected. However, the somewhat distinct behavior of Zr- and Hf-doped samples could be considered as quite surprising, bearing in mind the close chemical similarity, and identical metal and ionic radii of the elements. Nevertheless, similar discrepancies were observed previously during the investigation of Bi₂O₃-MO₂ systems, M = Zr or Hf,¹¹ and studies of mechanochemically treated 2Bi₂O₃·3ZrO₂²⁶ and 2Bi₂O₃·3HfO₂²⁷ mixtures.

SUPPLEMENTARY MATERIAL

Figures S1, S2 and S3, showing the experimental X-ray powder diffraction patterns, are available electronically at <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

ФАЗНИ САСТАВ УЗОРАКА Bi₂O₃ ДОПИРАНИХ Ti, Zr И Hf

ДЕЈАН ПОЛЕТИ¹, ЉИЉАНА КАРАНОВИЋ², МИОДРАГ ЗДУЈИЋ³ И ЧЕДОМИР ЈОВАЛЕКИЋ⁴

¹Каптедра за општу и неорганску хемију, Технолошко-металуршки факултет, Универзитет у Београду, Карнегијева 4, 11000 Београд, ²Лабораторија за кристалографију, Рударско-геолошки факултет, Универзитет у Београду, Ђушина 7, 11000 Београд, ³Институт за техничке науке САНУ, Кнез Михаилова 35, 11000 Београд и ⁴Институт за мултидисциплинарна истраживања, Универзитет у Београду, Кнеза Вишеслава 1а, 11000 Београд

Хомогенизоване смеше прахова α -Bi₂O₃ са 2, 5 и 10 mol % TiO₂, ZrO₂ или HfO₂ загреване су током 24 h на 820 °C и нагло хлађене на ваздуху до собне температуре. Тако припремљени узорци окарактерисани су методом рендгенске дифракције на поликристалним узорцима. Уочено је да у свим случајевима долази до стабилизације метастабилних модификација, γ -Bi₂O₃ или β -Bi₂O₃, које се појављују као једине или доминантне фазе. Показано је да додаток Ti⁴⁺ стабилизује γ -модификацију, док присуство Zr⁴⁺ и Hf⁴⁺ стабилизује β -модификацију. У узорцима са 2 и 5 mol % TiO₂ нађено је присуство чак две γ -Bi₂O₃ фазе (једињење Bi₁₂TiO₂₀ и допирани γ -Bi₂O₃ са веома малим садржајем Ti). Слично томе, у узорку са 2 mol % HfO₂ идентификоване су две β -Bi₂O₃ фазе. У раду су дискутовани фазни састави узорака, вредности параметара јединичних ћелија, као и истовремена појава две модификације са идентичном кристалном структуром а различитим параметрима јединичне ћелије.

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