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NOTE

## Phase composition of Bi<sub>2</sub>O<sub>3</sub> specimens doped with Ti, Zr and Hf

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**Abstract:** Powder mixtures of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> containing 2, 5 and 10 mol % of TiO<sub>2</sub>, ZrO<sub>2</sub> or HfO<sub>2</sub> 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 Bi<sub>2</sub>O<sub>3</sub> polymorphs,  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> or  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, were found as single or major phases. The addition of Ti<sup>4+</sup> stabilizes the  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> polymorph, while both Zr<sup>4+</sup> and Hf<sup>4+</sup> stabilize the  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> polymorph. In the samples with 2 and 5 mol % of TiO<sub>2</sub> the presence of even two  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> phases (the Bi<sub>12</sub>TiO<sub>20</sub> compound and a very low Ti-doped  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>) was established. Similarly, in the sample with 2 mol % of HfO<sub>2</sub>, two  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> 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; 4<sup>th</sup> 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, Bi<sub>2</sub>O<sub>3</sub>, is permanently in the focus of scientific interest. In addition to four well-known polymorphs:  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>,<sup>1–4</sup> three new Bi<sub>2</sub>O<sub>3</sub> polymorphs were described recently.<sup>5,6</sup> There is general agreement that only the  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> form is stable at room tempe-

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perature.<sup>2,7,8</sup> However, various metastable or high-temperature polymorphs, such as  $\beta$ -,  $\gamma$ - and  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>, can be readily stabilized by addition of proper dopants, which can be cations of any charge, usually added as the corresponding oxides.<sup>4,6,7,9–11</sup> Some bismuth(III) oxides of this kind, such as  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>, have valuable optical (photorefractive, photoluminescent, photoconductive) properties,<sup>12</sup> some other, such as  $\beta$ - and  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>, belong to the group of high oxide ion conductors.<sup>13,14</sup>

Although the Bi<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system should be considered as well-characterized since detailed phase diagrams are known,<sup>15</sup> in a previous study<sup>9</sup> the quite unusual co-existence of two Ti-doped  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> phases was observed in the Bi<sub>2</sub>O<sub>3</sub>-rich region. At the same time, Bi<sub>2</sub>O<sub>3</sub>–MO<sub>2</sub> systems, where M = Zr or Hf, are not so well known and the data are often contradictory, both for the Bi<sub>2</sub>O<sub>3</sub>-rich<sup>7,10,11,16</sup> and MO<sub>2</sub>-rich<sup>17,18</sup> region. For these reasons, a systematic crystallographic study of Bi<sub>2</sub>O<sub>3</sub> samples low-doped (2, 5 and 10 mole %) with Ti, Zr and Hf as 4<sup>th</sup> group elements is described herein.

#### EXPERIMENTAL

Four commercial powders: Bi<sub>2</sub>O<sub>3</sub> (> 99 % purity), TiO<sub>2</sub> (99.8 %), ZrO<sub>2</sub> (> 99 %) and HfO<sub>2</sub> (> 98.5 %) were used in this study. By means of the X-ray powder diffraction technique (XRPD), Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were identified as being in the  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> (bismite) and rutile form, respectively; ZrO<sub>2</sub> was mostly present as the baddeleyite modification, but contained about 5 mass % of the high-temperature tetragonal polymorph (JCPDS card No. 42-1164), whereas HfO<sub>2</sub> was in the monoclinic, analogous to baddeleyite, modification (JCPDS Card No. 34-0104) with about 1.5 mass % of ZrO<sub>2</sub> as an impurity.

Powder mixtures of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> containing 2, 5 and 10 mole % of TiO<sub>2</sub>, ZrO<sub>2</sub> or HfO<sub>2</sub> 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 $\alpha$  radiation,  $\lambda = 1.5418$  Å) in the  $2\theta$  range 10–90° (step-length: 0.02°  $2\theta$ , scan time: 1 s). The program PowderCell<sup>19</sup> was used for a semi-quantitative phase analysis. The unit cell parameters were calculated by the least-squares method using the program LSUCRIPC.<sup>20</sup>

#### RESULTS AND DISCUSSION

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

**Bi<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system.** The definite composition of the body-centered cubic  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> phase in this system is Bi<sub>12</sub>TiO<sub>20</sub> (14.3 mol % TiO<sub>2</sub>),<sup>3</sup> which was confirmed several times by crystal structure determination.<sup>9</sup> As briefly mentioned in the Introduction, if the quantity of TiO<sub>2</sub> was reduced to 7.7 mol %, a mixture of two phases, both with the  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> structure, was previously obtained.<sup>9</sup> 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 TiO<sub>2</sub> content. Thus, a quantity of only 2 mol % (0.35 mass %)

was sufficient to obtain mixed-phase specimens. One unit cell parameter ( $a_{\text{Ti}}$ , Table I) is in agreement with the literature data for the unit cell parameter of the Bi<sub>12</sub>TiO<sub>20</sub> phase ( $a \approx 10.18 - 10.19 \text{ \AA}$ ), while the other ( $a_{\text{ss}}$ , Table I) corresponds to the unit cell parameter of undoped  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> ( $a \approx 10.26 \text{ \AA}$ ).<sup>9</sup> As expected, with increasing Ti-content, the amount of the Bi<sub>12</sub>TiO<sub>20</sub> phase increased, showing the significance of the initial mixture stoichiometry. The co-existence of two phases with a  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> structure was also noticed and discussed by Guha *et al.*<sup>21</sup> in the Bi<sub>2</sub>O<sub>3</sub>-rich region of the Bi<sub>2</sub>O<sub>3</sub>-ZnO<sub>2</sub> system. After comprehensive research, they concluded that one phase was Bi<sub>38</sub>ZnO<sub>58</sub> (equivalent to Bi<sub>12</sub>TiO<sub>20</sub>), whereas the second phase was described as a  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> solid solution with no more than 2.2 mol % of ZnO. Very likely, an analogous solid solution exists in the Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system, although this was not predicted in the phase diagram. Preliminary results of EDS analysis also revealed traces of Ti in the present  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> solid solution.

TABLE I. Phase composition of the investigated samples and calculated unit cell parameters of the Bi<sub>2</sub>O<sub>3</sub> phases

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

<sup>a</sup>Due to the low content, it was not possible to calculate the precise lattice constant of the  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> phase

The appearance of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> in the sample with 10 mol % of TiO<sub>2</sub> was also surprising because under similar conditions Bi<sub>8</sub>TiO<sub>14</sub>, but not Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, may arise according to the phase diagram.<sup>15</sup>

*Bi<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> system.* As seen from Table I and Fig. S2 of the Supplementary material, in the Bi<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> system containing  $\leq 10$  mol % of ZrO<sub>2</sub>, single-phase  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> specimens that can be described as solid solutions with the general formula Bi<sub>2–x</sub>Zr<sub>x</sub>O<sub>3+x/2</sub> were obtained in all cases. Therefore, stabilization by Zr<sup>4+</sup> is the simplest way to obtain a tetragonal  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> 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  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>,<sup>22</sup> the unit cell volumes of the Zr-doped  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> were smaller due to the smaller radius of Zr<sup>4+</sup> with respect to Bi<sup>3+</sup>.<sup>23</sup> This also confirmed the presence of Zr<sup>4+</sup> in the prepared solid solutions. These results are in general agreement with data published by Abrahams and co-workers,<sup>10</sup> but their samples with  $x < 0.05$  were not single-phase and contained  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> as a secondary phase. A plausible explanation for such discrepancy could be different heat treatments applied.

*Bi<sub>2</sub>O<sub>3</sub>–HfO<sub>2</sub> system.* Apparently, Hf<sup>4+</sup> also tend to stabilize  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, since this phase predominated in all samples (Table I, Fig. S3 of the Supplementary material). With one exception, the unit cells of Bi<sub>2–x</sub>Hf<sub>x</sub>O<sub>3+x/2</sub> were larger than the unit cells of the corresponding Bi<sub>2–x</sub>Zr<sub>x</sub>O<sub>3+x/2</sub> solid solutions and undoped  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, implying a larger effective ionic radius of Hf<sup>4+</sup> in the Bi<sub>2</sub>O<sub>3</sub> host lattice. In comparison to the Bi<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> system, the main difference is that single-phase samples were not obtained, while in samples with higher Hf-contents, cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> appeared as a minor phase. In fact, trace amounts of HfO<sub>2</sub> were also observed in the sample doped with 10 mol % of HfO<sub>2</sub>, 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 Zr<sup>4+</sup> and Hf<sup>4+</sup> in the corresponding solid solutions with  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> structure. According to Sorokina and Sleight, the solubility of Hf<sup>4+</sup> is smaller than that of Zr<sup>4+</sup> and the limiting formulae are Bi<sub>1.84</sub>Zr<sub>0.16</sub>O<sub>3.08</sub> and Bi<sub>1.94</sub>Hf<sub>0.06</sub>O<sub>3.03</sub>.<sup>11</sup> Similarly, Ayala and López-García<sup>17</sup> found that the maximum concentration of Hf<sup>4+</sup> ions in Bi<sub>2–x</sub>Hf<sub>x</sub>O<sub>3+x/2</sub> solid solution was only about 5 mol %. An increased tendency of Hf<sup>4+</sup> to stabilize the cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> phase, as described in previous papers,<sup>24,25</sup> could also have some influence. The unit cell parameter of the  $\delta$ -phase in the sample doped with 10 mol % of HfO<sub>2</sub> was higher than the values reported (5.266–5.459 Å) for the corresponding  $\delta$ -phases containing Hf<sup>4+</sup>,<sup>11</sup> but lower than the values (5.655–5.665 Å) for undoped  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>.<sup>2,26</sup>

The most interesting result of this study was the appearance of two  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> phases in the sample with 2 mol % of HfO<sub>2</sub>. To the best of our knowledge, this has never been reported before and shows that there are some analogies between  $\gamma$ - and  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, *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,  $\beta_1$ -Bi<sub>2</sub>O<sub>3</sub> phase (Table I) are close to the

literature values<sup>17</sup> and JCPDS Card No. 43-0207 but the obtained very high unit cell parameters of the minor  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> 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 Bi<sub>2</sub>O<sub>3</sub> 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 Bi<sub>2</sub>O<sub>3</sub>-MO<sub>2</sub> systems, M = Zr or Hf,<sup>11</sup> and studies of mechanochemically treated 2Bi<sub>2</sub>O<sub>3</sub>·3ZrO<sub>2</sub><sup>26</sup> and 2Bi<sub>2</sub>O<sub>3</sub>·3HfO<sub>2</sub><sup>27</sup> 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 Bi<sub>2</sub>O<sub>3</sub> ДОПИРАНИХ Ti, Zr И Hf

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Хомогенизоване смеше прахова  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> са 2, 5 и 10 mol % TiO<sub>2</sub>, ZrO<sub>2</sub> или HfO<sub>2</sub> 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,  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> или  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, које се појављују као једине или доминантне фазе. Показано је да додатак Ti<sup>4+</sup> стабилизује  $\gamma$ -модификацију, док присуство Zr<sup>4+</sup> и Hf<sup>4+</sup> стабилизује  $\beta$ -модификацију. У узорцима са 2 и 5 mol % TiO<sub>2</sub> нађено је присуство чак две  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> фазе (једињење Bi<sub>12</sub>TiO<sub>20</sub> и допирани  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> са веома малим садржајем Ti). Слично томе, у узорку са 2 mol % HfO<sub>2</sub> идентификоване су две  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> 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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