

Influence of synthesis procedure on the morphology of bismuth oxide particles

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Abstract

A modified sol–gel procedure, based on the esterification reaction, was used to prepare the Bi₂O₃ precursor, which was then heated to 400 or 500 °C. β-Bi₂O₃ obtained at 400 °C showed well-shaped plate-like particles. The mixture β-Bi₂O₃/α-Bi₂O₃, obtained by prolonged heating at 400 °C, yielded pseudospherical particles having about 100 nm in size and much larger particles, as found by FE SEM. α-Bi₂O₃ obtained at 500 °C consisted of particles of varying shapes and sizes. Vitrification of α-Bi₂O₃ was also observed. XRD showed a small fraction of unidentified phase(s) in these samples. Different microstructures were obtained when the precipitation from aqueous Bi(NO₃)₃ solution with tetramethylammonium hydroxide at pH ~ 14 was used. The precipitation at pH ~ 3.5 yielded cloverleaf-like particles of good uniformity, which were assigned to BiOOH (isomorphous with (La_{0.26}Bi_{0.24})Bi_{0.5}OOH). It was found that these particles were made up of much smaller primary BiOOH particles.

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1. Introduction

In recent years the investigations of bismuth oxide (Bi₂O₃) polymorphs have been intensified, due to their possible applications in solid oxide fuel cells, oxygen sensors, varistors or electrochromic devices. In the electrical sense, Bi₂O₃ ceramics can be compared to the stabilized cubic ZrO₂ solid electrolyte; however, they are less stable and, in addition to that, their ionic conductivity depends on the type of Bi₂O₃ polymorph [1]. Ionic conductivity and stability against ageing can be improved significantly by doping Bi₂O₃ with lanthanide cations [2–5]. The addition of Bi₂O₃ component is critical for the formation of electrically active grain boundaries in ceramic varistors [6].

Chemical, microstructural and electrical properties of Bi₂O₃ powders depend on the synthesis route, and for that reason the researches investigated different routes in the synthesis of Bi₂O₃

[7–10]. β-Bi₂O₃ nanotubes were obtained by oxidizing metallic bismuth in air at 200–220 °C [11].

δ-Bi₂O₃ thin films were prepared on glass substrates by CVD (Chemical Vapour Deposition) of BiI₃ at atmospheric pressure [12]. Shimano et al. [13] prepared Bi₂O₃ thin films by vacuum evaporation technique and found that these films showed electrochromic behaviour. For example, a clear electrochromic change between transparent and dark brown on switching between anodic (+1.2 V) and cathodic (–2.0 V) polarization was observed.

In the present work we report new results of the synthesis of Bi₂O₃ polymorphs using a modified sol–gel procedure [14,15] and the thermal treatment of the corresponding precursor. Also, the precipitation from an aqueous Bi(NO₃)₃ solution using the tetramethylammonium hydroxide (TMAH) was investigated. The aim of the present work was to establish the conditions for the synthesis of single phase α-Bi₂O₃ or β-Bi₂O₃, as well as to investigate the morphology of the particles in dependence on the conditions of the synthesis. The morphology of β-Bi₂O₃ particles plays an important role in the technology of Bi₂O₃-based ceramics.

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2. Experimental

2.1. Chemicals

Bismuth isopropoxide, $\text{Bi}[\text{OCH}(\text{CH}_3)_2]_3$, supplied by Alfa Aeser[®], and p.a. *n*-heptanol ($\text{C}_7\text{H}_{16}\text{O}$), supplied by Fluka were used as received. Glacial acetic acid, supplied by Kemika, Zagreb, was additionally purified, as reported elsewhere [14]. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (p.a.) and HNO_3 (p.a.) were supplied by Kemika, Zagreb. Tetramethylammonium hydroxide [$(\text{CH}_3)_4\text{NOH}$; 25% w/w aqueous solution, electron grade (metal basis)] was supplied by Alfa Aeser[®]. Twice distilled and deionised water was prepared in our own laboratory.

2.2. Synthesis

The precursor of Bi_2O_3 was prepared by the modified sol–gel method as follows: 1.5 ml of purified glacial acetic acid was added to 2 g of $\text{Bi}(\text{OPr})_3$, then mixed with 7.5 ml of *n*-heptanol in a Teflon beaker. The Teflon beaker was set in a stainless steel autoclave, tightly sealed and heated in the laboratory oven at

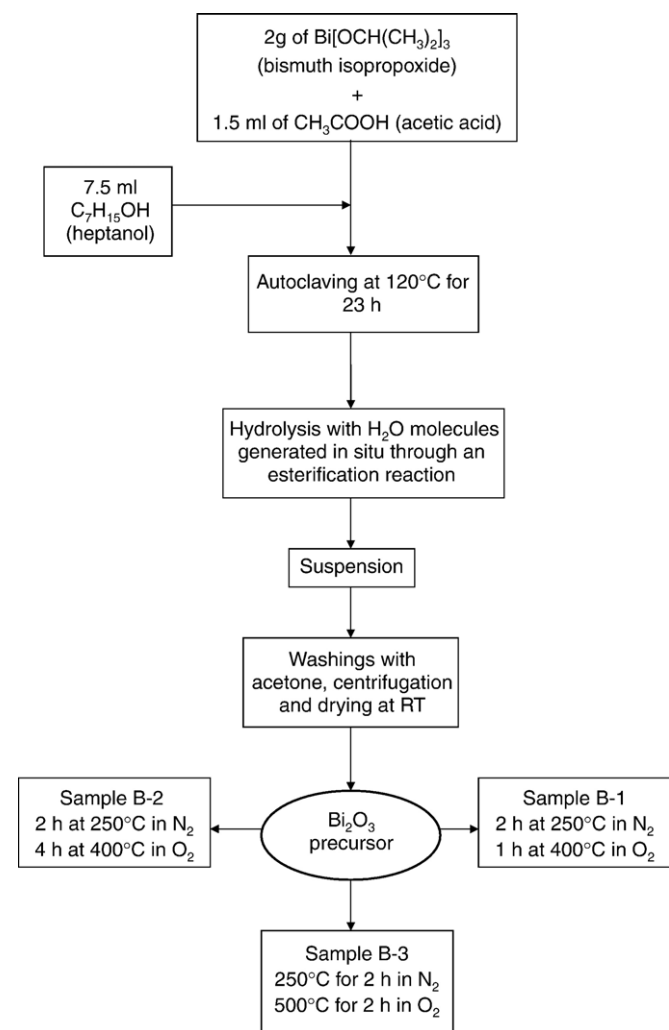


Fig. 1. Flow chart showing the syntheses of samples B-1 to B-3 by the modified sol–gel method.

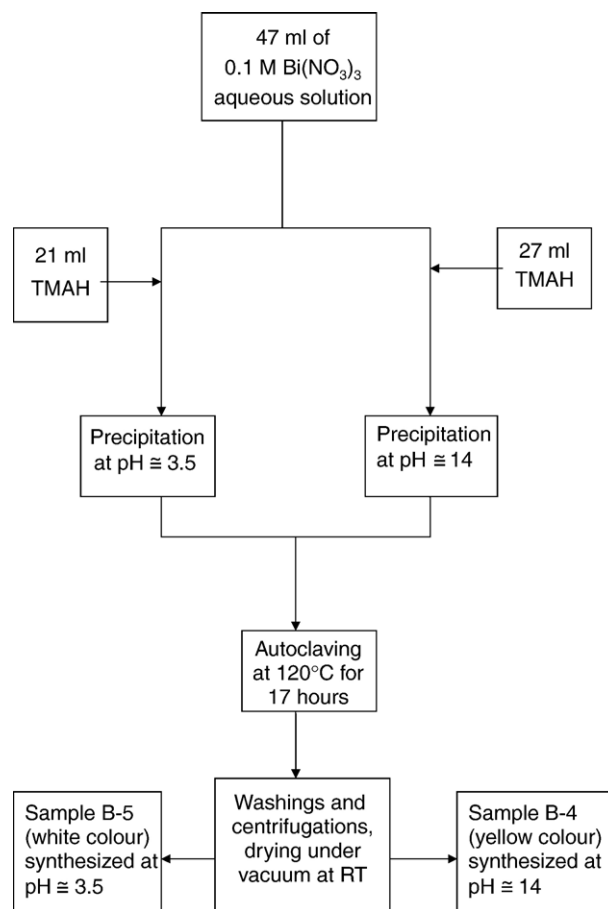


Fig. 2. Flow chart showing the syntheses of samples B-4 and B-5.

120 °C for 23 h. The precipitate thus obtained was quantitatively transferred into a broad Petri dish by washing with acetone, then dried under vacuum at room temperature (RT). Sample B-1 was obtained by heating the Bi_2O_3 precursor at 250 °C in a tubular furnace for 2 h in the stream of dinitrogen, then at 400 °C for 1 h in the stream of pure O_2 . By analogy, samples B-2 and B-3 were obtained by heating the Bi_2O_3 precursor at different temperatures and times, as shown in Fig. 1.

Samples B-4 and B-5 were prepared by a different experimental procedure. Firstly, an aqueous 0.1 M $\text{Bi}(\text{NO}_3)_3$ solution was prepared as follows: 9.796 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was weighted and quantitatively transferred into a 200 ml volumetric flask, followed by the addition of deionised water and drop by drop of concentrated nitric acid, swirling and shaking until the bismuth salt was completely dissolved. The final volume of deionised water was added to the calibration mark. pH 0.2 of this solution was measured with combined glass electrode and pH meter PHM-26 manufactured by Radiometer. Precipitation of bismuth ions was performed by a strong organic alkali (TMAH). TMAH was titrated to the aliquot of bismuth stock solution (47 ml) until the pH reached a value of ~ 3.5 or ~ 14 . Both suspensions were autoclaved at 120 °C for 17 h. The precipitates were isolated by repeated washing and centrifugation, then dried under vacuum at RT. The flow diagram of the preparation procedure for samples B-4 and B-5 is given in Fig. 2.

2.3. Instrumentation

X-ray powder diffraction (XRD) patterns were taken at RT using an automatic Philips diffractometer, model MPD 1880 (Cu K α radiation, graphite monochromator, proportional counter).

FE SEM micrographs were taken using a thermal field emission scanning electron microscope manufactured by JEOL Ltd. (model JSM-7000F) linked to the energy dispersive X-ray spectrometer manufactured by Oxford Instruments (model EDS/INCA 350).

3. Results

3.1. X-ray powder diffraction

Figs. 3 and 4 show characteristic XRD patterns of samples B-1, B-2, B-3 and B-4. XRD patterns of these samples were identified using data from JCPDS Powder Diffraction File [16]. XRD pattern of sample B-1 corresponded to the powder data for tetragonal β -Bi $_2$ O $_3$ [PDF card No. 78-1793, space group $P4_2/c$ (114), unit cell parameters $a=7.741(3)$, $c=5.634(2)$ Å at RT, $Z=4$; also card No. 27-0050]. XRD pattern recorded for sample B-2 corresponded to a mixture of monoclinic α -Bi $_2$ O $_3$ [PDF card No. 71-0465, space group $P2_1/c$ (14), unit cell parameters $a=5.850(1)$, $b=8.165(1)$, $c=7.510(1)$ Å, $\beta=112.38(1)$ at RT, $Z=4$; also card No. 41-1449] and tetragonal β -Bi $_2$ O $_3$. Sample B-3 was identified as monoclinic α -Bi $_2$ O $_3$. In these three samples, containing tetragonal and/or monoclinic Bi $_2$ O $_3$, a small fraction of unidentified phase(s) was observed. XRD patterns of sample B-4 showed a mixture of monoclinic and tetragonal Bi $_2$ O $_3$. Sample B-5 could be assigned to Bi(III)-oxyhydroxide (BiOOH) by comparison of XRD data obtained for this sample with those for isostructural La $_{0.26}$ Bi $_{0.74}$ OOH, for which there is a card in PDF, No. 82-1491 [space group $Pmm2$ (25), unit cell

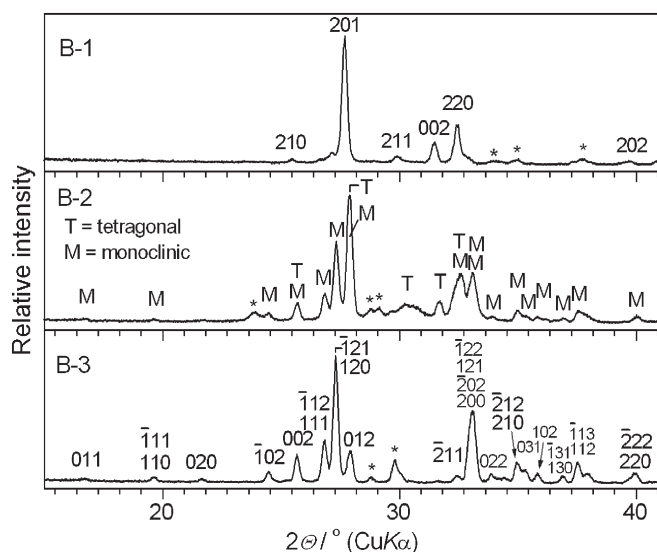


Fig. 3. Typical X-ray powder diffraction patterns of samples B-1, B-2 and B-3. XRD patterns of sample B-1 correspond to data for tetragonal β -Bi $_2$ O $_3$; sample B-2 is a mixture of monoclinic α -Bi $_2$ O $_3$ and tetragonal β -Bi $_2$ O $_3$; sample B-3 is a monoclinic α -Bi $_2$ O $_3$. For samples B-1 and B-3, above the diffraction maxima, hkl indices are indicated. Miller indices are indicated in the patterns of sample B-1 (tetragonal, β -Bi $_2$ O $_3$) and sample B-3 (monoclinic, α -Bi $_2$ O $_3$). For sample B-2, which is a mixture of monoclinic and tetragonal symmetry, T and M marks show the positions of diffraction lines of the tetragonal and monoclinic oxide, respectively. The asterisks indicate positions of XRD patterns of unidentified phase(s).

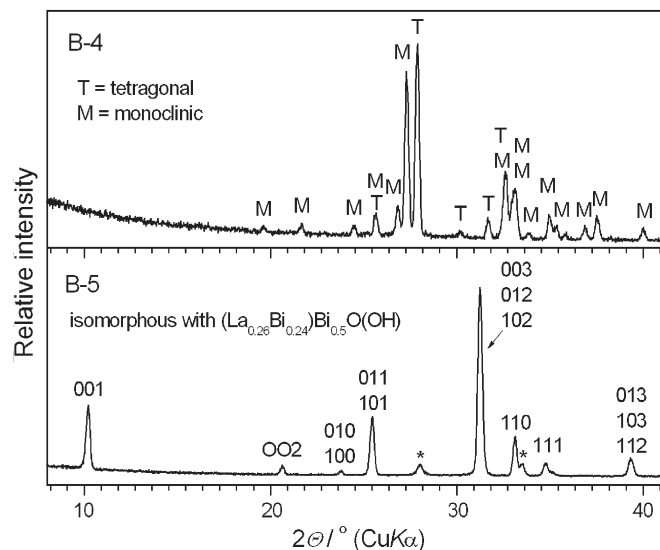


Fig. 4. Typical X-ray powder diffraction patterns of samples B-4 and B-5. Sample B-4 is a mixture of tetragonal and monoclinic Bi $_2$ O $_3$ (marks T and M). Sample B-5 is assigned to Bi(III)-oxyhydroxide (BiOOH), because its XRD patterns are very similar to data for (La $_{0.26}$ Bi $_{0.24}$)Bi $_{0.5}$ O(OH). The corresponding Miller indices are indicated. A small fraction of unidentified phase(s) is present (denoted by asterisks).

parameters $a=3.808(1)$, $b=3.811(1)$, $c=8.60(3)$ Å, $Z=2$). It is stated that bismuth oxyhydroxide is orthorhombic, and the values of the unit cell parameters a and b are little different. However, the interplanar spacings (d -values) for the two sets of lattice planes, hkl and khl (the first two indices permuted, index l the same), given in the card in PDF are the same (e.g. for 104 and 014, 213 and 123, etc.), as the structure was tetragonal. In sample B-5 in the present work, no splittings of diffraction lines hkl and khl were observed. The indices of diffraction lines of sample B 5 in Fig. 3 are those which appear in the card 82-1491.

Polymorphism is typical of Bi $_2$ O $_3$ and it may appear as α , β , γ or δ -phase. Generally, the low temperature monoclinic α -Bi $_2$ O $_3$ has a transition to cubic δ -Bi $_2$ O $_3$ at ~ 730 °C, which is stable up to the melting point at 825 °C. Followed by the cooling of δ -Bi $_2$ O $_3$ or melting to RT two metastable phases may appear, tetragonal (β -Bi $_2$ O $_3$) and body-centred cubic (γ -Bi $_2$ O $_3$). β -Bi $_2$ O $_3$ is obtained at 650 °C. Depending on the cooling history, γ -Bi $_2$ O $_3$ can also be obtained and continue to be stable up to RT. Doping of Bi $_2$ O $_3$ with metal cations, specifically with rare-earths, will significantly change the physical properties of Bi $_2$ O $_3$.

In the present work the Bi $_2$ O $_3$ precursor, obtained by the modified sol-gel procedure [14,15], upon heating for 2 h at 250 °C in N $_2$ atmosphere and 1 h at 400 °C in O $_2$ atmosphere yielded β -Bi $_2$ O $_3$ (sample B-1). Additional heating for 3 h at 400 °C in O $_2$ atmosphere induced a phase transition β -Bi $_2$ O $_3$ \rightarrow α -Bi $_2$ O $_3$, and in sample B-2 a mixture of these two phases was obtained. Upon increase in heating temperature to 500 °C, the α -Bi $_2$ O $_3$ as a single phase was detected by XRD. These results clearly showed that higher times of heating the precursor at 400 °C or 500 °C favoured the α -Bi $_2$ O $_3$ formation. On the other hand, "wet" precipitation from an aqueous Bi(NO $_3$) $_3$ solution by adding the aqueous solution of strong organic alkali (TMAH), followed by autoclaving, showed a strong dependence of the phase composition of the precipitate on the suspension pH. At pH ~ 3.5 bismuth (III)-oxyhydroxide isostructural with La $_{0.26}$ Bi $_{0.74}$ OOH was obtained, whereas at pH ~ 14 a mixture of oxide phases, α -Bi $_2$ O $_3$ and β -Bi $_2$ O $_3$, was obtained.

Reference literature reports a strong influence of the synthesis route on the phase composition of Bi $_2$ O $_3$ powders. For example, Jungk and Feldmann [7] synthesized α -Bi $_2$ O $_3$ powder using the polyol-mediated

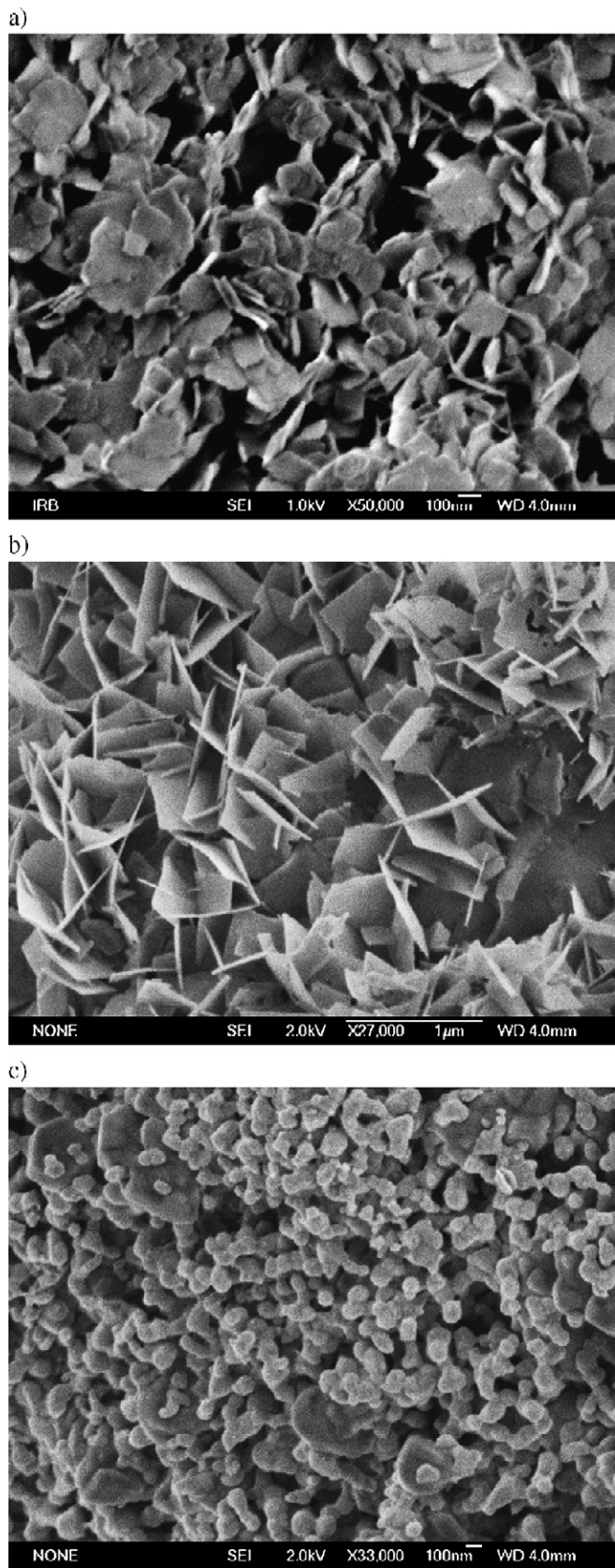


Fig. 5. FE SEM micrographs of the Bi_2O_3 precursor (a), sample B-1 (b) and sample B-2 (c).

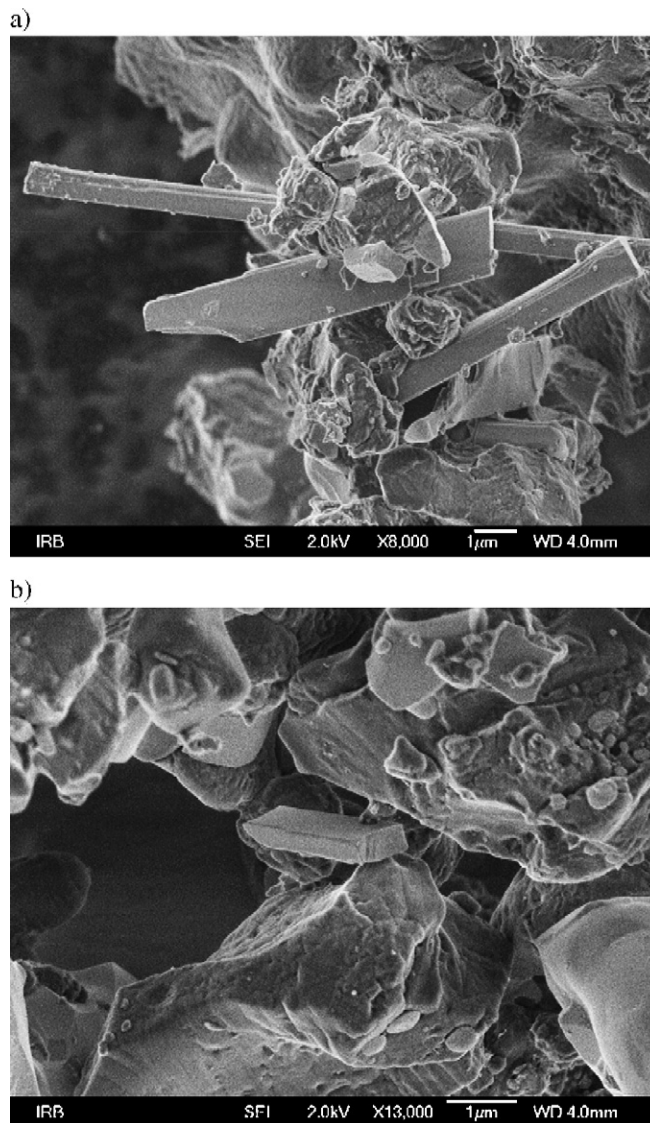


Fig. 6. FE SEM micrographs of sample B-3 (two details; a, b).

synthesis. This synthesis yielded 70–90 nm $\alpha\text{-Bi}_2\text{O}_3$ particles; however, these particles were heavily agglomerated in the powder. Yang et al. [8] synthesised acicular Bi_2O_3 by hydrothermal treatment of $\text{Bi}(\text{OH})_3$ at 120 °C for 0.5 h. Iha et al. [17] reported a synthesis of $\beta\text{-Bi}_2\text{O}_3$ by hydrolysis of Bi^{3+} ions in decomposing urea, followed by heating an isolated precipitate at 400 °C. On the other hand, Monnereau et al. [10] obtained $\beta\text{-Bi}_2\text{O}_3$ by decomposition of $\text{Bi}(\text{III})$ -oxalate between 250 and 300 °C. Thus obtained $\beta\text{-Bi}_2\text{O}_3$ was stable up to ~ 300 °C at which temperature transition to $\alpha\text{-Bi}_2\text{O}_3$ was observed. Mädler and Pratsinis [18] prepared $\beta\text{-Bi}_2\text{O}_3$ nanoparticles by flame spray pyrolysis of $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ dissolved in a solution of ethanol/nitric acid or ethanol/acetic acid.

3.2. FE SEM

A review of reference literature showed that researchers have been less focused on the particle morphology of Bi_2O_3 polymorphs although this is crucial in the applications of Bi_2O_3 powders. For that reason, we focused more on this problem by using high-resolution scanning electron microscopy. Fig. 5 shows FE SEM micrographs of the Bi_2O_3

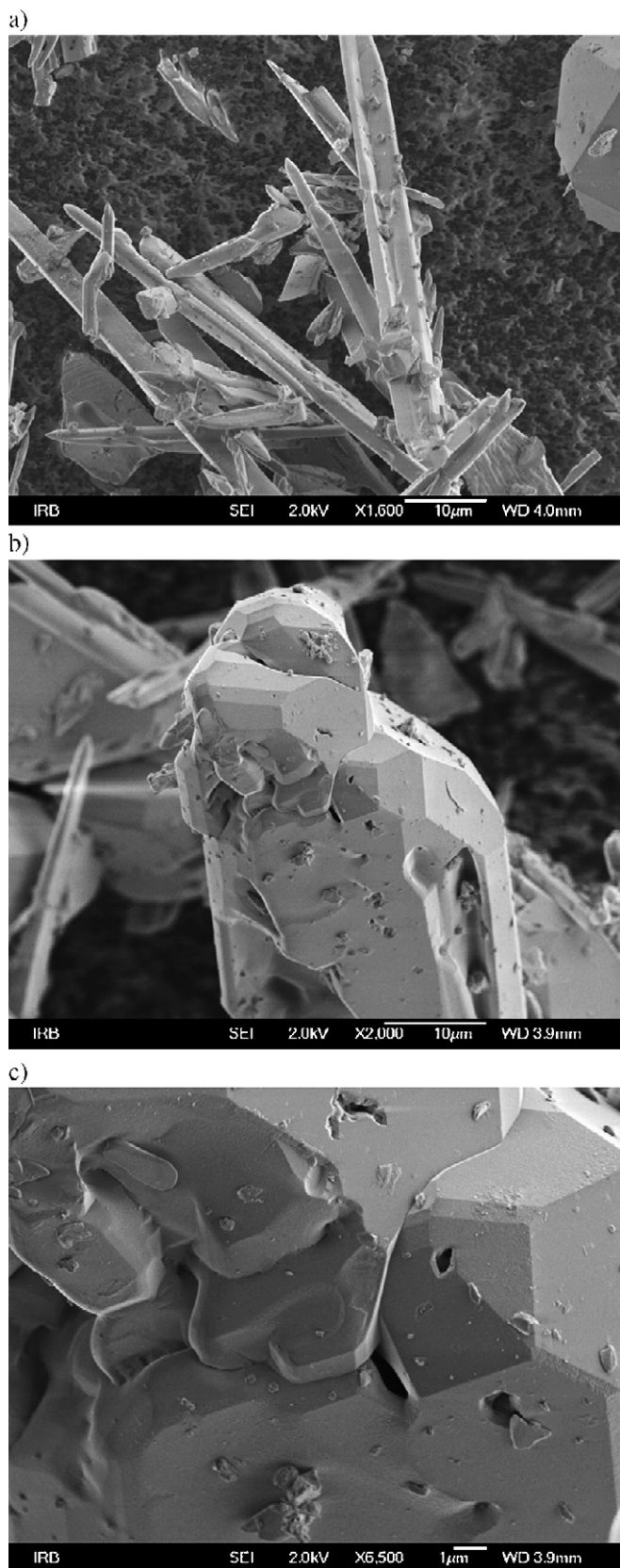


Fig. 7. FE SEM micrographs of samples B-4 (a) and B-5 (b). An enlarged part of micrograph (b) is shown (c).

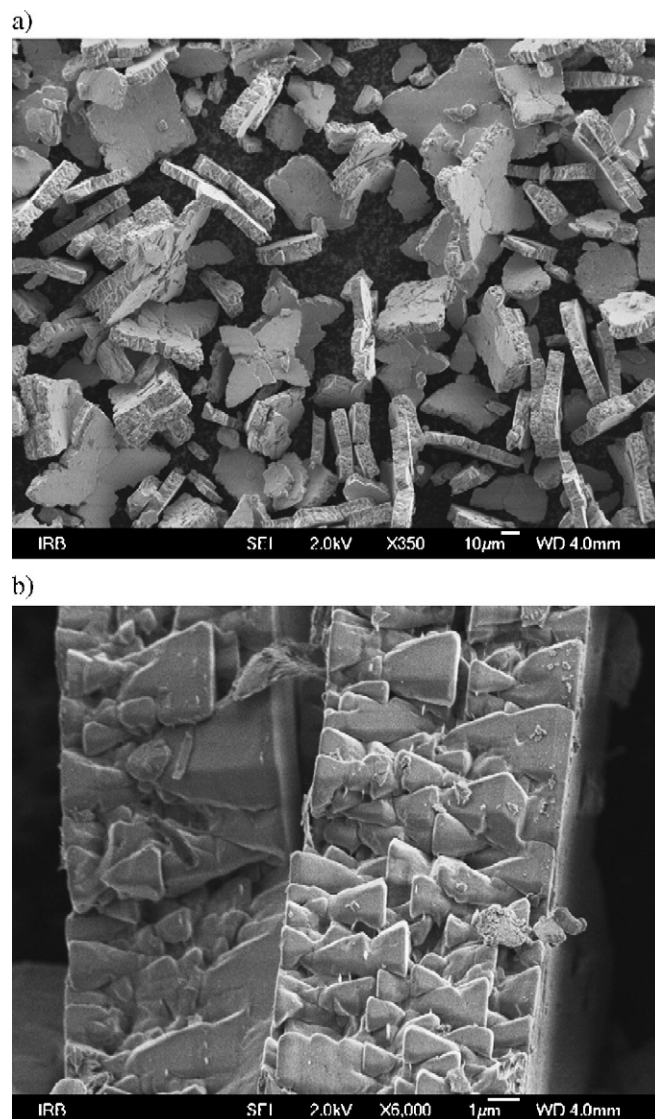


Fig. 8. FE SEM micrographs of sample B-5 (two details; a, b).

precursor and samples B-1 and B-2. The micrograph of the Bi_2O_3 precursor (Fig. 5a) shows plate-like particles of varying dimensions. On the other hand, sample B-1 obtained from that precursor by heating at 400 °C showed well-shaped plate-like $\beta\text{-Bi}_2\text{O}_3$ particles of almost identical widths (Fig. 5b). This morphology is not exhibited in sample B-2. Pseudospherical particles of about 100 nm and much larger particles are visible. FE SEM micrographs (two details; Fig. 6a, b) of $\alpha\text{-Bi}_2\text{O}_3$, prepared at 500 °C, show very large particles in the micrometer range. The beginning of $\alpha\text{-Bi}_2\text{O}_3$ vitrification of these large particles can be observed. The presence of a low fraction of small-sized $\alpha\text{-Bi}_2\text{O}_3$ particles is also visible in the same micrographs.

The mixture of $\alpha\text{-Bi}_2\text{O}_3$ and $\beta\text{-Bi}_2\text{O}_3$, precipitated from the aqueous $\text{Bi}(\text{NO}_3)_3$ solution by TMAH at pH ~ 14 (sample B-4) yielded different morphologies (Fig. 7) in relation to the previous synthesis route (Fig. 3c). Fig. 7 shows very long Bi_2O_3 rods of different sizes. This sample (B-4) also showed the formation of a unique microstructure, of which an example is shown in Fig. 7b. A large Bi_2O_3 particle is shown having a “robot-like” morphology. The shoulder of this “robot-like” particle is enlarged in Fig. 7c. These examples show a very high dependence of Bi_2O_3 microstructure on the synthesis route. BiOOH

particles (Fig. 8; two details) exhibit a cloverleaf morphology (Fig. 8a). The micrograph of the cross-section of one particle (Fig. 8b) shows that these particles possess a substructure, *i.e.* they are made up of much smaller primary BiOOH particles. It can also be noticed that BiOOH particles are so arranged that the width of the secondary particle has almost the same value at different surface points.

4. Conclusion

- A modified sol–gel procedure [14,15] was used to prepare the Bi₂O₃ precursor which was transformed into β-Bi₂O₃ at 400 °C, or into a mixture of β-Bi₂O₃/α-Bi₂O₃ with prolonged heating at the same temperature. β-Bi₂O₃ obtained at 400 °C consisted of well-shaped plate-like particles as shown by FE SEM. The mixture of β-Bi₂O₃/α-Bi₂O₃, also obtained at 500 °C, showed two kinds of particles. Pseudospherical particles of about 100 nm and much larger particles were found by FE SEM. α-Bi₂O₃ obtained by heating the Bi₂O₃ precursor at 500 °C showed particles of varying size and a beginning of α-Bi₂O₃ vitrification. β-Bi₂O₃ and α-Bi₂O₃ prepared by the modified sol–gel procedure contained a small fraction of unidentified phase(s), as found by XRD.
- Precipitation from the aqueous Bi(NO₃)₃ solution showed a different microstructure in relation to the modified sol–gel procedure. A particle precipitated at pH ~ 14 by adding TMAH showed very long Bi₂O₃ rods of varying size. The formation of a unique microstructure (“robot-like”) was observed. On the other hand, precipitation at pH ~ 3.5 yielded cloverleaf-like particles of good uniformity, which can be assigned to BiOOH (isomorphous with (La_{0.26}Bi_{0.24})Bi_{0.5}OOH). FE SEM showed that these particles are composed of much smaller primary BiOOH particles.

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