

Thermal transformations of bismuth (III) tartrates

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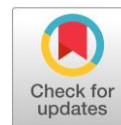
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Abstract

The processes of oxidative thermolysis of bismuth tartrates $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ and $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ precipitated from bismuth nitrate solutions was studied by the methods of X-ray diffraction, thermal analysis, IR spectroscopy and chemical analysis. The staging of thermal transformation processes was determined. Morphological studies of initial precursors and the final products of their thermal transformations were carried out. The expediency of obtaining fine-crystal powders of the tetragonal bismuth oxide modification $\beta\text{-Bi}_2\text{O}_3$ with uniform sized particles by oxidative thermolysis of $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ was shown.

Keywords

bismuth tartrates
thermal transformations
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tetragonal bismuth (III) oxide
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IR spectroscopy
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1. Introduction

Tartaric acid salts are used as compounds showing antimicrobial activity [1–3] and precursors for the synthesis of metal nanoparticles [4, 5], oxides [6, 7] and complex oxide materials [8, 9]. Bismuth compounds with tartaric acid also find applications in these areas. Bismuth tartrates have a long history of medical use against various kinds of bacterial infections [10, 11] and are promising as substances for the treatment of infections caused by protozoan parasites [12]. However, the use of bismuth tartrate as a precursor for the synthesis of oxide materials has not yet been sufficiently reported in the literature.

A method for obtaining bismuth oxide used in the production of enamels and ceramic paints from bismuth tartrate synthesized by treatment of metallic bismuth with tartaric acid while grinding in a mortar followed by heating the resulting mixture in the presence of water at 50–60 °C was proposed [13]. The composition of bismuth tartrate was not indicated, nor was the polymorphic modification of the resulting oxide. Analysis of the literature data allows assuming that at bismuth tartrate heat treatment temperatures of 270–300 °C, the target product is the tetragonal modification $\beta\text{-Bi}_2\text{O}_3$. In order to obtain nanoparticles of the monoclinic $\alpha\text{-Bi}_2\text{O}_3$ modification, a synthesis using polyeth-

ylene glycol 2000 and the initial bismuth-containing compound of two-dimensional coordination polymer composition $\{[\text{Bi}(\mu\text{-C}_4\text{H}_4\text{O}_6)(\text{NO}_3)(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}\}_\infty$ [14] was proposed. The above mixture was heated at 500 °C for 3 h. For the synthesis of a bismuth-containing compound, an expensive medium, bismuth nitrate, was used, which was treated at a temperature of 25 °C in stages with tartaric acid solution at a molar ratio of tartrate ions to bismuth of 0.5. The resulting precipitate was filtered off, and the mother liquor was kept at 4 °C until colorless crystals of the desired composition were obtained.

Bi_2O_3 , an important metal oxide semiconductor, has attracted particular attention because of its excellent optical and electrical properties, such as wide bandwidth, high refractive index, high dielectric constant and good photoconductivity. Due to these unique characteristics, bismuth oxides can be used in various fields such as fuel cells, sensor technology, oxide varistors, ionic conductors, photovoltaic materials, high temperature superconductors and functional ceramics. Bi_2O_3 is also an important component in the production of transparent ceramic glass, optical coatings and catalysts [15]. Bismuth oxide (III) is included as a radiopaque agent in dental materials, including hydraulic silicate cements; it is a preferred material for some endodontic procedures [16].

Recently, a large number of studies have been devoted to the photocatalytic activity of bismuth oxides, with a higher activity of the tetragonal modification β - Bi_2O_3 compared to the monoclinic α - Bi_2O_3 being noted [17]. Tetragonal bismuth oxide is also used in the synthesis of pigments for the production of coatings, enamels and ceramic paints [18, 19].

The process of obtaining bismuth compounds for engineering and medicine is associated with the hydrolytic processing of bismuth nitrate solutions, as HNO_3 is the best solvent for metallic bismuth and its alloys [20]. Precipitation of the compounds is carried out by diluting bismuth-containing solutions with water or by adding carboxylic acids and their salts to them.

The purpose of this work was to investigate the oxidative thermolysis of bismuth tartrate obtained as a result of processing nitric acid solutions to produce β - Bi_2O_3 . Two objects of study were chosen: the medium bismuth tartrate of the composition $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$, which contains a minimum amount of tartrate ions and is used in medicine as an anti-bacterial substance, and the bismuth nitrate-tartrate of the composition $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$; the latter was selected to determine the role of nitrate ions in the process of oxidative thermolysis [21].

2. Experimental

All reagents in this work were of analytical grade and were used without further purification. Bismuth stock solution in nitric acid ($420 \text{ g} \cdot \text{l}^{-1} \text{ Bi}^{3+}$, $100 \text{ g} \cdot \text{l}^{-1}$ free HNO_3) was prepared by dissolving pure grade bismuth oxide in 7 M nitric acid.

Precipitation of bismuth nitrate-tartrate $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ and bismuth tartrate $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ was carried out in Teflon or glass vessels equipped with stirrers and temperature-controlled using water baths by adding bismuth-containing solutions to aqueous solutions of *L*(+)-tartaric acid $\text{C}_4\text{H}_6\text{O}_4$ and sodium tartrate $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$, respectively, with a molar ratio of tartrate ions to bismuth equal to 1.1. The mixtures were stirred for 1 h at 25 °C. The precipitates were filtered off and dried in air.

Chemical determination of macro quantities of Bi (III) in solutions was carried out by titration with a complexon III solution in the presence of the xylenol orange indicator. Micro quantities of Bi (III) were determined photocolometrically using potassium iodide. Carbon, nitrogen and hydrogen contents in the obtained samples were determined by the modified Pregle method with gravimetric termination.

The phase compositions of the samples were analyzed using X-ray diffraction technique (XRD) on a diffractometer (Bruker D8 Advance, Germany) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray diffraction data were collected in scanning mode at a scanning speed of $0.5^\circ \text{ min}^{-1}$ in the range of $4^\circ < 2\theta < 70^\circ$. Phase analysis was performed using the ICDD PDF-4 database (2011).

The infrared absorption spectra were recorded with the IR-Fourier spectrometer Scimitar FTS 2000 (Digilab) in the range of $400\text{--}4000 \text{ cm}^{-1}$. The samples were prepared as tablets with calcined KBr. Microstructure of the samples was studied by scanning electron microscopy (SEM) using a Hitachi TM 1000 Scanning Electron Microscope.

Thermal analysis of the samples was carried out on a synchronous thermoanalytical complex STA 449 F1 Jupiter (Netzsch) dynamically under heating in an Ar/O_2 atmosphere ($80/20$; O_2 $10 \text{ ml} \cdot \text{min}^{-1}$; Ar $40 \text{ ml} \cdot \text{min}^{-1}$). Samples weighing 180–200 mg were placed in crucibles of Pt-10% Rh alloy and heated at a rate of $10^\circ \cdot \text{min}^{-1}$ to 350–500 °C. The mass spectra of the gaseous products formed in the course of the heat treatment were recorded in the multi-ion detection mode at m/z of 18, 28, 30 and 44 with a QMS 403D quadrupole mass spectrometer (Netzsch).

3. Results and Discussion

3.1. Synthesis and characterization of bismuth tartrate

According to the data of chemical analysis, when a nitric acid bismuth-containing solution is added to a solution of *L*(+)-tartaric acid at a molar ratio of tartrate ions to bismuth n equal to 1.1 and temperatures of 25 and 60 °C, the samples contain (%): Bi – 45.0, C – 10.71, H – 1.59 and N – 2.98, and the molar ratio of bismuth (III) to tartrate and nitrate ions in the precipitate is 1:1:1. A comparison of the diffractograms of precipitation products with a reference XRD pattern plotted according to [14] (Figure 1, 1 and 2) shows significant differences in the structures of the studied nitrate-tartrate. This suggests that, under these conditions, the compound $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$, the formation of which was reported earlier in [21], is precipitated. Studies have shown that this compound is also formed after the treatment of medium bismuth nitrate of the composition $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ by tartaric acid solution at a molar ratio of tartrate ions to bismuth in the system of 1–1.1 at 25 °C.

The compound $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ becomes X-ray amorphous as a result of multiple washings with water (Figure 1, 3). Amorphization of the product is already observed after a single washing with water. For a complete purification from nitrate ions 5–7 washes at room temperature are necessary. The content of nitrate ions in the obtained samples does not exceed 0.02%. According to chemical analysis the samples contain (%): Bi – 55.9, C – 12.7, H – 1.34, which corresponds to the molar ratio of bismuth (III) to tartrate ions of 1:1 and indicates that the obtained precipitates, as will be shown below, are bismuth tartrate of the composition $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$. Further conclusions about the composition of the compound are based on the analysis of its IR spectra in comparison with those of tartaric acid, bismuth nitrate-tartrate and tartrates of other metals.

In the IR spectrum of tartaric acid (Figure 2, 1), the presence of a carboxyl group appears as weak absorption bands at 3206 and 3112 cm^{-1} , corresponding to the valence vibrations of the O–H bond bound in carboxyl group dimers [22].

The complex band with maxima at 1740 and 1720 cm^{-1} corresponds to the valence vibrations of the C=O bond of the unsubstituted carboxyl group [23]. These bands are absent in the spectra of carboxylic acid salts, but there are bands in the region of $\sim 1550\text{--}1610$ and $\sim 1300\text{--}1400$ cm^{-1} , respectively, related to asymmetric and symmetrical valence vibrations of ionized groups of COO^- [24]. If in the examined compounds the tartrate anion associated with the bismuth cation has at least one non-dissociated group — COOH , bands in the ~ 1700 cm^{-1} region should be present in the IR absorption spectra of salt [25].

For the IR spectrum of the bismuth nitrate-tartrate $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ (Figure 2, 2), along with the absorption bands of the carboxylate group (1590 and 1390 cm^{-1}) [26], we observed band broadening in the region of 1400–1280 cm^{-1} and the appearance of a significant shoulder at 1310 cm^{-1} , which appears to be due to the absorption of nitrate ions [27]. A broad band with a maximum at 3400 cm^{-1} relates to the valence vibrations of the O–H bond of water molecules and oxo- groups of tartrate ions involved in the formation of hydrogen bonds [28].

In the IR spectrum of the bismuth tartrate with the composition $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ (Figure 2, 3), a number of characteristic features are observed in comparison with the spectra of tartaric acid. In the spectra of the compound there are no valence vibration bands $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ of carboxylic tartaric acid groups indicating the presence of a twice deprotonated tartaric acid anion. Bands of valence vibrations of carboxylate groups of asymmetric $\nu_{\text{as}}(\text{COO}^-)$ with a maximum at 1570 cm^{-1} and symmetrical $\nu_{\text{s}}(\text{COO}^-)$ at 1385 and 1360 cm^{-1} appear, which indicates the substitution of protons in carboxyl groups of carboxylic acid for the Bi cation [29]. A wide absorption band with a maximum at 1070 cm^{-1} indicates the presence of dissociated oxo- groups in the compound under study [25, 26]. In the spectrum of the nitrate-tartrate complex two bands are observed in this region, indicating the presence of unsubstituted protons of alcohol groups. Weak wide bands with maxima at 470 and 140 cm^{-1} are related to the valence and deformation vibrations of the Bi–O bond, respectively [27]. The presence of water in the compound is indicated by a wide diffuse band in the area of 3650–2800 cm^{-1} , corresponding to valence $\nu(\text{OH})$ vibrations of water, as well as a band of plane deformation $\delta(\text{OH})$ vibrations of water at 1700–1640 cm^{-1} , which show as a shoulder with a maximum at 1638 cm^{-1} [29].

Thus, as a result of repeated washings of $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ with water, bismuth tartrate monohydrate $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ is formed, the composition of which is in good agreement with the physico-chemical investigations and the results of IR spectroscopy.

By adding a bismuth nitrate solution to a sodium tartrate solution, X-ray amorphous samples were obtained, the IR spectra of which coincided with those of $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$. It should be noted that in this case there is no effective purification of the product from nitrate ions, which is appar-

ently associated with the coprecipitation of bismuth oxonitrates at the stage of adding a bismuth solution to the alkaline salt solution.

3.2. Thermal analysis of bismuth tartrate

According to thermal analysis data, the process of oxidative thermolysis of $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ has a complex nature with a predominance of exothermic stages (Figure 3) and, as follows from analysis of the obtained mass spectra of gaseous products, involves internal oxidation of tartrate ions by nitrate ions, as a result of which nitrate nitrogen is reduced to N_2 (Table 1). This is confirmed by the registered amount of NO ($m/z = 30$), which is 20 times less than the amount of CO_2 ($m/z = 44$). Based on the ratio of the amount of nitrogen and carbon in the initial compound, in the absence of the oxidation process the ionic current integral of NO would be about 4 times smaller than for CO_2 .

Also, the ionic current integral for $m/z = 28$ (N_2 or CO) is too large to be related only to the ionization fragment of CO_2 (for CO about 10% of the integral for $m/z = 44$).

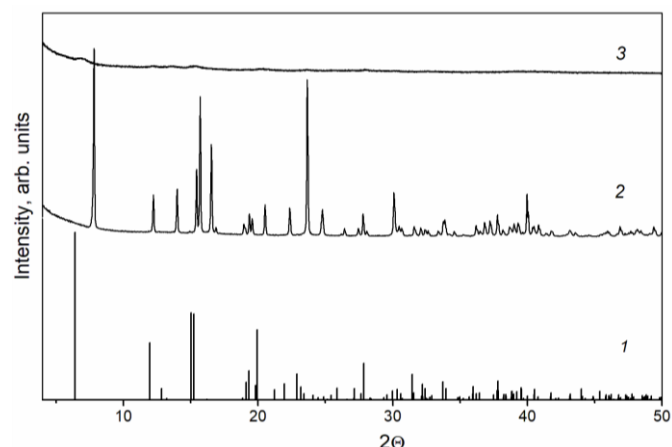


Figure 1 Reference XRD pattern of $\{[\text{Bi}(\mu\text{-C}_4\text{H}_4\text{O}_6)(\text{NO}_3)(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}\}_\infty$ (1) modeled on the basis of the literature data [14] and X-ray powder diffraction patterns of $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ (2) and the product of its washing with water (3).

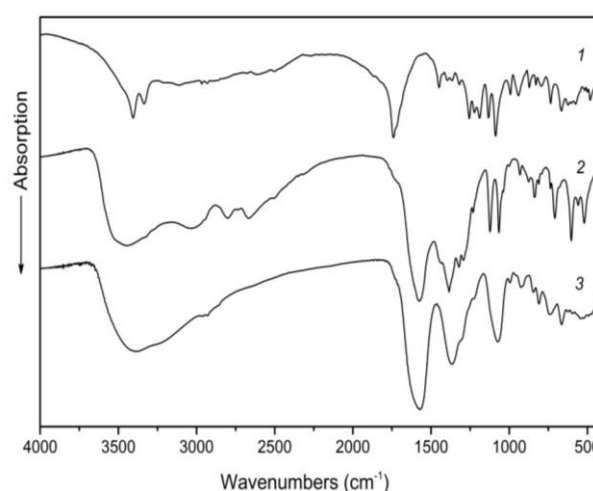


Figure 2 IR absorption spectra of tartaric acid $\text{C}_4\text{H}_6\text{O}_6$ (1) and bismuth tartrates $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ (2) and $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ (3).

Table 1 Results of mass spectra analysis of gaseous products.

m/z	Ionic current integral, A·s
18	$81.83 \cdot 10^{-9}$
28	$24.30 \cdot 10^{-9}$
30	$5.19 \cdot 10^{-9}$
44	$109.27 \cdot 10^{-9}$

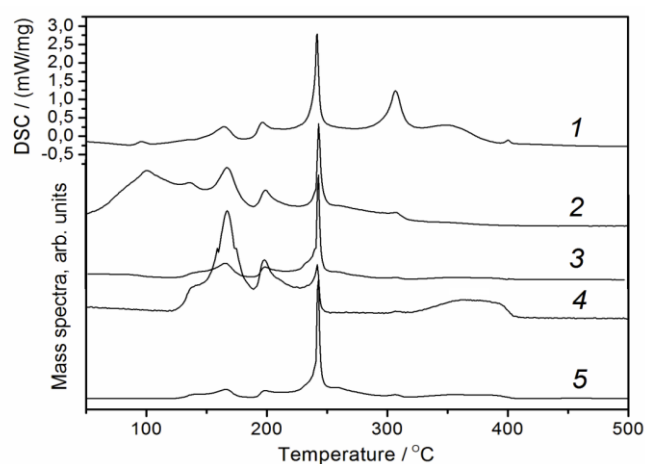
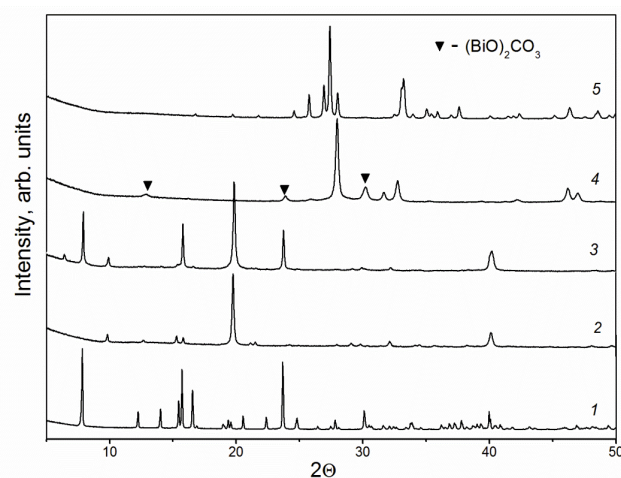
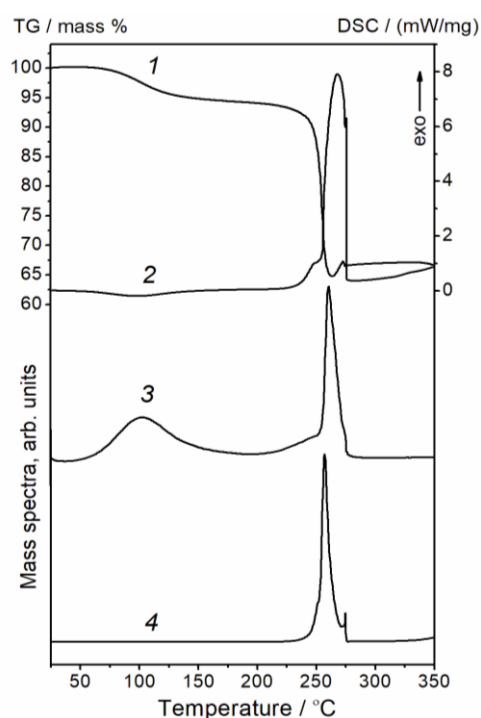
Based on the DSC data, the temperatures corresponding to the most pronounced thermal effects were determined, at which the $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ samples were kept consecutively for 3 h and analyzed by X-ray diffraction (Figure 4).

According to the XRD data (Figure 4), when $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ is kept at 100 °C for 3 h, the diffraction pattern changes significantly (Figure 4, 1 and 2) and corresponds to a partially dehydrated initial compound. This process is reversible, since when the samples heated at 100 °C are kept in air for several days, the main reflections of nitrate-tartrate reappear on the diffraction patterns (Figure 4, 3). The samples obtained at temperatures of 150, 200, and 250 °C are X-ray amorphous. The diffraction pattern of the sample aged at 300 °C clearly shows reflexes of the tetragonal modification of $\beta\text{-Bi}_2\text{O}_3$ (ICDD 010-77-5341) and bismuth oxocarbonate $(\text{BiO})_2\text{CO}_3$ (ICDD 000-41-1488) (Figure 4, 4). The increase of curing time at 300 °C up to 6 h also yields the $\beta\text{-Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$ composite. Further increase in temperature leads to the $\beta \rightarrow \alpha$ phase transition, the product is the monoclinic modification $\alpha\text{-Bi}_2\text{O}_3$ (ICDD 040-03-2034) (Figure 4, 5).

The results of the thermal analysis of $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ are presented in Figure 5. The TG curve shows several different stages of weight loss. The process of oxidative thermolysis of bismuth tartrate monohydrate begins with the removal of one molecule of crystallization water (the endothermic effect at 100 °C). The weight loss at this stage of decomposition is 4.8%, which corresponds to the expected composition of $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$.

According to mass spectrometry data, two successive exothermic effects at 250 and 270 °C are associated with the release of H_2O and CO_2 due to the decomposition of tartrate ions. Thus, a rather low decomposition temperature of the compound in the reaction range 240–280 °C and the absence of nitrate ions in the composition make the medium bismuth tartrate a more preferable precursor for the production of $\beta\text{-Bi}_2\text{O}_3$, compared with tartrates containing nitrate ions. Based on the data obtained, the temperature regime and duration of annealing of the $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ samples were chosen.

According to the XRD data, in the diffractogram of the initial sample $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ (Figure 6, 1), kept at a temperature of 240 °C, reflections of bismuth oxocarbonate $(\text{BiO})_2\text{CO}_3$ clearly appear in the region of the X-ray amorphous halo (Figure 6, 2), and the product of annealing at 270 °C is a mixture of $\beta\text{-Bi}_2\text{O}_3$ and $(\text{BiO})_2\text{CO}_3$ (Figure 6, 3); upon further heating of the sample at 280 °C, the main reflections of bismuth oxocarbonate disappear (Figure 6, 4). Powders of single-phase $\beta\text{-Bi}_2\text{O}_3$ were obtained by keeping $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ for 6 h at 280 °C.

**Figure 3** DSC (1) and mass spectra curves (2–5) of decomposition of $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$. m/z : 18 (2), 28 (3), 30 (4), 44 (5).**Figure 4** X-ray powder diffraction patterns of $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ (1) and the products of its oxidative thermolysis for 3 h at 100 (2), 300 (4), 320 °C (5) and the product of thermolysis at 100 °C kept in air (3).**Figure 5** TG (1), DSC (2) and mass spectra curves (3, 4) of decomposition of $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$. m/z : 18 (3), 44 (4).

Researching the mechanisms of thermal decomposition of tartrates has been mainly limited to the processes occurring in an inert atmosphere [30, 31]. Thus, in the thermal decomposition of tartrates of alkaline-earth [30] and rare-earth elements [31] the formation of metal oxalates as intermediate products with their subsequent transformation into carbonates and corresponding oxides was indicated. In our study of oxidative thermolysis process of the bismuth tartrate, based on the XRD data, the formation of bismuth oxalate with the proposed composition $\text{BiC}_2\text{O}_4(\text{OH})$ [32] as an intermediate product was not established. However, the stage of bismuth oxocarbonate formation was confirmed.

SEM images indicate that the samples of the $\beta\text{-Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$ composite and $\beta\text{-Bi}_2\text{O}_3$ obtained by oxidative thermolysis of $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ and $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$, respectively, retain the morphology of the original precursors (Figure 7). A sample of the $\beta\text{-Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$ composite obtained from $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ is a large aggregate of plate crystals with signs of a block structure, just like the original $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ (Figure 7, *a* and *b*). The samples of $\beta\text{-Bi}_2\text{O}_3$ synthesized from $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ are aggregates consisting of uniformly sized (1–2 μm) amorphous particles (Figure 7, *c* and *d*).

4. Conclusions

The final product of the oxidative thermolysis of bismuth tartrates of the compositions $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ and $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ is bismuth oxide, whose samples retain the morphology of the initial precursors. Oxidative thermolysis processes of the precursor compounds include a bismuth oxocarbonate $(\text{BiO})_2\text{CO}_3$ formation stage as an intermediate product, and in the case of the bismuth nitrate-tartrate – also redox reactions involving tartrate and nitrate ions. Thus, fine-crystalline powders of tetragonal bismuth oxide $\beta\text{-Bi}_2\text{O}_3$ with uniformly sized particles are expediently obtained by oxidative thermolysis of $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ at 280 °C for 6 h.

Supplementary materials

No supplementary materials are available.

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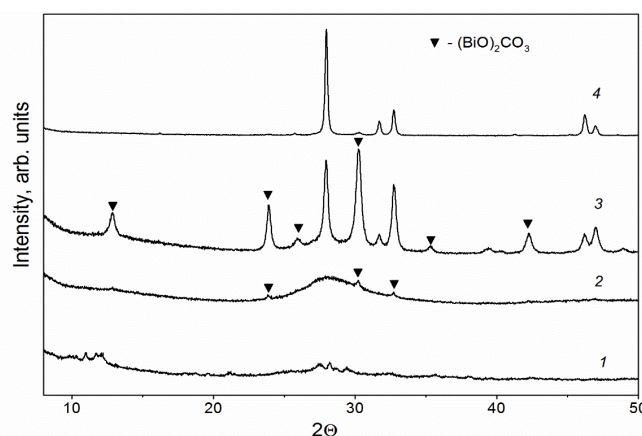


Figure 6 X-ray powder diffraction patterns of $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ (1) and the products of its oxidative thermolysis for 3 h at 240 (2), 270 (3) and 280 °C (4).

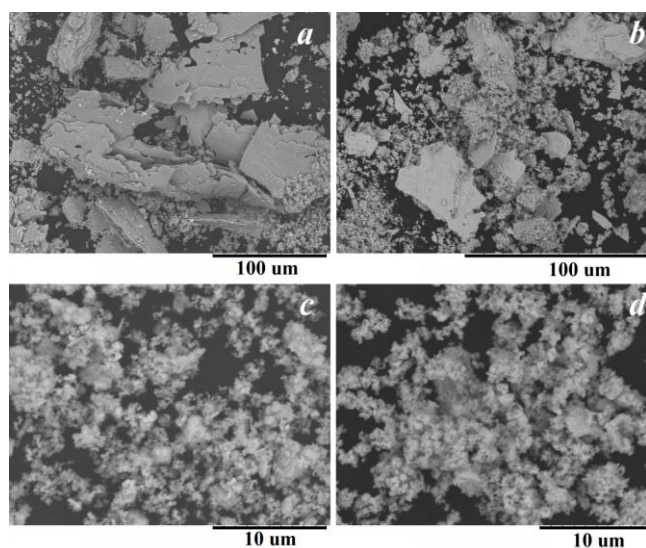


Figure 7 SEM images of $[\text{Bi}(\text{NO}_3)(\text{C}_4\text{H}_4\text{O}_6)] \cdot 3\text{H}_2\text{O}$ (*a*), $\text{BiC}_4\text{H}_3\text{O}_6 \cdot \text{H}_2\text{O}$ (*c*) and the products of its oxidative thermolysis: $\beta\text{-Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$ (*b*) and $\beta\text{-Bi}_2\text{O}_3$ (*d*).

Author contributions

Conceptualization: E.V.T.
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Formal Analysis: K.B.G., L.I.A.
Funding acquisition: E.V.T., Yu.M.Y.
Investigation: T.E.T., K.B.G., L.I.A.
Methodology: E.V.T., Yu.M.Y.
Project administration: E.V.T.
Resources: Yu.M.Y., K.B.G.
Supervision: E.V.T., Yu.M.Y.
Validation: L.I.A., T.E.T.
Visualization: E.V.T., L.I.A.
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Conflict of interest

The authors declare no conflict of interest.

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