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SYNTHESIS AND THERMAL DECOMPOSITION OF BISMUTH PEROXOTITANATE TO $Bi_2Ti_2O_7$

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Bi-peroxotitanate was synthesized by a peroxo method and after thermal decomposition $Bi_2Ti_2O_7$ was obtained. DTA, TG and DSC curves of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ were recorded and used to determine isothermal conditions suitable for obtaining the intermediate samples corresponding to the phases observed during the thermal decomposition. The samples were identified by quantitative analysis, IR spectroscopy and X-ray analysis. The experimental results were used to propose a mechanism of thermal decomposition of the investigated compound to a nanosized $Bi_2Ti_2O_7$. The optimum conditions were also determined for obtaining $Bi_2Ti_2O_7$, which is applicable for piezosensors.

Keywords: *$Bi_2Ti_2O_7$, bismuth peroxotitanate, DSC, DTA, TG*

Introduction

The titanates have a broad application in electronics and this defines the great interest for their obtaining [1–4]. Bismuth titanates are used for the production of piezoceramics not containing Pb^{2+}. The following find application: $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$ [5–8], $SrBi_4Ti_4O_{15}$ [6], $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ [8], $Bi_4Ti_3O_{12}$–IrO_2 [9], $Bi_4Ti_7O_{20}$ [10], $Bi_{4-x}La_xTi_3O_{12}$ [11], etc. Some of the materials are in their pure form and others are dotted with Nb_2O_5, Ta_2O_5, Sb_2O_5, WO_3, V_2O_5 [12–14].

Bismuth titanates have a number of advantages compared to the classic piezomaterials. They are distinguished for a relatively high piezoelectric charge constant d_{33} [12] in a wide temperature range from 20 to 600°C and pressure of 0 to 300 MPa. They have a high Curie temperature T_C, as well as great parameter stability in time [5, 6]. That is why ceramics on the basis of bismuth titanates are very suitable for piezosensor functioning at high temperatures and high frequencies.

Bismuth titanates are obtained mainly with conventional technology from Bi_2O_3 and TiO_2 at T=900–1050°C for a period of time from 5 to 100 h [12]. In [7] $Bi_4Ti_3O_{12}$ is synthesized using $Bi(NO_3)_3$ and $(NH_4)_2TiO_3$ solutions at a relatively low temperature.

$Bi_2Ti_2O_7$ was obtained with conventional synthesis technology. Its obtaining by the peroxo method is of particular scientific and practical interest. This method from technological point of view exhibits some important advantages compared with the conventional methods for obtaining titanates: significantly lower temperature of synthesis, shorter reaction time, avoiding the milling and homogenizing of the raw materials and the final product. As a result the obtained metatitanates are of higher purity, with fine crystaline structure and homogeneous grain-size composition.

The aim of this study is to synthesize Bi-peroxotitanate by the peroxo method and follow its thermal decomposition to obtain a nanosized $Bi_2Ti_2O_7$. A mechanism for thermal decomposition of Bi-peroxotitanate to $Bi_2Ti_2O_7$ is suggested on the base of the data from DTA, TG, DSC, quantitative and X-ray analyses. The optimal conditions for obtaining fine-crystalline $Bi_2Ti_2O_7$ applicable for piezosensors were determined.

Experimental

The Bi-peroxotitanate with composition $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ were synthesized by the peroxo method [15]. The essence of the method can be illustrated with the following chemical reaction:

$$TiCl_4+Bi(NO_3)_3+H_2O_2+OH^-\rightarrow Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$$

A 18% aside solution of $Bi(NO_3)_3$ and a 30% solution of H_2O_2 in a mol ratio of 2:2:10 were added to a 40% solution of $TiCl_4$ in HCl. It was alkalized to pH=7.5 with a 12% solution of NH_3. A temperature of 10–15°C was maintained during the synthesis. Amorphous sediment of Bi-peroxotitanate was obtained. The latter was used as a precursor for obtaining $Bi_2Ti_2O_7$. For this purpose the dried sediment (in an ae-

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rial environment at T≈20°C) with composition $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ was subjected to a thermal decomposition at T=550–600°C as a result of which $Bi_2Ti_2O_7$ crystallizes.

The final product, $Bi_2Ti_2O_7$, was characterized by X-ray diffraction using a Zeiss TUR-M-62 apparatus with CuK_α radiation.

The composition of Bi-peroxotitanate and the composition of the intermediate compounds obtained following the thermal decomposition were proved using the quantitative analysis and the IR spectroscopy. The peroxo groups were determined permanganometrically [16], and Bi^{3+} and Ti^{4+} spectroscopically with an ICP-AES-spectrometer Vista MPX CCD Simultaneous of the manufacturer Varian. The hydroxyl groups are defined by Chernev's method [17] and hydrate water, by Fisher's method [18]. The IR spectra were taken on a Philips PV 9700 spectrometer in the region 4000 to 400 cm^{-1} in KBr tablets and, in the region of stretching vibrations of H_2O, as a suspension in hexachloro-1,3-butadiene.

Besides the methods described above, simultaneous DTA and TG analysis were used during the study of the mechanism of Bi-peroxotitanate thermal decomposition. The DTA and TG curves were recorded on MOM-OD-102 apparatus between 20 and 900°C at a heating rate of 10°C min^{-1} in air. The enthalpy changes were measured by DSC on a Perkin-Elmer DSC-4 apparatus in air and nitrogen, in the temperature interval 20 to 400°C, at a heating rate of 10°C min^{-1}.

Results and discussion

The Bi-peroxotitanate synthesized by the peroxo method was used as a precursor for obtaining nanosized $Bi_2Ti_2O_7$. Its IR-spectrum and the spectra of the intermediate compounds obtained following the thermal decomposition are illustrated on Figs 1 and 2, and the data of the quantitative analysis are shown on Table 1.

The Bi-peroxotitanate has the following composition: $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$. The typical absorption band of the peroxo groups bonded to the titanium forming a triangle at 830 cm^{-1} can be observed in its IR spectra (Figs 1 and 2a) [19, 20].

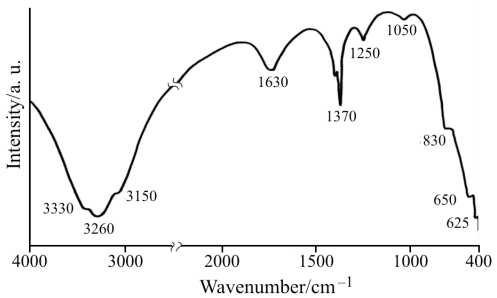

Fig. 1 IR spectra of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$

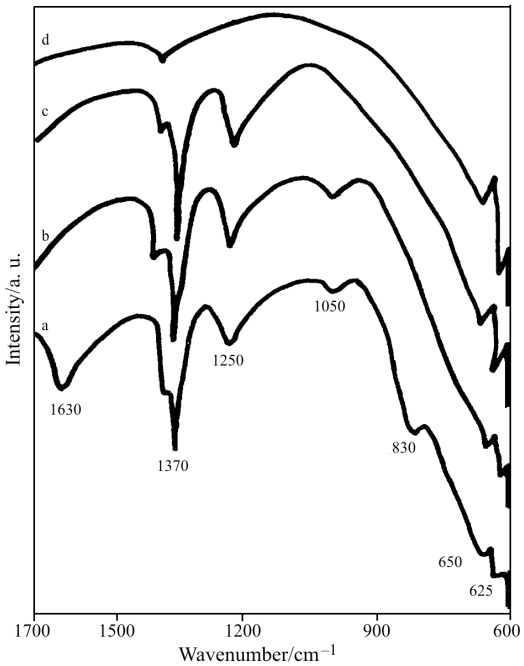

Fig. 2 IR spectra of: a – $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ at T=20°C, b – heated sample at T=120°C, c – heated sample at T=300°C and d – heated sample at T=620°C

This also corresponds to the data of the quantitative analysis (Table 1). The stretching vibrations of the Ti–O groups are registered at 625 and 650 cm^{-1} [21]. The absorption bands at 1050, 1250 and 1370 cm^{-1} are of interest in the observed spectrum. The first one is associated with the bending vibration of the terminal hydroxyl groups Ti–OH [22], and the other two are associated with the bridging hydroxyl groups Ti–O(H)–Ti [23]. The information concerning the

Table 1 Data from quantitative analyses of samples of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ partially decomposed under isothermal conditions

Temperature/°C	Quantitative composition/mass%					Mol ratio	Δm/%	
	Bi^{2+}	Ti^{4+}	O_2^{2-}	OH^-	H_2O	$Bi:Ti:O_2^{2-}:OH^-:H_2O$	exp.	calc.
20	49.9	11.8	15.0	12.5	11.1	1.00:1.03:1.95:3.08:2.58	–	–
120	70.0	14.7	–	15.3	–	1.00:1.05:–:3.08:–	19.3	18.5
300	63.8	15.2	–	5.0	–	1.00:1.04:–:0.96:–	23.4	22.9
620	66.1	15.6	–	–	–	1.00:1.03:–:–:–	24.8	25.1

Table 2 Data from DTA, TG and DSC curves of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$

DTA			DSC		Δ*m*/%	
Interval/°C	T_{max}/°C	T_{onset}/°C	T_{max}/°C	ΔH^0/kJ mol^{-1}	exp.	calc.
30–225	145	67	147.3	107±1.0	18.7	18.5
280–400	335	282	217.0	35±0.5	23.3	22.9
400–475	448	–	–	<0	–	–
475–580	520	–	–	0>	25.5	–
580–700	645	–	–	<0	–	25.1

OH^- is also increased by the observed absorption bands in the region of their stretching vibrations at 3330, 3260 and 3150 cm^{-1}. Considering their number, the presence of three different types OH^- groups can be clearly identified: of the hydrate water, the terminal and the bridging groups. The existence of OH^- groups belonging to the hydrate water is proved with δ_{H_2O} 1630 cm^{-1}[22].

DTA, TG and DSC curves of the Bi-peroxotitanate are shown on Figs 3 and 4, and the DTA and DSC data are presented on Table 2.

As seen on Fig. 3, the first large endothermal effect in the temperature range of 30 to 225°C with T_{max}=145°C is associated with the separation of peroxo groups and hydrate water. These two processes are simultaneous and complete. In confirmation of this statement are the following facts: to this effect in the TG curve (Fig. 3) corresponds the reduction of the mass $\Delta m_{exp.}$=18.7% at $\Delta m_{calc.}$=18.5%. In spite of the greater preciseness of the DSC method, just one effect of endothermal character with T_{max}=147.3°C and ΔH^0=107±1.0 kJ mol^{-1} (Table 2) was registered in the range of 30 to 225°C of the DSC curve (Fig. 4). The quantitative analysis data on a sample isothermally heated at 120°C (Table 1) prove the complete separation of the peroxo groups and the hydrate water. The reduction of the mass of this sample is $\Delta m_{exp.}$=19.0% and it corresponds to a composition $Bi_2[Ti_2O_4(OH)_6]$. The absorption bands of the triangle peroxo group at 830 cm^{-1} and of the hydrate water at 1630 cm^{-1} are absent in the IR spectrum of this sample (Fig. 2b).

The second endothermal effect is within the temperature range of 280 to 400°C and has maximum value at 335°C. It is due to the separation constitutionally bound water obtained as a result of splitting of the terminal hydroxyl groups. To this effect in the TG curve (Fig. 3) corresponds the reduction of the mass of the sample $\Delta m_{exp.}$=22.3% at $\Delta m_{calc.}$=22.9%. An endothermal effect with T_{max}=326.5°C is observed on the DSC curve (Fig. 4) within the discussed range. The enthalpy of this phase transition is ΔH^0=171.6±1.0 kJ mol^{-1} (Table 2). In support of the above statement are the quantitative analysis data (Table 1). In the sample isothermally

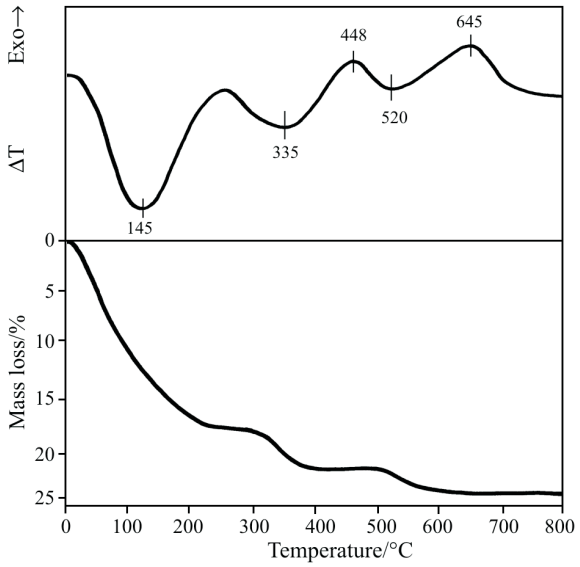

Fig. 3 DTA and TG curves of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$

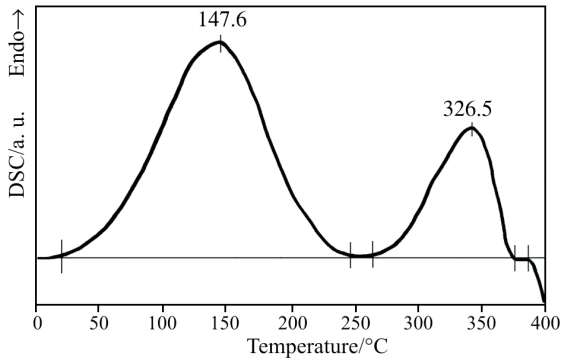

Fig. 4 DSC curve of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$

heated at 300°C the content of OH^- groups is reduced from 3.08 to 0.96 mol, and the reduction of the mass of the sample is $\Delta m_{exp.}$=23.4%. The composition of this sample is $Bi_2[Ti_2O_6(OH)_2]$. Its X-ray analysis shows an amorphous phase. The absorption bands of the terminal hydroxyl groups Ti–OH at 1050 cm^{-1} are not observed in its IR spectrum (Fig. 2c).

The third endothermal effect with T_{max}=448°C (Fig. 3) is due to the separation of the water as a result of splitting of the bridging hydroxyl groups. A reduc-

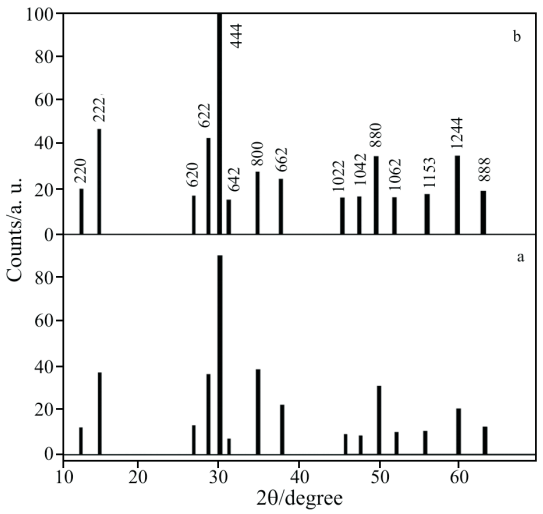

Fig. 5 Schematic diagram of the X-ray diffraction lines for $Bi_2Ti_2O_7$ obtained at: a – 550°C for 5 h and b – 600°C for 3 h

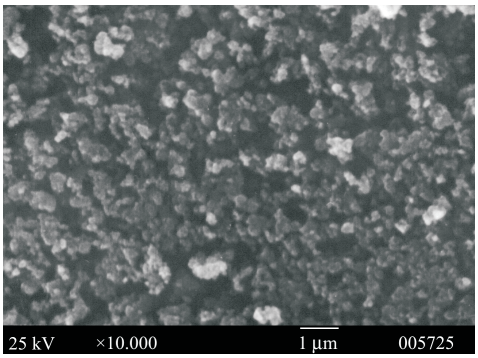

Fig. 6 SEM of the $Bi_2Ti_2O_7$ obtained at T=600°C for 3 h

tion of the mass $\Delta m_{exp.}$=25.5% at $\Delta m_{calc.}$=21.5% is observed on along the TG curve. This corresponds to the separation of one molecule of water. This information correlates with the quantitative analysis data and the IR spectra. The reduction of the mass of the sample isothermally heated at 620°C is $\Delta m_{exp.}$=24.8% (Table 1). The absorption bands of the bending vibrations of the bridging Ti–O(H)–Ti group at 1250 and 1370 cm^{-1} are absent in the IR spectrum of this sample.

The X-ray analysis of this sample shows a crystalline phase and has the following composition: $Bi_2Ti_2O_7$ [24].

Two exothermal effects are registered in the progress of the DTA curve at T_{max}=520°C and T_{max}=645°C (Fig. 3). No change of the mass is observed on the TG curve (Fig. 3) in relation to these effects. It could be assumed that they are due to substance restructuring processes in phases more stable thermodynamically. The X-ray analysis of the $Bi_2Ti_2O_7$ obtained from DTA at T=645°C shows an amorphous phase. No other exothermal effect is observed to the end of the DTA curve (900°C) which allows the presupposition that the sample does not crystallize at the speed of making the derivatogram (10°C min^{-1}). However, samples of the $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ isothermally heated in an aerial atmosphere at 550°C for 5 h and at 600°C for 3 h decomposed to fine-crystalline $Bi_2Ti_2O_7$. The last one is X-ray crystal (Fig. 5), without admixtures and with homogeneous granulometric composition and size of the particles from 70 to 200 nm (Fig. 6) applicable to piezosensors.

On the basis of the data of DTA, DSC, IR spectroscopy, quantitative and X-ray analysis, the most probable mechanism has been proposed for the thermal decomposition of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ to $Bi_2Ti_2O_7$:

$$Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O_{(s)} \xrightarrow{30-225°C} Bi_2[Ti_2O_4(OH)_6]_{(s)} + 2O_{2(g)} + 5H_2O_{(g)}$$

$$Bi_2[Ti_2O_4(OH)_6]_{(s)} \xrightarrow{280-400°C} Bi_2[Ti_2O_4(OH)_2]_{(s)} + 2H_2O_{(g)}$$

$$Bi_2[Ti_2O_4(OH)_2]_{(s)} \xrightarrow{475-580°C} Bi_2Ti_2O_{7(s)} + H_2O_{(g)}$$

Conclusions

Bi-peroxotitanate was synthesized by a peroxo method and after thermal decomposition $Bi_2Ti_2O_7$ was obtained.

Based on DTA, TG, DSC, IR spectra and the quantitative analysis results, here is the most probable mechanism of thermal decomposition of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ to $Bi_2Ti_2O_7$.

The optimal conditions for obtaining fine-crystalline $Bi_2Ti_2O_7$ applicable for piezosensors were determined: heating of $Bi_2[Ti_2(O_2)_4(OH)_6]\cdot 5H_2O$ in an aerial atmosphere at 550°C for 5 h and at 600°C for 3 h. The $Bi_2Ti_2O_7$ so obtained is without any admixtures and has homogeneous granulometric composition and size of the particles from 70 to 200 nm.

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