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INVESTIGATION OF SYNTHESIS AND MICROSTRUCTURE OF BISMUTH TITANATES WITH TiO_2 RICH COMPOSITIONS

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Preliminary examinations regarding formation of bismuth titanates in a part of Bi_2O_3–TiO_2 system rich with TiO_2 have been carried out. Bismuth titanates have been synthesized from mixtures of Bi_2O_3 and TiO_2 (anatase) by the conventional solid-state method at the temperatures ranged from 1273 to 1473 K. Differential thermal analysis (DTA), powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used to study the formation of bismuth titanates. The following compounds have been achieved: $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$ and $Bi_2Ti_4O_{11}$. Existence of controversial bismuth titanate of formula $Bi_2Ti_3O_9$ in the Bi_2O_3–TiO_2 system has not been confirmed.

Keywords: *bismuth titanates, DTA, microstructure, SEM, synthesis, XRD*

Introduction

Bismuth titanates represent characteristic dielectric material of high dielectric constant and interesting ferroelectric properties [1–3]. In 1965 Speranskaya *et al.* [1] using the DTA technique, identified three incongruently – melting compounds in the Bi_2O_3–TiO_2 system, namely the bismuth rich phase Bi_8TiO_{14} (melting point 1138 K), $Bi_4Ti_3O_{12}$ (melting point 1483 K) and the titanium rich $Bi_2Ti_4O_{11}$ (melting point 1548 K). The data of Bruton [4] are similar to those given by Speranskaya *et al.* [1], except that the bismuth rich compound is $Bi_{12}TiO_{20}$, melting incongruently at 1148 K. The bismuth rich compound has also been identified as $Bi_{12}TiO_{20}$ by Levin and Roth [5] who suggested that it is congruently melting, and by Morrison [6] who concluded that the experimental evidence favored congruent melting but that the departure from congruent melting was small.

The results obtained by various authors about the existence of the compound $Bi_2Ti_3O_9$ are contradictory. According to Belyaev *et al.* [7] and Skanavi *et al.* [8] $Bi_2Ti_3O_9$ does exist as indicated by the X-ray diffraction patterns, but the crystal structure was not discussed. According to Yordanov *et al.* [9] ceramics with composition $Bi_2Ti_3O_9$ is a composite between $Bi_2Ti_4O_{11}$ and $Bi_2Ti_2O_7$ [10]. Hence, the X-ray diffraction patterns of $Bi_2Ti_3O_9$ must be a superposition of the patterns of these two compounds. According to Speranskaya *et al.* [1] $Bi_2Ti_3O_9$ does not exist. Yordanov *et al.* [9] explain this discrepancy with the peculiarities of the compounds in system Bi_2O_3–TiO_2. Some of these compounds exist only in solid state phase and they can not be observed in liquid phase. They decompose on melting. The formation of the different bismuth titanates depends on the starting composition and on the conditions of the solid state reaction. A solid phase chemical transformation of the bismuth titanates with separation of Bi_2O_3 or TiO_2 at certain temperature is possible. For example, a separation of Bi_2O_3 by heat treatment of $Bi_4Ti_3O_{12}$ at $T\approx1473$ K was observed. During heating $Bi_2Ti_4O_{11}$ beyond about 1498 K, it appeared to dissociate into TiO_2 and other titanates ($Bi_2Ti_2O_7$ and $Bi_4Ti_3O_{12}$) [11].

The most recent references related to bismuth titanates presents mainly examination results $Bi_4Ti_3O_{12}$ synthesis as well as its properties [3, 12–16]. Ferroelectric $Bi_4Ti_3O_{12}$ ceramics are potential candidates for device applications due to their high dielectric constant, high Curie temperature and high breakdown strength. However, there is no more recent examinations related to such bismuth titanates rich in TiO_2 as: $Bi_2Ti_2O_7$, $Bi_2Ti_4O_{11}$ as well as controversial compound $Bi_2Ti_3O_9$. There are no description of microstructure in older examinations from 1960–1983 of the said titanates.

The aim of the present work was to study, which titanates create in part of system Bi_2O_3–TiO_2 rich in TiO_2, taking a position on basic references which frequently are contradictory ones as well as comparison of microstructure of titanates conventionally prepared. Bismuth titanates are almost always

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prepared by a solid state reaction. It is classical ceramic method which used oxides, hydroxides or carbonates as precursors [17, 18].

Differential thermal analysis and X-ray diffraction were applied to investigate the syntheses of titanates. Scanning electron microscopy was used to observe bismuth titanates particles morphology.

Experimental

A conventional process involving the calcination of mixed oxides was used to prepare the bismuth titanates. Starting materials were dry reagent grade: Bi_2O_3 (POCH – Gliwice, Poland, purity 99.4%) and TiO_2 in the form of anatase (‘Police’ Chemical Factory, Poland, purity 99.5%). These two precursors were weighted according to the compositions (x Bi_2O_3 y TiO_2, y:x=1.5, 2, 3, 4). They were mixed in an agate mortar under isopropanol and then dried. All dried mixtures of precursors were subjected to DTA. The selected mixture of precursors (molar ratio Bi_2O_3:TiO_2=1:3) has been additionally subjected to mechanical activation by means of milling in vibration mill during 4 h.

DTA was performed using a MOM type derivatograph (Hungary) in static air atmosphere. The 2000 mg sample was placed in platinum crucible, α-Al_2O_3 powder was used as reference material. Heating rate was 10 K min^{-1}. DTA sensitivity was equal 1/10.

The precursors mixtures were mixed with organic binder of 5 mass% PVA, and then were compacted under pressure of 98 MPa into disc samples of 18 mm in diameter and $\approx$3 mm in height. The green compacts were heated at temperatures between 1273 and 1473 K for 4 h in air. Two samples of the same composition have been heated up each time. After thermal treatment different methods of samples cooling were applied, namely:

- rapid cooling by taking the sample out of the furnace i.e. sample was quenched in air without slow cooling,
- natural cooling in the furnace down to room temperature.

The phases in each sample were identified from the X-ray diffraction (XRD) patterns using DRON-2.0 diffractometer (Russia) with CuK_α radiation. Joint Committee Powder Diffraction Standards (JCPDS) powder diffraction files were consulted for all phase analyses.

The morphology of the starting materials and samples after calcination and cooling was observed by scanning electron microscopy, SEM (Tesla BS 340, Czech Republic). Microscope observations were made after coating the samples surface with a thin layer of gold.

Results and discussion

Figure 1 presents the curves of DTA of mixtures of precursors. In the paper, TG and DTG curves have not been presented, because oxides as precursors were used and samples mass did not change during synthesis. DTA provided the first information about the temperature region of the bismuth titanates formation. Compositions of the mixtures, conditions of thermal treatment and resulting phases as determined by X-ray powder diffraction are listed in Table 1. Phase composition of the samples of assumed starting composition was the same, regardless of the method of cooling down. Cooling down method did not distinctly influence their microstructure. Raw materials and selected samples microstructures are shown in Figs 2–5.

The DTA curve for the mixture 1 (molar ratio Bi_2O_3:TiO_2=2:3) shows exothermic peak with the initial temperature about 913 K due to the formation of $Bi_4Ti_3O_{12}$. The strong and sharp endothermic peak located at a minimum of 973 K, indicates the polymorphic transformation of $\alpha \rightarrow \delta$ Bi_2O_3 (monoclinic to cubic). It is agreement with the previously reported values in the literature [19]. According to Hedvall’s effect, when the reacting substances undergo polymorphic transformation at reaction temperature, rate of such reaction is increased. Formation of $Bi_4Ti_3O_{12}$ within the range of temper-

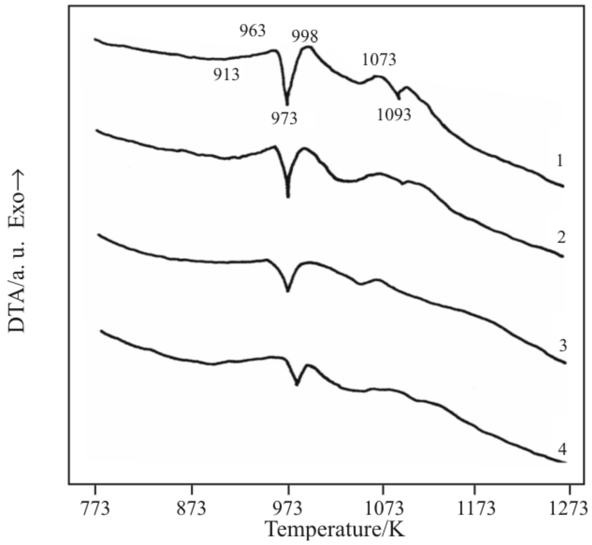

Fig. 1 DTA curves of mixtures; 1 – molar ratio Bi_2O_3:TiO_2=2:3, 2 – molar ratio Bi_2O_3:TiO_2=1:2, 3 – molar ratio Bi_2O_3:TiO_2=1:3, 4 – molar ratio Bi_2O_3:TiO_2=1:4

Table 1 Compositions of the mixtures and phases detected

No. of mixtures of precursors	Molar ratio Bi_2O_3:TiO_2	Thermal treatment/K	Phases detected
1	2:3	1273^*	$Bi_4Ti_3O_{12}$
		1273	$Bi_4Ti_3O_{12}$
2	1:2	1273^*	$Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$
		1273	$Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$
		1473	$Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$
3	1:3	1273^*	$Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$
		1273	$Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$
		1473	$Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$
		1473^{**}	$Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$
4	1:4	1273^*	$Bi_2Ti_4O_{11}$
		1273	$Bi_2Ti_4O_{11}$
		1473	$Bi_2Ti_4O_{11}$

*the sample after DTA, **the mixture of precursors was milled in a laboratory vibrating mill

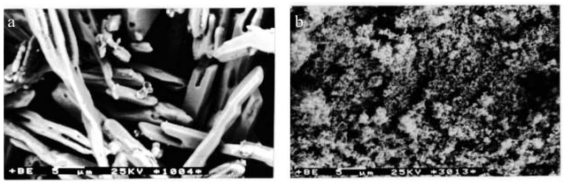

Fig. 2 SEM micrographs of the starting materials: a – Bi_2O_3, b – TiO_2 anatase

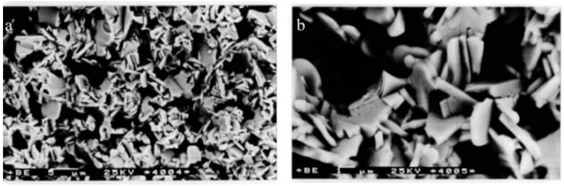

Fig. 3 SEM micrographs of mixture 1 after thermal treatment at 1273 K ($Bi_4Ti_3O_{12}$): a – magn. 5000×, b – magn. 15000×

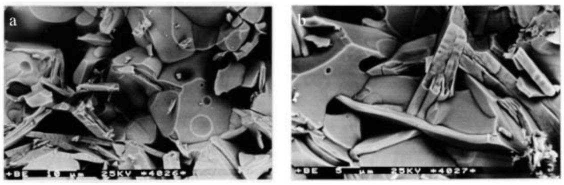

Fig. 4 SEM micrographs of mixture 2 after thermal treatment at 1473 K ($Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$): a – magn. 2500×, b – magn. 4000×

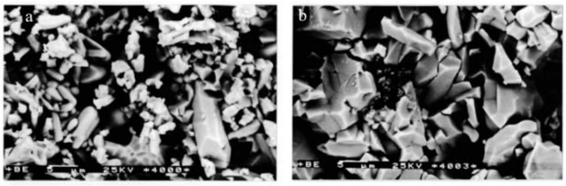

Fig. 5 SEM micrographs of mixture 4 after thermal treatment ($Bi_2Ti_4O_{11}$) at: a – 1273, b – 1473 K; magn. 5000×

atures 913–1073 K, has been confirmed by X-ray analysis of mixture 1, the thermal analysis of which has been finished at 1073 K. On the other hand, the formation of $Bi_4Ti_3O_{12}$ is not completed at a temperature 1073 K, we have observed an endothermic peak, located at 1093 K, which is due to the melting non-reacted Bi_2O_3. Melting of Bi_2O_3 facilitates further course of $Bi_4Ti_3O_{12}$ synthesis. After heat treatment at 1273 K, the sample contains the final product only (Table 1). Microstructural studies revealed platelike grains (Fig. 3). This typical platelet formation in $Bi_4Ti_3O_{12}$ has been previously reported in the literature [20–22].

The DTA curve of mixture 2 (Fig. 1) with molar ratio Bi_2O_3:TiO_2=1:2 is similar to the DTA curve of mixture 1. Less area of endothermic peak of melting of non-reacted Bi_2O_3 results from lesser content of Bi_2O_3 in a mixture of raw materials.

The X-ray diffraction pattern of the sample 2 after heat treatment at 1273 K did not show formation of $Bi_2Ti_2O_7$ compound. The major phase was identified as $Bi_4Ti_3O_{12}$, and the phase of $Bi_2Ti_4O_{11}$ was also observed. After 4 h at 1473 K sample 2 contains $Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$ (Table 1). Figure 4 shows the microstructure of sample 2 after thermal treatment at 1473 K, where the grains with two different morphologies were determined. The sample shows platelike grains of $Bi_4Ti_3O_{12}$ and irregularly shaped grains of $Bi_2Ti_2O_7$. The different morphologies of grains were attributed to this complex phase constitution.

The DTA curve of mixtures 3 (molar ratio Bi_2O_3:TiO_2=1:3) and 4 (molar ratio Bi_2O_3:TiO_2=1:4) also show endothermic peak of Bi_2O_3 polymorphic transformation (Fig. 1). However, these curves do not show endothermic melting peak of Bi_2O_3. The thermal treatment of all samples of mixture 3 produces $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$ (Table 1). The $Bi_2Ti_3O_9$ phase was not found in the XRD patterns at any of the temperatures. The same phase composition after thermal treatment has shown mixture 3, activated before synthesis by milling in vibration mill.

According to Yordanov *et al.* [9] the $Bi_2Ti_3O_9$ compound exists. The authors have specified the X-ray data of this compound, however they consider the ceramics $Bi_2Ti_3O_9$ as a composite between $Bi_2Ti_2O_7$ and $Bi_2Ti_4O_{11}$.

After thermal treatment only $Bi_2Ti_4O_{11}$ appears in the samples 4 (Table 1). SEM shows that the $Bi_4Ti_4O_{11}$ disc consists of grains of columnar shape (Fig. 5). Examination presented in this paper has proved that at temperature 1473 K $Bi_2Ti_4O_{11}$ shows thermal stability.

None DTA curve has shown distinct peak of polymorphic transformation of anatase into rutile, that proceed at temperature about 1173 K [23]. This proves complete reaction of TiO_2 with Bi_2O_3.

Conclusions

Heat treatment within the range 1273–1473 K of four mixtures of Bi_2O_3 and TiO_2 has been accomplished, corresponding with their composition to different bismuth titanates which potentially occur in a part of Bi_2O_3–TiO_2 composition rich with TiO_2. Three out of four assumed final products have been obtained, namely: $Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$ and $Bi_2Ti_2O_7$ (this compound mixed with $Bi_4Ti_3O_{12}$). It has been found that compound $Bi_4Ti_3O_{12}$ creates plate-like crystals, and $Bi_2Ti_2O_7$ creates irregular polyhedral crystals. $Bi_2Ti_4O_{11}$, i.e. bismuth titanate of highest TiO_2 content of all examined ones (80 mol% TiO_2) creates elongated crystals with columnar habit.

The results related to $Bi_2Ti_3O_9$ are not identical to results cited in basic references. Controversial compound $Bi_2Ti_3O_9$ has not been obtained from the mixture of precursors in mole ratio of Bi_2O_3:TiO_2 equal to 1:3, but the mixture of compounds $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$. The compound $Bi_2Ti_3O_9$ has not been obtained as a result of non-isothermal heating up to temperature 1273 K. The compound did not create under isothermal conditions (temperature 1273 and 1473 K, isothermal heating time equal 4 h). Mechanic activation of precursor mixture Bi_2O_3+3TiO_2, using milling did not influence the phase composition of post-synthesis material.

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