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THERMOANALYTICAL STUDY OF THE SYNTHESIS OF $Na_{0.5}Bi_{0.5}TiO_3$ FERROELECTRIC

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The study presents results of examination on $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) ferroelectric synthesis through intermediate binary compound $Bi_4Ti_3O_{12}$ (BIT). The first stage of the study related to obtaining BIT from oxide precursors, i.e. Bi_2O_3 and TiO_2. The second stage included obtaining NBT from $Bi_4Ti_3O_{12}$, Na_2CO_3 and TiO_2. Two polymorphic modifications of TiO_2 (anatase, rutile) and diversified initial homogenization of raw material batches were applied during examination.

Keywords: *bismuth titanate, DTA, sodium–bismuth titanate, synthesis, TG, XRD*

Introduction

At present, lead zirconate titanate (PZT)-based ceramics are the most widely applied piezoelectric materials because of their superior electrical properties [1]. However, the evaporation of toxic lead during the fabrication of the ceramics causes an environmental problem. Therefore, there is an increasing interest of investigating lead-free piezoelectric materials to replace PZT-based piezoelectric ceramics. Sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is a kind of perovskite-type ferroelectric with a relatively high Curie temperature (T_c=320°C) and is considered to be an excellent candidate for use in lead-free piezoelectric ceramics. NBT was discovered by Smolenskii *et al.* [2] and subsequently studied by several other researchers [3–11].

Obtaining the perovskites is a multi-stage process where intermediate compounds are formed, thus the necessity to determine the sequence of their formation. The phenomenon of multi-stage thermal reaction of solid bodies and achieving the thermodynamic equilibrium via series of unstable phases or intermediate compounds still belong to insufficiently recognized. In the chemistry of solid several methods of examination of physical and chemical processes sequence are applied, which proceed in homogenized mixtures of precursors subject to thermal treatment. The most frequently applied methods are static and dynamic thermal analyses. The dynamic thermal analysis provides the opportunity to obtain the results in fast way.

The study presents results of examinations on NBT ferroelectric synthesis through intermediate binary compound $Bi_4Ti_3O_{12}$ (BIT). The examinations performed were supposed to make possible the comparison of anatase and rutile reactivity as well as to determine the influence of homogenization method of raw material batches on temperature ranges at witch synthesis reactions of intermediate compounds and final product proceeded. Mechanical treatment is one of methods to increase the reactivity of solids [12–18]. Preliminary tests were made whose aim was to establish NBT synthesis course.

Experimental

Starting materials were dry reagent grade:

- Na_2CO_3 (POCH – Gliwice, purity 100.0%)
- Bi_2O_3 (POCH – Gliwice, purity 99.4%)
- TiO_2 in the form of anatase and rutile ('Police' Chemical Works, purity 99.4%).

Precursors mixtures were prepared, weighed in amounts that corresponded to molar ratios of oxides in $Bi_4Ti_3O_{12}$ ($2Bi_2O_3{\cdot}3TiO_2$) and $Na_{0.5}Bi_{0.5}TiO_3$ ($Na_2O{\cdot}Bi_2O_3{\cdot}4TiO_2$) compound, respectively. The mixtures prepared in amount of 100 g were subject to:

- manual homogenization using isopropyl alcohol in agalite mortar for 30–40 min,
- manual homogenization as above and then the mechanical one (combined with grinding) in laboratory vibrating mill for 1 h.

All dried mixtures of precursors were subject to differential thermal analysis (DTA) and thermogravimetric analysis (TG). From the DTA curves of individual mixtures, the temperature ranges, in which the chemical reactions and phase transformations occurred, have been determined.

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DTA and TG was carried out using a MOM type derivatograph (Hungary) in static air atmosphere at temperature range 20–1000°C, the mass of sample in all runs was 2000 mg. The reference material was alumina. Heating rate was 10 K min^{-1}.

The BIT synthesis has been carried out using two stages:

- the first stage: at temperature 700°C (in case of all mixtures of precursors),
- the second stage: at higher temperature, i.e. at 750 or 850°C.

Materials obtained using mixtures homogenized mechanically, after thermal treatment, were reground by means of laboratory vibration mill during one hour. Using this method BIT was obtained, which was then used as raw material in NBT synthesis examinations. The NBT synthesis was also carried out with two stages:

- the first stage: at temperature 700°C (in case of all mixtures of precursors),
- the second stage: at higher temperature, i.e. at 800 or 850°C.

Both in case of BIT and NBT, the time of keeping at preset temperature at every stage of synthesis was 1 h.

After thermal treatment, all materials were subjected to X-ray analysis to control reaction of precursors.

Examinations over NBT synthesis course were carried out using non-isothermal method i.e. under conditions of linear temperature increase. After the preset temperature (in range from 600 up to 800°C) was achieved, the samples were rapidly cooled by removing them from heating zone. Cooled samples were subject to X-ray analysis.

The X-ray investigation of the samples was carried out using XRD-3003 TT type diffractometer (Seifert), equipped with a copper anode generating Ni-filtered CuK_{α} radiation. Diffraction patterns were analysed using JCPDS PDF-2 powder diffraction data base [19].

Results and discussion

Figure 1 presents the curves of thermal differential analysis of mixtures of mole composition $2Bi_2O_3$+$3TiO_2$, which has been prepared using two types of polymorphic forms TiO_2 as well as various methods of homogenization. It was limited to DTA curves because synthesis reactions of bismuth titanate of used precursors proceeds basically without changes of sample mass. Table 1 presents phase composition of samples of mixtures after thermal treatment.

Exothermic effect of $Bi_4Ti_3O_{12}$ (BIT) creation can be seen in DTA curves. In case of mechanically homogenized mixtures the initial temperature of this effect is about 600°C, and in case of manually homogenized mixtures – about 620°C. The distinct endothermic effect superimposes on this effect ($T_{\max}$~720°C) of polymorphic transformation Bi_2O_3. The area of this peak proves the quantity of non-reacted Bi_2O_3. In case of grinded mixtures the area of this peak is smaller as compared with mixtures homogenized manually. The course of DTA curve of the mixture based on anatase as TiO_2 source and homogenized mechanically (Fig. 1a) indicates to the greatest reactivity of this mixture. The least area of endothermic peak of Bi_2O_3 polymorphic transformation proves the significant reaction of bismuth oxide with TiO_2 already at the temperature below 700°C (the distinct maximum of endothermic effect at temperature 650°C). The biggest amount of non-reacted Bi_2O_3 (the biggest peak area of polymorphic transformation Bi_2O_3) can be observed on DTA curves of manually homogenized mixtures (Figs 1c and d). Polymorphic transformation of Bi_2O_3 probably accelerates creation of $Bi_4Ti_3O_{12}$ due to increased mobility of atoms during polymorphic transformation. Non-reacted Bi_2O_3 melts, which fact is confirmed by distinct endothermic effect with $T_{\max}$x within the range 820–830°C on

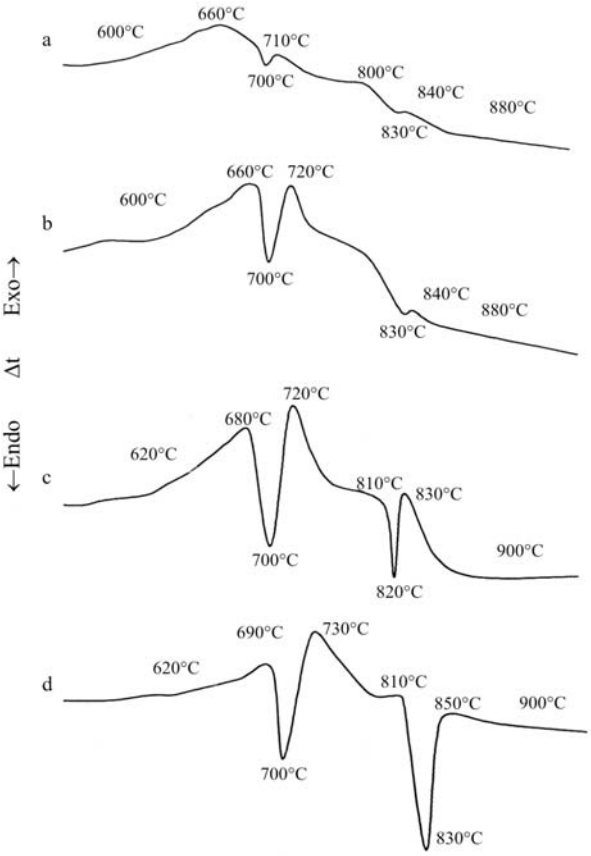

Fig. 1 DTA curves of mixtures of mole composition $2Bi_2O_3$+$3TiO_2$: a – based on anatase, mechanically homogenized, b – based on rutile, mechanically homogenized, c – based on anatase, manually homogenized and d – based on anatase, manually homogenized

Table 1 Phase composition of samples of mixtures of mole composition $2Bi_2O_3+3TiO_2$ after thermal treatment

Symbol of a mixture	TiO_2 type	Method of homogenization	Final synthesis temperature/°C	Phase composition
1A	anatase	manual	850	$Bi_4Ti_3O_{12}$ $Bi_{12}TiO_{20}$
1R	rutile	manual	850	$Bi_4Ti_3O_{12}$ $Bi_{12}TiO_{20}$
2A	anatase	mechanical	850	$Bi_4Ti_3O_{12}$
2R	rutile	mechanical	850	$Bi_4Ti_3O_{12}$
3A	anatase	mechanical	750	$Bi_4Ti_3O_{12}$ $Bi_{12}TiO_{20}$
3R	rutile	mechanical	750	$Bi_4Ti_3O_{12}$ $Bi_{12}TiO_{20}$

DTA curves of manually homogenized mixtures (Figs 1c and d). The bigger area of melting peak of Bi_2O_3 in Fig. 1d proves lesser reactivity of the mixture that contains rutile. Melting of Bi_2O_3 probably makes easier the further course of BIT synthesis. In case of mechanical homogenized mixtures the Bi_2O_3 melting effects is very slightly evident (Figs 1a and b). Slightly bigger reactivity of anatase can result from result from lesser graining of anatase as compared with rutile graining. The anatase creates aggregates composed of very fine grains ~0.1 µm. As compared to anatase the rutile creates aggregates composed of slightly bigger grains.

Bismuth titanate rich in Bi_2O_3 i.e. $Bi_{12}TiO_{20}$ in an intermediate compound during $Bi_4Ti_3O_{12}$ synthesis process. This compound occurs in samples after thermal treatment: manually homogenized mixtures (final temperature of the synthesis is 840°C) as well as mechanically homogenized mixtures, when final temperature of the synthesis was 750°C (Table 1). Lack of $Bi_{12}TiO_{20}$ in mechanically homogenized mixtures after thermal treatment at 840°C shows that precursors have completely reacted to final product $Bi_4Ti_3O_{12}$. These samples underwent partial sintering.

Figures 2–7 present DTA, TG and DTG curves of mixtures of mole composition that corresponds to $Na_{0.5}Bi_{0.5}TiO_3$ i.e. $Bi_4Ti_3O_{12}+2Na_2CO_3+5TiO_2$. The phase composition test results after thermal treatment are presented in Table 2.

Slight loss of mass can be observed on TG curves within the range of temperatures up to 400°C result from loss of samples moisture as well as decomposition of admixtures that were present in Bi_2O_3. The basic loss of mass at temperature above 400°C results from volatilization of CO_2 that was created as a result of Na_2CO_3 decomposition, which reacted with the other components of mixtures. Loss of CO_2 runs gradually, which fact is confirmed by TG courses as well as distinct peaks on DTG curves and corresponding endothermic effects on DTA curves.

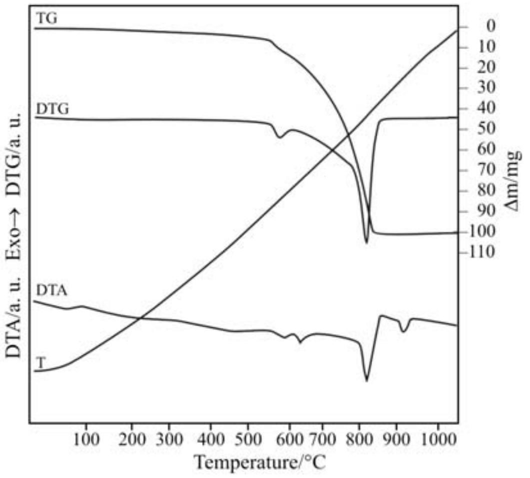

Fig. 2 DTA, TG and DTG curves of Z1 manually homogenized mixture

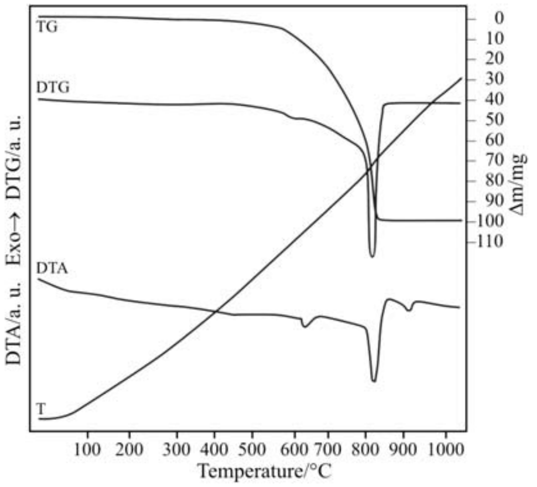

Fig. 3 DTA, TG and DTG curves of Z2 manually homogenized mixture

The maximum temperature of the strongest endothermic effect – in case mechanically homogenized mixtures Z3 and Z5 (anatase) as well as Z4 and Z6 (rutile) is 620 and 640°C, respectively (Figs 4–7). In case of Z1 and Z2 manually homogenized mixtures

Table 2 Phase composition of samples of mixtures of mole composition $Bi_4Ti_3O_{12}$+$2Na_2CO_3$+$5TiO_2$ after thermal treatment

Symbol of a mixture	BIT type	TiO_2 type	Method of homogenization	Final synthesis temperature/°C	Phase composition
Z1	1A	anatase	manual	850	NBT
Z2	1R	rutile	manual	850	NBT
Z3	2A	anatase	mechanical	800	NBT
Z4	2R	rutile	mechanical	800	NBT
Z5	3A	anatase	mechanical	800	NBT
Z6	3R	rutile	mechanical	800	NBT

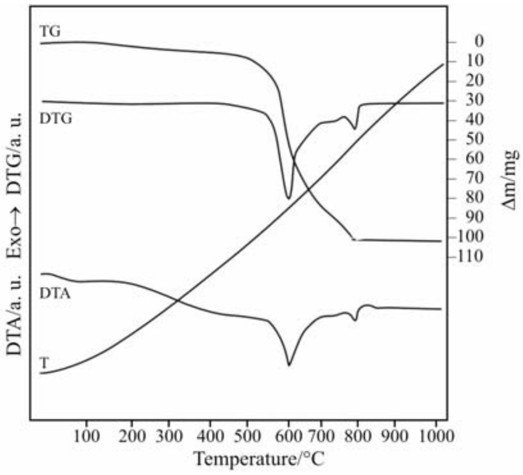

Fig. 4 DTA, TG and DTG curves of Z3 mechanically homogenized mixture

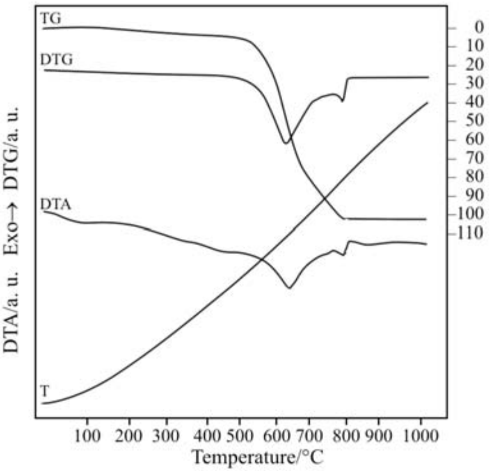

Fig. 5 DTA, TG and DTG curves of Z4 mechanically homogenized mixture

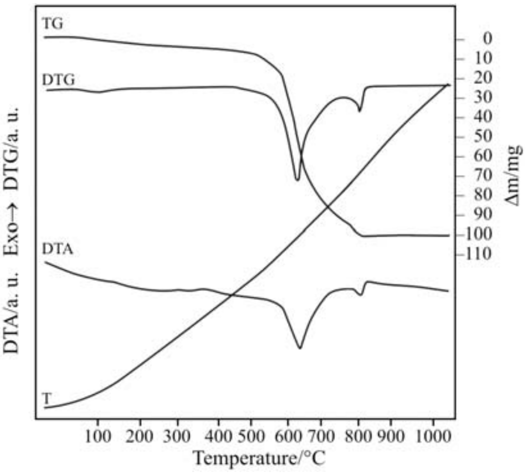

Fig. 6 DTA, TG and DTG curves of Z5 mechanically homogenized mixture

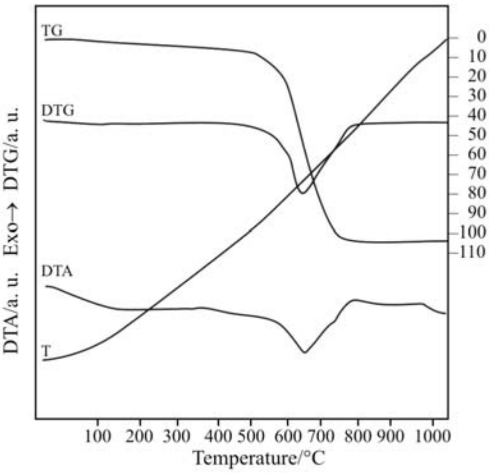

Fig. 7 DTA, TG and DTG curves of Z6 mechanically homogenized mixture

the T_{max} of the strongest endothermic effect is higher and is about 810°C (Figs 2 and 3). On DTA curves of Z1 and Z2 mixtures, the endothermic effect is evident at T_{max} 920°C, which does not occur on DTA curves of mechanically homogenized mixtures. This effect is not correlated with sample weight change thus it indicates probably melting. The manually homogenized mixtures are less reactive ones, so it is possible in these samples that incomplete reacted Na_2CO_3 occurs (the melting temperature of Na_2CO_3 is 852°C) or binary intermediate compound, i.e. sodium titanate.

The X-ray analysis of all sample after thermal treatment proved the complete reaction of precursors to the final products NBT (Table 2), regardless the BIT synthesis temperature (750, 850°C), the method of homogenization of mixtures (manual, mechanical ones) or type of TiO_2 polymorphic modification used (anatase, rutile). The influence of synthesis conditions on NBT sintering temperature as well as on microstructure and NBT ceramics properties shall be the subject of further examination.

On the basis of preliminary examinations over NBT synthesis course from $Bi_4Ti_3O_{12}$, Na_2CO_3 and TiO_2 mixture we did not obtain clear-cut information, whether intermediate sodium titanates occur in the process. In comparison, in [20] it was found that ternary compound $K_{0.5}Bi_{0.5}TiO_3$ (KBT) was formed through the intermediate binary compounds, i.e. bismuth titanates and potassium titanates rich in TiO_2. However these examinations confirmed that mechanically homogenized mixtures are more reactive and NBT synthesis runs at lower temperatures.

Conclusions

It was found that method of precursors mixtures homogenization influences temperature ranges at which $Bi_4Ti_3O_{12}$ (BIT) and $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) syntheses proceeded. Type of applied polymorphic modification of TiO_2 does not significantly influence temperatures ranges. Slightly bigger reactivity of anatase can result from lesser graining of anatase as compared with rutile graining.

NBT synthesis is a multi-stage process, which fact is proved by the results of thermal analysis. Several stages of NBT synthesis are distinctly pointed out on DTA, TG and DTG curves. However, we did not manage to identify intermediate sodium titanates. To this end, isothermal method should probably be applied, i.e. long (many hours) heating at the preset temperatures, waiting for better crystallization of created intermediate binary compounds.

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