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APPLICATION OF THERMAL ANALYSIS TO STUDY OF THE SYNTHESIS OF $K_{0.5}Bi_{0.5}TiO_3$ FERROELECTRIC

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Abstract

Synthesis of potassium bismuth titanate ferroelectric by heating of mixtures prepared using oxide precursors, i.e. Bi_2O_3, TiO_2 and K_2CO_3 was investigated. DTA, TG, XRD and SEM methods were used to study the formation of intermediate compounds and the final product. Usage of associated homogenization and grinding of precursors mixture permits to decrease the temperature of formation of $K_{0.5}Bi_{0.5}TiO_3$.

Keywords: DTA, potassium bismuth titanate, SEM, synthesis, TG, XRD

Introduction

The ferroelectric ceramic capable of working at elevated temperatures is based on ferroelectrics of high Curie temperature such as e.g. $PbTiO_3$ (T_C=490°C) and $K_{0.5}Bi_{0.5}TiO_3$ (T_C=380°C) [1]. The increasing demand for environmentally benign materials points in the direction of lead-free ceramic materials for different electronic applications. Both potassium bismuth titanate $K_{0.5}Bi_{0.5}TiO_3$ and sodium bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (T_C=320°C) belong to perovskites composed of $A^{+}_{0.5}Bi^{3+}_{0.5}B^{4+}O_3$, which are relatively little known. Previous works have shown that $K_{0.5}Bi_{0.5}TiO_3$ (KBT) and $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) were synthesized by the mixed oxide method [2–4], but the available literature does not contain any information about the mechanism of KBT and NBT syntheses.

The purpose of present paper was an attempt at establishing the kinetics and mechanism of KBT synthesis using diversified homogenization of precursors mixtures. 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 solids 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. In presented exam-

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inations the dynamic thermal analysis was applied, which is carried out at gradual, usually linear increase (or decrease) of temperature. This method provides the opportunity to obtain the results in fast way. In practice, the examinations carried out were to make possible determining the homogenization effect of precursors mixtures (including grinding) on temperature intervals magnitude in which intermediate compounds synthesis were performed and final product reacted. Mechanical treatment is one of methods to increase the reactivity of solids [5–10].

Experimental

Starting materials were dry reagent grade:

– K_2CO_3 (POCH – Gliwice, purity 99.8%),
– Bi_2O_3 (POCH – Gliwice, purity 99.4%),
– TiO_2 in the form of anatase ('Police' Chemical Works, purity 99.3%).

Precursors mixtures were prepared, weighed in amounts that corresponded to molar ratios of oxides in $K_{0.5}Bi_{0.5}TiO_3$ ($K_2O{\cdot}Bi_2O_3{\cdot}4TiO_2$) compound. The mixtures prepared in amount of 200 g were subject to:

– manual homogenization using isopropyl alcohol in agalite mortar for 40 min,
– manual homogenization as above and then the mechanical one (combined with grinding) in laboratory vibrating mill for 10, 20 and 60 min.

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. Homogenization of the mixtures was controlled using the TG, i.e. mass losses were read off from the TG curves and compared with losses of CO_2, resulting from the assumed amounts of K_2CO_3.

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}.

Investigation of KBT and intermediate compounds synthesis consisted in heating the mixtures up to temperature range from 540 up to 1000°C, determined on the basis of derivatograms courses. Examinations were done under non-isothermal conditions, i.e. under continuous linear temperature increase. The products obtained during DTA interrupted at various temperatures were cooled to room temperature by removing the sample in platinum crucible from the furnace and identified by means of X-ray powder diffractometry.

The X-ray investigation of the samples was carried out using DRON-2.0 diffractometer (Russia), equipped with a copper anode generating Ni-filtered CuK_α radiation. Diffraction patterns were analysed using ICPDS PDF–2 powder diffraction data base [11].

The microstructure of precursors and selected samples subjected to thermal treatment was studied using Tesla scanning electron microscopy.

Results and discussion

Figure 1 shows DTA curves of K_2CO_3+Bi_2O_3+4TiO_2 mixtures homogenized by means of various methods. Homogenization method affects significantly the temperature range, in which intermediate compounds and final product reactions i.e. KBT formation take place. Phase composition of samples after thermal treatment at selected temperatures is presented in Table 1.

Table 1 Phase composition of samples after thermal treatment

Temperature/°C	Phase composition	
	Manual homogenization	Mechanical homogenization (1 h)
540	K, B, T	K, B, T
680	K, B, T, B_6T	K, B, T, B_6T, phase 'X'
740	K, B, T, B_6T, KT_6	B, T, B_6T, B_2T_3, KT_6, KBT
840	T, B_6T, B_2T_3, phase 'Y', KBT	B_2T_3, phase 'Y', KBT
1000	B_2T_3, phase 'Y', KBT	KBT

Code: K – K_2CO_3, B – Bi_2O_3, T – TiO_2 (anatase), B_6T – $6Bi_2O_3{\cdot}TiO_2$, B_2T_3 – $2Bi_2O_3{\cdot}3TiO_2$, KT_6 – $K_2O{\cdot}6TiO_2$, KBT – $K_{0.5}Bi_{0.5}TiO_3$

Figure 2 presents exemplary DTA–TG curves of manually homogenized precursor mixtures as well as by means of mechanical methods using vibrating mill for 1 h. Every sample showed gradual loss of CO_2, therefore intermediate compounds formation at lower temperatures, rich in TiO_2. This fact is proved by mass loss on TG curves and corresponding endothermic effects on DTA curves. The sharp endothermic effect with minimum at 700°C results from polymorphic transformation of α-Bi_2O_3 (polymorphic form stable room temperature) [12]; in case of ground sample it is suppressed by endothermic effect connected with formation of intermediate potassium titanate.

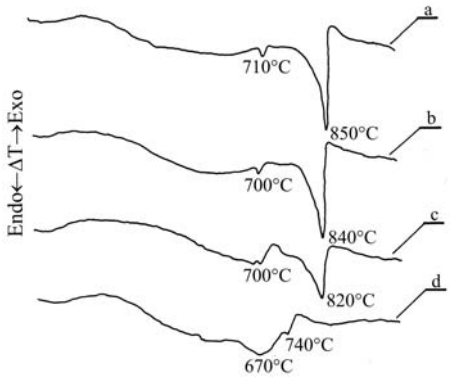

Fig. 1 DTA curves of homogenized solids with molar formula K_2CO_3+Bi_2O_3+4TiO_2: a – manually, b –, c –, d –mechanically for 10, 20 and 60 min, respectively

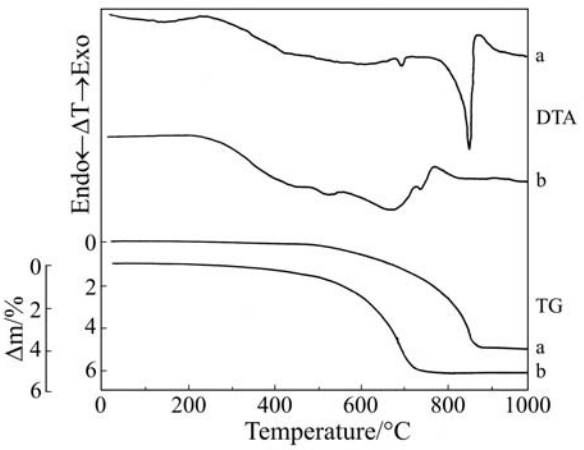

Fig. 2 DTA–TG curves of homogenized solids with molar formula $K_2CO_3+Bi_2O_3+4TiO_2$: a – manually, b – mechanically for 60 min

DTA curves do not show the endothermic effect of melting K_2CO_3 at 895°C; this fact proves the complete reaction of this precursor in mixture under analysis.

We can suppose that the main reason of lower temperature of chemical reactions in mechanically homogenized precursors mixture (ground one) and lower amount of energy to origin these reactions is reactivity of particles (grains) obtained as a result of grinding. This activity affects the reaction rate. In vibrating mills, we can obtain sharp-edge grains, very active ones, because charges which are not saturated on edges of broken lattice improve the chemical activity of this system [13]. The bigger reactivity of ground precursor mixture is confirmed by results of X-ray diffraction analysis of samples which were subject to thermal treatment (Table 1). In case of a sample ground for 1 h the final product i.e. KBT occurs in sample heated up to the temperature 740°C.

The identification of intermediate compounds formed in the solid-state process of KBT synthesis was difficult because potassium titanates rich in TiO_2 no strong peaks on XRD patterns. The only strong peak with d-spacing 3.27 Å which appeared on XRD pattern of ground mixture heated up to 680°C was attributed to unidentified 'X' phase (Table 1), being probably formed as a result of anatase transformation at the temperature about 640°C [14]. We did not manage to identify the 'Y' phase by means of X-ray methods (the strongest peaks on XRD pattern: 2.85; 1.66; 4.60 Å), i.e. the intermediate phase rich in K_2O, which was formed at the final stage of synthesis (Table 1). The same problem was encountered by Lencka *et al*. [15] who studied hydrothermal synthesis of sodium and potassium bismuth titanates.

Scanning electron micrographs of the starting materials are presented in Figs 3 and 4 show scanning electron micrographs of mixed solids with molar formula $K_2CO_3+Bi_2O_3+4TiO_2$ heated up to 740, 840 and 1000°C. Grains can be seen in Figs 4a and b of intermediate compounds and of final product KBT, in Fig. 4c only KBT are seen.

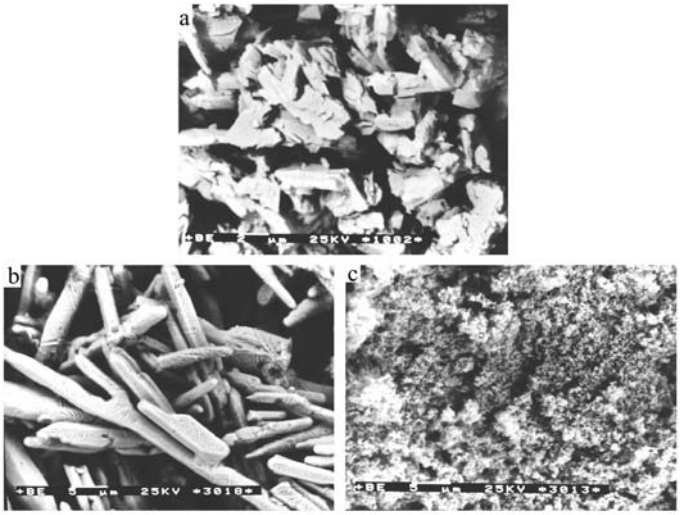

Fig. 3 Scanning electron micrographs of the starting materials: a – K_2CO_3, b – Bi_2O_3, c – TiO_2 – anatase

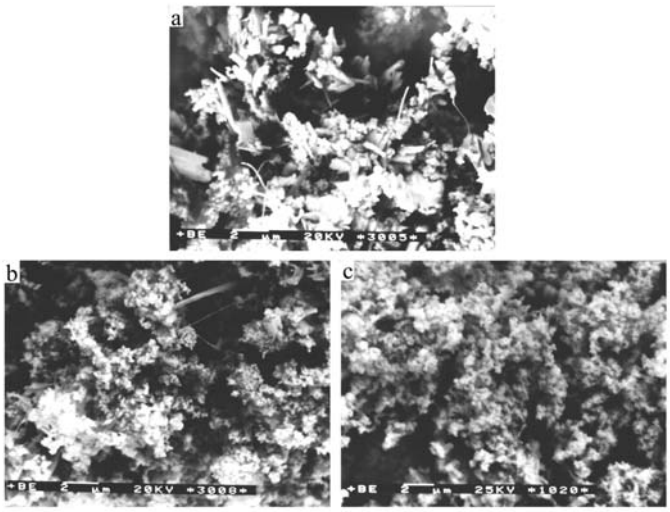

Fig. 4 Scanning electron micrographs of reaction products in the mixtures corresponding to molar formula K_2CO_3+Bi_2O_3+4TiO_2, heated up to temperature: a – 740, b – 840 and c – 1000°C

Conclusions

Investigation of synthesis of potassium bismuth titanate produced by heating the mixtures with molar formula K_2CO_3+Bi_2O_3+4TiO_2, was carried out using thermal and X-ray phase analyses. Various methods of homogenization of mixtures of starting

materials were applied. It was found that ternary compound $K_{0.5}Bi_{0.5}TiO_3$ was formed only through the intermediate binary compounds, i.e. bismuth titanates and potassium titanates rich in TiO_2. Associated mixing and grinding of precursor mixture in vibrating mill permits to decrease the temperature of formation of final product.

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