Journal of Thermal Analysis, Vol. 54 (1998) 63-69

SYNTHESIS OF SOLID SOLUTIONS IN THE (1–x)$PbZrO_3$–$xK_{0.5}Bi_{0.5}TiO_3$ SYSTEM

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Abstract

DTA, TG, XRD and IR methods were used to study the formation of solid solutions in the selected subsolidus range of the $PbZrO_3$–$K_{0.5}Bi_{0.5}TiO_3$ system by heating mixtures prepared using oxide substrates, i.e. PbO, Bi_2O_3, ZrO_2, TiO_2 and K_2CO_3. It was found that solid solutions are formed in the reaction of PbO and ZrO_2 with intermediate compound, i.e. $K_{0.5}Bi_{0.5}TiO_3$. $PbZrO_3$ was not found to be formed as an intermediate phase.

Keywords: DTA, IR, $K_{0.5}Bi_{0.5}TiO_3$, $PbZrO_3$, solid solution, TG, XRD

Introduction

Perovskite ferroelectric solid solutions are excellent materials for different piezoelectric devices applications, such as piezoelectric transducers, filters and resonators. The ferroelectric ceramics capable of working at elevated temperatures are based on ferroelectrics of high Curie temperature such as e.g. $PbTiO_3$ (PT) and $K_{0.5}Bi_{0.5}TiO_3$ (KBT). However PT and KBT are technologically slow-sintering materials in densification process which, together with a so-called high ferroelectrical hardness, is limiting their direct application [1–3].

$PbZrO_3$–$PbTiO_3$ (PZT) solid solutions have found the most wide-scale application, because show a number of interesting properties. On the other hand, PZT ceramic materials are characterized by high sintering temperature ranging from 1200 to 1360°C, at which the PbO volatilization problem occurs [4]. Solid solutions of the $PbZrO_3$–$K_{0.5}Bi_{0.5}TiO_3$ system (abbreviated as PZ–KBT hereafter) sinter at temperatures lower than those for PZT ceramic materials. Dielectric and piezoelectric properties of PZ–KBT ceramics were described by Rogova *et al.* [5] and Zaremba [6].

The aim of study was to determine the course of synthesis of the solid solutions in the selected subsolidus range of (1–x)$PbZrO_3$–$xK_{0.5}Bi_{0.5}TiO_3$ system.

1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Investigations of solid solutions synthesis in the (1–x)PZ–x KBT system were performed for $0 \leq x \leq 0.3$. The blends were prepared from the following substrates:

- K_2CO_3 (analytical reagent grade, POCh-Gliwice),
- Bi_2O_3 (analytical reagent grade, POCh-Gliwice),
- PbO (analytical reagent grade, POCh-Gliwice) – massicot (orthorhombic structure),
- TiO_2 (Tytanpol RC grade, 'Police' Chemical Works) – rutile,
- ZrO_2 imported (CS 10 grade, SEPR - France) – baddeleyite.

Potassium carbonate was calcined at 400°C to remove crystallization water, immediately prior to mixtures preparation. The other raw materials were dried at 110°C and weighted using laboratory balance with an accuracy 0.0001 g. The blends were mixed manually using isopropyl alcohol for 30–40 min. After drying out blends were subject to DTA and TG on an OD-102 Derivatograph (MOM, Budapest) under the following conditions: air atmosphere, sample mass 2000 mg, heating rate 10 deg min^{-1}, Al_2O_3 as reference material, temperature interval 20–1000°C. From the DTA curves of individual blends, the temperature ranges, in which solid solutions were synthesized, have been determined. Homogenization of the blends was controlled using the thermogravimetric analysis, 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.

Blends formed into briquettes under 30 MPa pressure were heated in air in a box furnace under conditions that assured stabilization of equilibrium state, i.e.:

$$400^\circ C \rightarrow 450^\circ C\ (24\ h) \rightarrow 500^\circ C\ (24\ h) \rightarrow 550^\circ C\ (24\ h) \rightarrow$$
$$\rightarrow 600^\circ C\ (24\ h) \rightarrow 650^\circ C\ (24\ h) \rightarrow 700^\circ C\ (24\ h) \rightarrow 750^\circ C\ (24\ h)$$

Heat treatment was started at a temperature of 400°C to find in what conditions PbO (massicot) is oxidized to Pb_3O_4. Phase composition of the reaction products was examined using X-ray diffraction (XRD) following every heating cycle. The diffraction patterns were recorded with a DRON-2,0 diffractometer; Ni-filtered CuK_α radiation was used. Joint Committee Powder Diffraction Standards (JCPDS) powder diffraction files were consulted for all phase analyses.

IR spectroscopic examinations of obtained solid solutions were conducted using a UR-20 spectrophotometer and KBr disc technique. IR spectra were recorded in the range from 400 to 1800 cm^{-1}.

Results and discussion

Figure 1 shows TG, DTG and DTA curves of the selected blend with the composition described by the formula (0.7PZ+0.3KBT). Table 1 demonstrates a

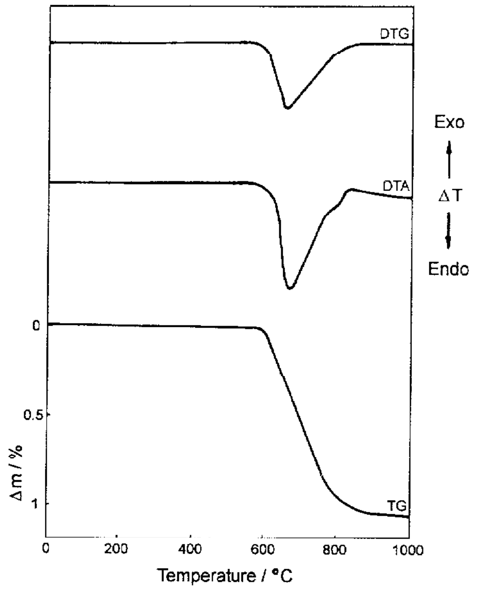

Fig. 1 TG, DTG and DTA curves of (0.7PZ+0.3KBT) blend

Table 1 Mass loss (Δ*m*) due to heat treatment of (1–*x*)PZ–*x*KBT blends

x	Δ*m*/%	
	Theoretical	Measured by TG method
0.1	0.32	0.3
0.2	0.67	0.7
0.3	1.05	1.1

theoretical mass loss in blends under examination (as calculated from their assumed composition) and the mass loss read off from TG curves within the range of 550–900°C; synthesis of solid solutions occurred in this temperature range, and the CO_2 loss due to decomposition of K_2CO_3 was recorded on TG curves. The phase composition examination results for the (1–*x*)PZ–*x*KBT for $0 \le x \le 0.3$ isothermally heated within the temperature range of 400–700°C, with the phases expressly identified on the X-ray diffraction patterns are presented in Table 2. Illustrative diffraction patterns of the blend with formula (0.7PZ+0.3KBT), under 24 h heat treatments within the temperature range of 400–700°C, are shown in Fig. 2. Fragments of IR spectra for obtained solid solutions and $PbZrO_3$ are drawn up in Fig. 3.

It has been found that Pb_3O_4 is formed within the temperature range of 400–450°C with respect to all analysed blends which were isothermally heated

Table 2 Isothermal heating of selected (1–x)PZ–xKBT powders in air

Temperature/ °C	Phase composition			
	x=0	x=0.1	x=0.2	x=0.3
400	P_M, Z, traces of M	P_M, Z, B, T, M	P_M, Z, B, T, M	P_M, Z, B, T, M
450	P_M, Z, M	Z, B, T, M, traces of P_M	Z, B, T, M, traces of P_M	Z, B, T, M, traces of P_M
500	Z, M	Z, B, T, M	Z, B, T, M	Z, B, T, M
550	Z, M, traces of P_L	Z, B, T, P_L, P_M, KBT	Z, P_L, P_M, KBT	Z, P_L, P_M, KBT
600	Z, P_M, P_L	Z, P_M, KBT, SS	Z, P_M, KBT, SS	Z, P_M, KBT, SS
650	Z, P_M, traces of PZ	SS	SS	SS
700	PZ, traces of Z, P_M	SS	SS	SS
750	PZ	SS	SS	SS

Denotations: B – Bi_2O_3, M – Pb_3O_4, P_L – PbO (litharge), P_M – PbO (massicot), T – TiO_2, Z – ZrO_2, KBT – $K_{0.5}Bi_{0.5}TiO_3$, PZ – $PbZrO_3$,
SS – Solid solution

Remark: In the Table potassium carbonate presence is not indicated as K_2CO_3 reflections on the X-ray diffraction patterns are weak and suppressed by reflections of other phases during 24 h. Oxidation of massicot to Pb_3O_4 proceeds slowly, since the DTA and TG of blends studied (heating rate 10°C min^{-1}) have not revealed Pb_3O_4 formation; and lack of suitable exothermic effect was noted on DTA curves and associated with it a mass gain on TG curves (Fig. 1). It is in agreement with the Munson's and Riman's test results [7] that with heating rates of 10 deg min^{-1} or greater, formation of Pb_3O_4 is not observed.

In the samples $(1-x)$PZ–x KBT for $x>0$, and consequently containing, apart from PbO and ZrO_2, also K_2CO_3, Bi_2O_3 and TiO_2 – minium occurs in small quantities just after heating at a temperature of 400°C (Table 2, Fig. 2). These samples, on heat treatment at 450°C, in practice do not already contain any free PbO but only Pb_3O_4. Formation of Pb_3O_4 in a blend with a composition corresponding to $PbZrO_3$, proceeds more slowly.

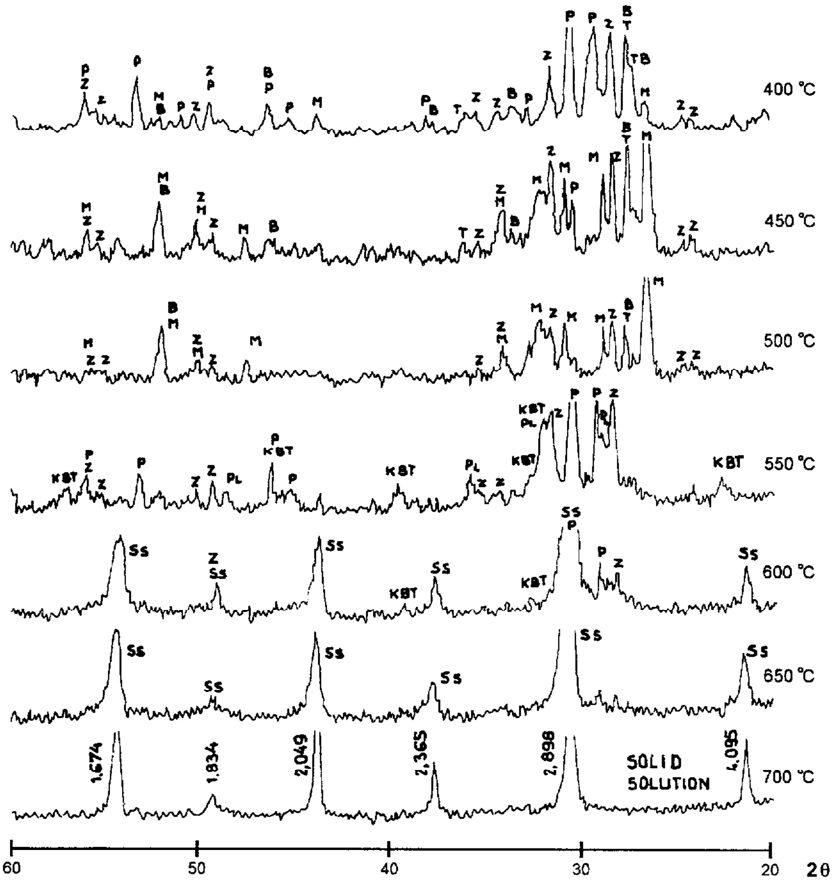

Fig. 2 XRD patterns of (0.7PZ+0.3KBT) blend isothermally heated within the temperature range of 400–700°C, B – Bi_2O_3, M – Pb_3O_4, P_L – PbO litharge, P – PbO massicot, T – TiO_2, Z, – ZrO_2, KBT – $K_{0.5}Bi_{0.5}TiO_3$, SS – solid solution

Further heating of samples up to 550–600°C makes decomposition of Pb_3O_4; on X-ray diffraction patterns PbO lines occur again. The coexistence of litharge (PbO_L) and massicot (PbO_M) was observed in this study. In the sample of blend whose composition is conforming with $PbZrO_3$, after heating at 600°C, the intensity of PbO_M peaks increases, however that of PbO_L peaks decreases until their complete decay in the sample heated at 650°C. According to Munson and Riman [7] Pb_3O_4 reduces to litharge at about 560°C. At temperatures greater than 560°C, litharge converts to massicot.

No formation of $PbZrO_3$ as an intermediate phase in the process of solid solutions synthesis was observed, whereas the presence of $K_{0.5}Bi_{0.5}TiO_3$ was found. The KBT reflections were markedly insolated on the diffraction patterns of blends for $x>0$ after heating at 550°C. These reflections decay on diffraction patterns in samples heated at 650°C as the reflections of solid solutions appear. The $PbZrO_3$ synthesis process progresses at higher temperatures than that of solid solutions synthesis. The blend whose composition is conforming with $PbZrO_3$ ($x=0$) becomes practically homogeneous after being heated at 700–750°C, however the blends in which composition corresponds to solid solutions – already at a temperature of about 650°C.

A number of authors [8–10] investigating the mechanisms of synthesis of $Pb(Zr, Ti)O_3$ solid solutions, which are known long since, observed $PbZrO_3$ formation as an intermediate compound only when ultrafine ZrO_2 was used as a substrate. In a case when commercial ZrO_2 is used the only intermediate compound occurring in the process of PZT solid solutions is $PbTiO_3$.

Analysis of IR spectra of obtained solid solutions (Fig. 3) has shown displacement of maxima of absorption bands towards higher wave numbers as the KBT concentration in solutions increases, as well as clear broadening of bands and their asymmetry.

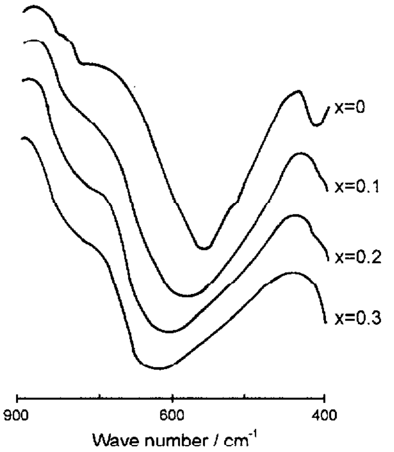

Fig. 3 IR spectra of (1–x)PZ–xKBT solid solutions

Conclusions

When oxide substrates are used the solid solutions of the $(1-x)PbZrO_3-xK_{0.5}Bi_{0.5}TiO_3$ system (for $0<x\leq0.3$) are formed within the temperature range of 600–650°C as a result of PbO and ZrO_2 reaction with $K_{0.5}Bi_{0.5}TiO_3$ constituting intermediate compound in the synthesis process. PbO (massicot) slowly oxidizes to the Pb_3O_4 phase within the temperature range of 400–450°C and reduces to litharge at a temperature of about 550°C. At temperatures greater than 550°C, litharge converts to massicot. With heating rates of 10 deg min^{-1}, formation of Pb_3O_4 is not observed.

No formation of $PbZrO_3$ as an intermediate phase in the process of solid solutions synthesis is observed. $PbZrO_3$ is formed within the temperature range of 650–750°C.

Infrared spectroscopy of solid solutions of $PbZrO_3-K_{0.5}Bi_{0.5}TiO_3$ system has shown displacement of maxima of absorption bands towards higher wave numbers as the KBT concentration in solutions increases. The IR method can provide a complement for the thermal analysis and X-ray diffraction during investigations on synthesis of solid solutions in multicomponent systems, and their identification as well.

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