The devitrification of PbO-B₂O₃-ZnO glass doped with Li₂O

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In this paper the effect of the addition of Li₂O on the crystallization behavior of PbO-B₂O₃-ZnO glass was investigated by the differential thermal analysis (DTA) and X-ray powder diffraction (XRPD) methods. The crystallization ability, as well as the crystalline phases which develop during devitrification of the glass were examined. The results of DTA and XRPD analysis showed that the addition of Li₂O varies the sequence of the crystallization as well as the phase composition of the crystalline phase. The glasses with Li₂O crystallize at a lower temperature (360 ºC) with 4Li₂O·4ZnO·3B₂O₃ as the major crystalline phase. The base PbO-B₂O₃-ZnO glass crystallizes at 480 ºC with PbO·2ZnO·B₂O₃ as the major crystalline phase.

Keywords: glass, devitrification, DTA, XRPD.

INTRODUCTION

Low-melting oxide glasses with a high content of lead are widely used in various fields of technology. In recent years considerable attention has been paid to their use in electronics and microelectronics (solder or sealing glasses, thick film capacitors and resistors, *etc*.) because of their thermal stability.[1,2]

The basis for the development of these glasses are the PbO-B₂O₃-SiO₂ and PbO-B₂O₃-ZnO glassy systems. In order to improve the physicochemical and electrical characteristics, a small amount of different oxides (Na, Li, B, Cu, Al, *etc*). are usually added to the denoted ternary systems.[2–8]

The basic data of these glasses can usually be found in the patent literature, but systematic investigations of their properties especially their ability to crystallize are rare.

The purpose of the present study was to determine the effect of the addition of small amounts of Li₂O on the crystallization behavior of PbO-B₂O₃-ZnO glass. The crystallization ability, as well as the crystalline phases which develop during devitrification of the glass were examined by the DTA and XRPD methods.

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EXPERIMENTAL

Four glasses with different amounts of Li_2O were chosen for study. The chemical compositions of the glasses are given in Table I.

TABLE I. Composition of the synthesized glasses w_i, (wt. %)

Oxide	Glass			
	1	2	3	4
PbO	66.6	66.3	66.0	65.3
B_2O_3	17.6	17.5	17.4	17.2
ZnO	15.8	15.7	15.6	15.5
Li_2O	–	0.5	1.0	2.0

The glasses were prepared by the standard procedure of melting previously homogenized mixtures of reagent grade Pb_3O_4, H_3BO_3, ZnO and Li_2CO_3 in a zirconia crucible. Melting was performed in a laboratory electric furnace at 1100 ºC for 2 h. The melts were quenched in air by pouring into a 50 mm diameter steel mould. The X-ray diffraction patterns of the obtained samples showed that no crystalline phases were formed.

The DTA curves of glass powder (granulation DIN 100) were recorded in air at a heating rate of 10 ºC min^{-1}. A "MOM" - Hungary differential thermal analyser, with α- Al_2O_3 powder as the reference material, was used.

The powder X-ray diffraction data were collected by the step-scan procedure with an automatic powder diffractometer Philips PW1710 using the graphite-monochromated CuKα radiation.

The crystallization ability of the synthesized glasses was determined by the method of continuously cooling the glass melts at low rates,[9] as well as by the isothermal treatment of the glass samples at 360, 480, 570 and 720 ºC for different times up to 24 h ("rapid quenching method"). The quoted temperatures were chosen on the basis of previously performed DTA of the PbO-B_2O_3-ZnO glasses.[9-11] The glass samples previously prepared by the ASTM 829-81 procedure were placed into platinum crucibles and put into furnace (t = 800 ºC). After one hour the furnace was turned off and samples inside were cooled to room temperature.

The isothermal experiments were carried out by the heating of the glass samples placed in the platinum crucibles at the chosen temperature at different time. After heating the samples were quickly transfered out of furnace and then cooled in the air. The obtained samples were then analyzed by XRPD.

RESULTS AND DISCUSSION

The DTA curves of glasses 1, 2 ,3 and 4 are presented in Fig. 1. The transition temperature t_g, temperature of crystallization peaks t_c and $t_{c,1}$, melting temperature t_m and $t_{m,1}$ and flow temperature t_f for the glasses 1, 2, 3 and 4 determined from the DTA curves in Fig. 1 are given in Table II.

On the basis of the obtained results for the transition and flow temperature of the glasses it is obvious that increasing the Li_2O content leads to a decrease in the transition and flow temperature.

The results obtained by the method of continuously cooling the glass samples at a low rate showed that all the investigated glasses have a small tendency to crystallization. Only glass 1 (base glass) crystallized during the experiment. The X-ray diffraction
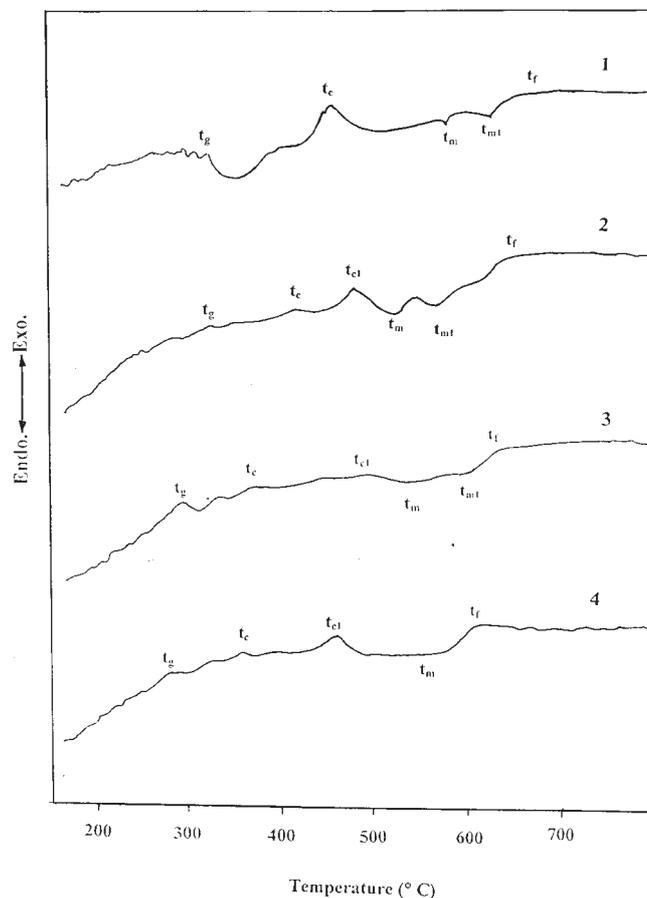
Fig. 1. DTA curves of glass samples 1, 2, 3 and 4; t_g, transition temperature, t_c and $t_{c,1}$, temperature of the crystallization peak; t_m and $t_{m,1}$, melting temperature, t_f, flow temperature.

pattern of glass sample 1 is shown in Fig. 2. No crystalline phases were detected in the glasses 2, 3 and 4 (glasses with Li_2O).

TABLE II. Transition temperature, temperature of the crystallization peak, melting temperature and flow temperature of glasses 1, 2, 3 and 4

Glass	t_g ºC	t_c ºC	$t_{c,1}$ºC	t_m ºC	t_{m1}ºC	t_fºC
1	340	480	–	580	630	650
2	320	400	490	530	580	630
3	300	360	490	530	588	624
4	290	360	460	500	–	612

Analysis of the diffraction patterns of the partially crystallized glass samples 1, showed that the glass phase is dominant. The crystalline phase is present in a very small amount. However, $3ZnO \cdot B_2O_3$ (JCPDS-27-983) was determined as the possible crys-
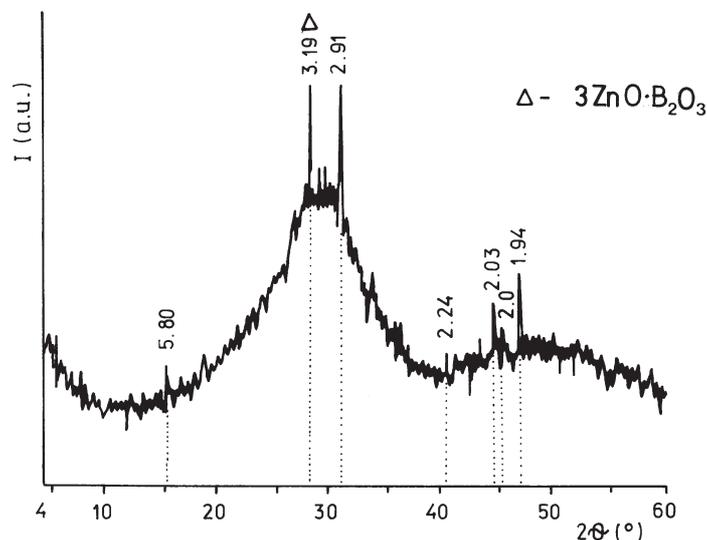
Fig. 2. X-ray diffraction pattern of the glass sample 1 (continuous cooling of the glass melt at a low rate).

talline phase. It should be noted that, owing to the very small amount of crystalline material and the presence of very big humps of the glass phase which overlap reflections, unambiguous phase identification was very difficult.

The results of the XRPD analysis of the isothermally treated samples are summarized in Table III.

TABLE III. Results of the XRPD analysis of the isothermally treated glass samples

Glass	Temperature/°C	Time/h	Crystalline phases identified[*]
1	360	2–24	–
	480–570	2–24	$PbO \cdot 2ZnO \cdot B_2O_3$[1]
			$2PbO \cdot ZnO \cdot B_2O_3$[2]
	630–720	2–24	no crystals
2, 3 and 4	360	2–24	$4Li_2O \cdot 4ZnO \cdot 3B_2O_3$[3]
			$Li_2O \cdot 2ZnO \cdot B_2O_3$[4]
	480–570	2–24	$Li_2O \cdot 2ZnO \cdot B_2O_3$
	630–720	2–24	no crystals

[*]JCPDS 19–709[1]; JCPDS 19–711[2]; JCPDS 36–638[3]; JCPDS 20–1443[4]

The X-ray diffraction patterns of the isothermally treated glasses 1 and 4 at 360 °C and 480 °C are shown in Figs. 3, 4 and 5.

Glass sample 1 (base glass), thermally treated for 2–24 h at 480–580 °C, crystallized with $PbO \cdot 2ZnO \cdot B_2O_3$ as the main crystalline phase. The presence of the $2PbO \cdot ZnO \cdot B_2O_3$ crystalline phase was also detected in the samples. Analysis of the X-ray diffraction patterns shows that the glass phase is dominant in sample 1. The crystalline phases are present to a small extent even after 24 h of thermal treatment of glass
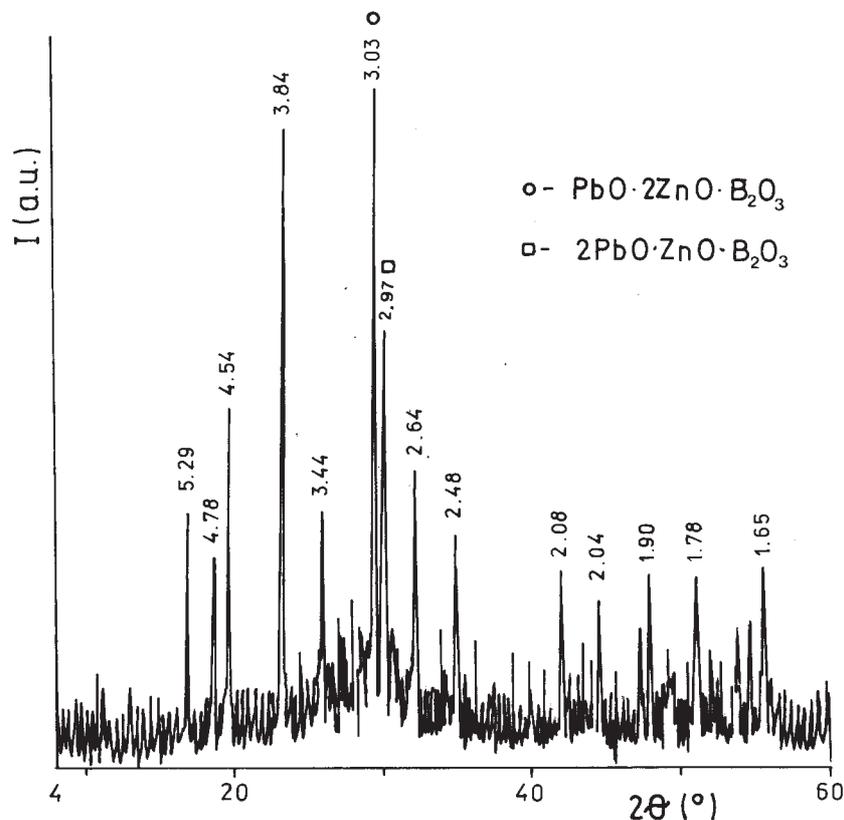
Fig. 3. X-ray diffraction pattern of the glass sample 1 thermally treated at 480 ºC for 24 h.

sample (Fig. 3). The existence of these phases in the $PbO-B_2O_3-ZnO$ system was previously described by Lee *et al.*[10] and Petzoldt.[12]

The glasses 2, 3 and 4 with Li_2O were crystallized at 360 ºC for 2–24 h with $4Li_2O \cdot 4ZnO \cdot 3B_2O_3$ being the crystalline phase in all the samples. In addition, all samples thermally treated at 360 ºC for 24 h showed different reflections of other crystalline phases. Because of the overlapping and the very small content, identification of the crystalline phase was not reliable, but $Li_2O \cdot 2ZnO \cdot B_2O_3$ was tentatively identified (Fig. 4).

The glasses 2, 3 and 4 thermally treated at 480 ºC for 2–24 h crystallized with $Li_2O \cdot 2ZnO \cdot B_2O_3$ as the crystalline phase (Fig. 5). As in the glass sample 1, the detected crystalline phase is present to a small extent even after 24 h of thermal treatment of the samples 2, 3 and 4. The glass phase is dominant in all samples.

The glass sample 1 (base glass), thermally treated for 2–24 h at 630–720 ºC and glass samples 2, 3 and 4 (with Li_2O) thermally treated for 2–24 h at 520–720 ºC did not crystallize.

Considering the results of DTA and XRPD analysis, it can be concluded that:
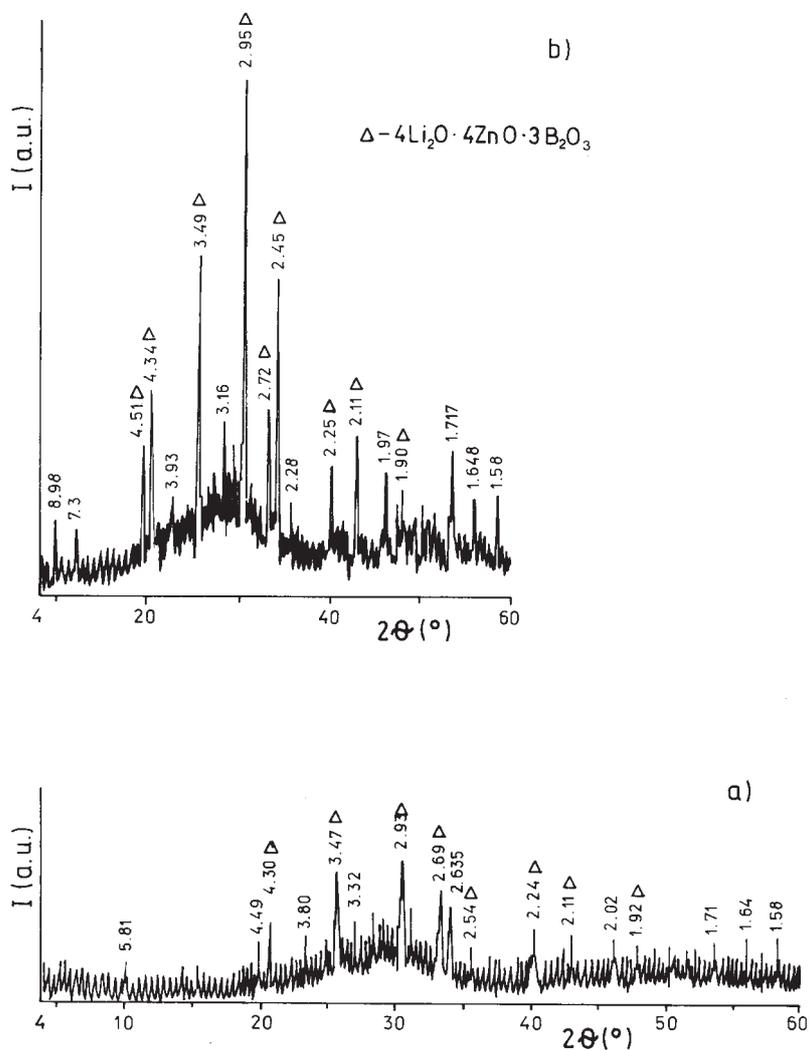
Fig. 4. X-ray diffraction pattern of the glass sample 4 thermally treated at 360 ℃ for 2 h (a) and 24 h (b).

– The exothermic effect observed on the DTA curve 1 for glass 1, in Fig. 1, corresponds to the formation and crystallization of $PbO·2ZnO·B_2O_3$ and $2PbO·ZnO·B_2O_3$ with the temperature of the crystallization peak, $t_c = 480$ ℃. The shape of this peak indicates the crystallization of two phases.

– As expected, two endothermic peaks which corresponds to the melting of $PbO·2ZnO·B_2O_3$ and $2PbO·ZnO·B_2O_3$ are observed with melting temperature $t_m = 580$ ℃ and $t_{m1} = 630$ ℃. The difference in the size of the exothermic peak and the two endothermic peaks confirms the assumption that these two phases were formed.
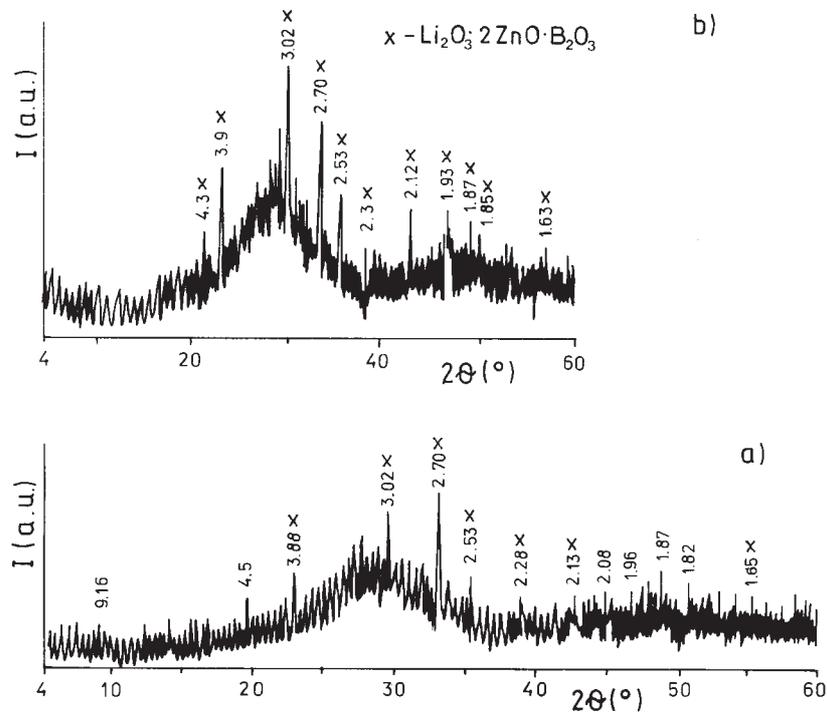
Fig. 5. X-ray diffraction pattern of the glass sample 4 thermally treated at 480 ºC for 2 h (a) and 24 h (b).

– With glasses containing Li_2O, new crystalline phases were formed. For glasses 2, 3 and 4, the first exothermic peak corresponds to the crystallization of the $4Li_2O \cdot 4ZnO \cdot 3B_2O_3$ phase, and the second exothermic peaks to the crystallization of the $Li_2O \cdot 2ZnO \cdot 3B_2O_3$ phase. The observed endothermic peaks correspond to the melting of these phases. The sizes of these endothermic peaks are similar to the sizes of the exothermic peaks. This fact indicate that $4Li_2O \cdot 4ZnO \cdot 3B_2O_3$ and $Li_2O \cdot 2ZnO \cdot 3B_2O_3$ are formed during the synthesis of glasses 2, 3 and 4.

– The temperature of the crystallization peak for $4Li_2O \cdot 4ZnO \cdot 3B_2O_3$ decreases with increasing Li_2O content. Thus, for the glass 4 the temperature of the crystallization peak is 360 ºC (t_c). This trend of the crystallization peak also appears with $Li_2O \cdot 2ZnO \cdot 3B_2O_3$ and in this case, the temperature of the crystallization peak is 460 ºC ($t_{c,1}$) for glass 4. For glass 4 the intensity of the diffraction patterns and the size of the crystallization peaks indicate that only small quantities of the crystalline phases are present.

CONCLUSION

The effect of the addition of Li_2O on the crystallization behavior of PbO-B_2O_3-ZnO glass was investigated in this study.

On the basis of the obtained results it may be concluded that the addition of small amounts of Li_2O causes the sequence of crystallization and the phase compositon of the crystalline phase formed during crystallization to vary. The glasses containing Li_2O

crystallize at a low temperature (360 ºC) with $4Li_2O \cdot 4ZnO \cdot 3B_2O_3$ being the main crystalline phase. The base glass 1 (without Li_2O) crystallize at a higher temperature (480 ºC) with $PbO \cdot 2ZnO \cdot B_2O_3$ being the main crystalline phase. Increasing the Li_2O content leads to a decrease in the transition temperature and the flow temperature.

The changes in the crystallization behavior may be explained by the influence Li_2O exerts on the PbO-B_2O_3-ZnO glass network structure. As a modifying oxide, Li_2O weakens the base glass network structure, and induces the atomic rearrangement necessary for the formation of the compounds $4Li_2O \cdot 4ZnO \cdot 3B_2O_3$ and $Li_2O \cdot 2ZnO \cdot 3B_2O_3$ during the synthesis of the glasses with Li_2O which crystallized during thermal treatment.

И З В О Д

РАСТАКЉИВАЊЕ PbO-B_2O_3-ZnO СТАКЛА СА ДОДАТКОМ Li_2O

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У овом раду методом диференцијално-термијске анализе и рендгенске дифрактометрије праха испитиван је утицај додатка Li_2O на кристализацију PbO-B_2O_3-ZnO стакла. Резултати испитивања су показали да увођење малих количина Li_2O у основно PbO-B_2O_3-ZnO стакло мења ток кристализације и фазни састав кристалне фазе. Стакла која садрже Li_2O кристалишу на нижој температури (360 ºC) уз издвајање $4Li_2O \cdot 4ZnO \cdot 3B_2O_3$ као основне фазе. Основно PbO-B_2O_3-ZnO стакло кристалише на вишој температуре (480 ºC) уз издвајање $PbO \cdot 2ZnO \cdot B_2O_3$ као кристалне фазе.

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