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X-ray diffraction studies of phase transformations in heavy-metal fluoride glasses

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The crystallization of five ZrF_4-based glasses has been investigated using powder X-ray diffraction and differential scanning calorimetry. The crystalline phase in Zr–Ba–La–Pb fluoride glass was found to be β-$BaZrF_6$. In other glasses the crystal phases could not be identified. Reversible polymorphic phase transformations occur in Zr–Ba–La–Li and Zr–Ba–La–Na fluoride glasses when heated to higher temperatures.

1. Introduction

The heavy-metal fluoride glasses (HMFG) are potential materials for various optical and other applications [1]. The most significant use is as extremely low-loss, long-distance, repeaterless optical waveguides for telecommunication data transmission and sensing.

However, these glasses are highly susceptible to devitrification during glass formation and fibre drawing. In order to prepare low-loss fibres the formation of microcrystallites, which act as light-scattering centres resulting in unacceptable loss of the optical signal, has to be avoided. It is therefore important to understand the crystallization behaviour of the HMFG.

The crystallization kinetics of a number of fluorozirconate glasses have been studied [2–5] with isothermal and athermal differential scanning calorimetry (DSC), and with optical and electron microscopy. The devitrification of Zr–Ba–La–Al fluoride glass has been studied by Weinberg and co-workers [6, 7] and Sr–Mg–Y–Al fluoride glass by Kanamori [8].

The structure and composition of the crystalline phases separating in HMFG on heating are of considerable interest. We have reported [9] phase transformation studies of three ZrF_4 glasses using X-ray diffraction (XRD) and DSC. Results of a similar investigation for five additional fluorozirconate glasses are presented in this communication.

2. Experimental procedure

The glass compositions used in this investigation are presented in Table I. The method of glass synthesis was essentially the same as described elsewhere [2–5]. The constituent metal fluorides (Cerac) were mixed with $NH_4F \cdot HF$ and heated to $\sim 500°$ C to remove oxide impurities. The contents were melted in a vitreous carbon crucible by heating in stages to $\sim 900°$ C under a reactive atmosphere of 3% Cl_2 in nitrogen in a resistance furnace. The melt was cooled to $\sim 650°$ C and quenched in brass moulds, followed by annealing for ~ 5 min near the glass transition temperature, and then allowed to cool slowly to room temperature. The ZBLALi and ZBLALiPb glasses (see Table I for acronyms) were melted in a platinum crucible under an inert argon atmosphere at the Naval Research Laboratory, Washington, DC.

Small pieces of glass were crystallized by heating in a differential scanning calorimeter (Perkin-Elmer Model DSC IV) up to various stages of the DSC curve at the rate of $10°\,C\,min^{-1}$, or isothermally heated for different times and cooled to ambient temperature at $300°\,C\,min^{-1}$. The devitrified glass samples were finely powdered and the X-ray diffraction patterns were recorded with a

TABLE I Acronyms and batch compositions of heavy-metal fluoride glasses

Component	Composition of glass (mol%)				
	ZBLPb	ZBLLi	ZBLN	ZBLALi*	ZBLALiPb*
ZrF_4	58.8	58	58	50.7	49.83
BaF_2	31.4	15	15	20.7	16.96
LaF_3	4.8	6	6	5.2	5.06
PbF_2	5.0	–	–	–	4.09
LiF	–	21	–	20.2	20.09
NaF	–	–	21	–	–
AlF_3	–	–	–	3.2	3.16

*Analysed compositions

Phillips Norelco diffractometer using nickel filtered Cu$K\alpha$ radiations at 1/2° or 1° (2θ) per minute from 10 to 65°.

3. Results and discussion

Values of some characteristic parameters [5] of the HMFG are listed in Table II. The reduced parameter $(T_x$-$T_g)/T_g$, where T_g is the glass transition temperature and T_x is the temperature for the onset of crystallization, for these glasses is higher than for the binary ZrF_4-BaF_2 (ZB) glass [5, 9]. According to Cooper and Angell [10], the value of this reduced parameter indicates the glass-forming ability. The multicomponent glasses with higher values of the reduced parameter are better glass formers and more stable against devitrification. The binary ZB glass could only be prepared as thin sheets by fast quenching of the melt by pressing between two metal plates. It was easier to cast the multicomponent glasses as bulk samples.

3.1. ZrF_4–BaF_2–LaF_3–PbF_2 (ZBLPb) glass

The DSC output for the ZBLPb glass at a heating rate of 10° C min^{-1} is given in Fig. 1. A number of glass samples were heated up to different points of the DSC curve as shown in Fig. 1, followed by recording of their powder X-ray diffraction at room temperature. Sample PB6 was heated at 345° C for 12 min. Typical X-ray diffractograms are presented in Fig. 2. In Samples PB6 to PB2 the positions and relative intensities of the XRD peaks correspond to a β-$BaZrF_6$ phase. In PB1, peaks for β-$BaZrF_6$ are present along with some additional peaks at $2\theta = 21.45$, 23.75, 25.75 and 27.2°, of which the peak at $2\theta = 21.45°$ is the most prominent. These peaks did not match with any of the known phases in the JCPDS File [11]. In Fig. 1, P1 is the glass transition peak and P2 and probably also P3 are the crystallization exotherms.

3.2. ZrF_4–BaF_2–LaF_3–LiF (ZBLLi) glass

A complete DSC thermogram for the ZBLLi glass at a scan rate of 10° C min^{-1} is presented in Fig. 3. The XRD patterns of a number of glass samples after different heat treatments (Fig. 3) are shown in Fig. 4. The endotherm P1 is the glass transition and P2 is the glass crystallization exotherm. The peak positions in the X-ray diffractograms of L1, L2 and L3 are the same; the peak intensities increased from L1 to L2 and L3. Additional peaks are present in the XRD of L4, which perhaps indicates that the DSC peak P3 results from the crystallization of a new crystal phase from the glass. A comparison of the XRD spectra of L4 and L5 reveals the same peak positions in both. This probably shows that the endotherm P4 in Fig. 3 is due

TABLE II Characteristic parameters of the fluorozirconate glasses studied [5]

Glass	Glass transition temperature* T_g (K)	Onset of crystallization temperature* T_x (K)	Reduced parameter $(T_x - T_g)/T_g$
ZBLPb	576	637	0.11
ZBLLi	509	615	0.21
ZBLN	520	604	0.16
ZBLALi	524	638	0.22
ZBLALiPb	518	618	0.19

*From DSC scans at a heating rate of 10° C min^{-1}.

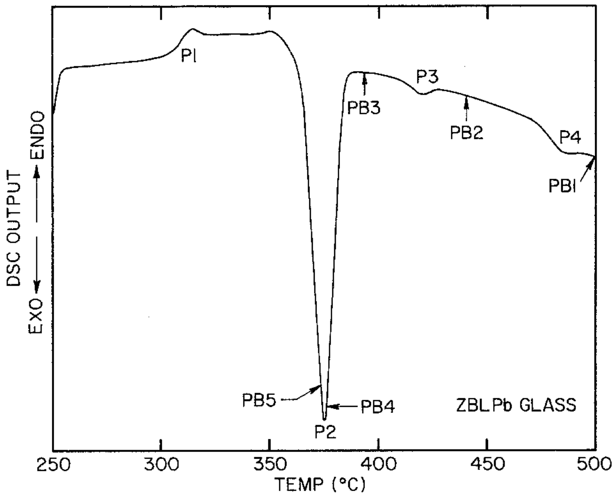

Figure 1 DSC thermogram for ZrF_4–BaF_2–LaF_3–PbF_2 glass heated at 10° C min^{-1}. PB1, PB2 etc. indicate the stages of heat treatment of various glass samples.

to a reversible transformation of a low-temperature phase into its high-temperature stable analogue. XRD data are available in the JCPDS file [11] and elsewhere [12–15] for a large number of fluoride compounds of Zr–Li, Zr–Ba etc., but it was not possible to identify the crystalline phases in this system.

3.3. ZrF_4–BaF_2–LaF_3–NaF (ZBLN) glass

A complete DSC curve for the ZBLN glass heated at 10° C min^{-1} is shown in Fig. 5. A number of peaks are present. To unscramble the processes responsible for these peaks, a number of glass samples were heated in the DSC up to various stages (see Fig. 5) at 10° C min^{-1}, quickly cooled, and

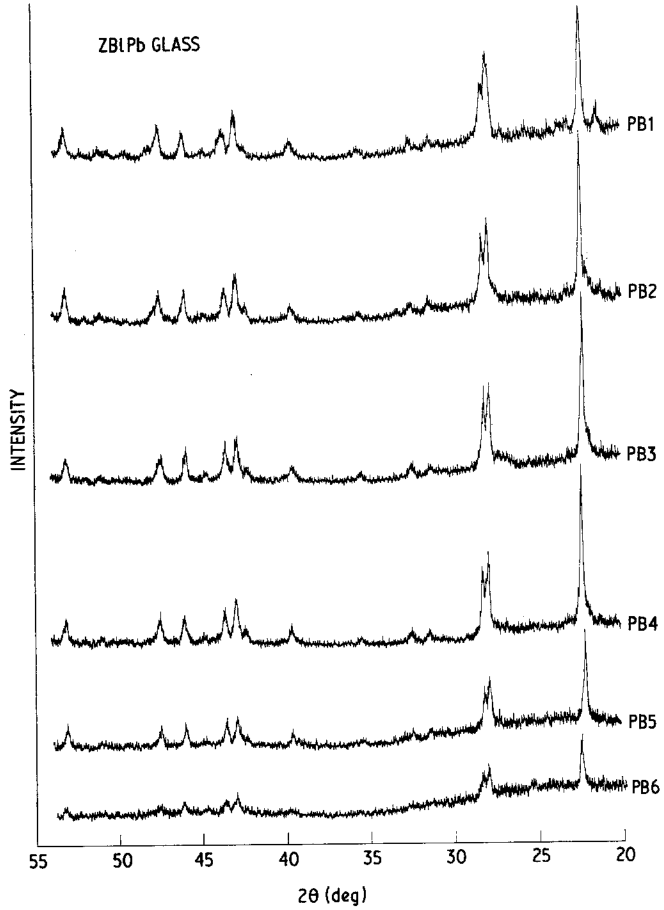

Figure 2 Powder X-ray diffraction patterns of ZrF_4–BaF_2–LaF_3–PbF_2 glasses after various heat treatments; for details see text.

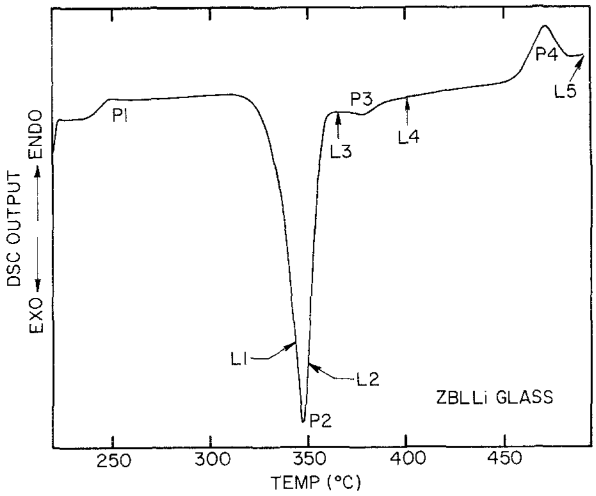

Figure 3 DSC trace of ZrF_4–BaF_2–LaF_3–LiF glass heated at 10° C min^{-1}. L1, L2 etc. indicate the points up to which the different glass samples were heated.

subjected to powder X-ray diffraction. The XRD patterns are presented in Fig. 6.

The DSC peak P1 is due to the glass transition and P2, P3 are the glass crystallization exotherms. The crystallization of glass was complete at the end of P3 but not at the end of P2. This was confirmed from a simple experiment [16]. A DSC scan was terminated at the end of P3, the sample quickly cooled below T_g and reheated at 10° C min^{-1}. No glass transition or crystallization peaks were found in the rescan. However, in a similar experiment where the DSC scan was stopped at the end of P2, an exothermic peak was found to be present in the rescan.

Comparison of the XRD pattern of Samples N3 and N4 indicates the presence of additional peaks in the XRD of N4. This probably shows that the DSC peak P3 is due to the crystallization of a new phase from the glass. The XRD patterns of Samples N4 and N5 are similar. This indicates that the

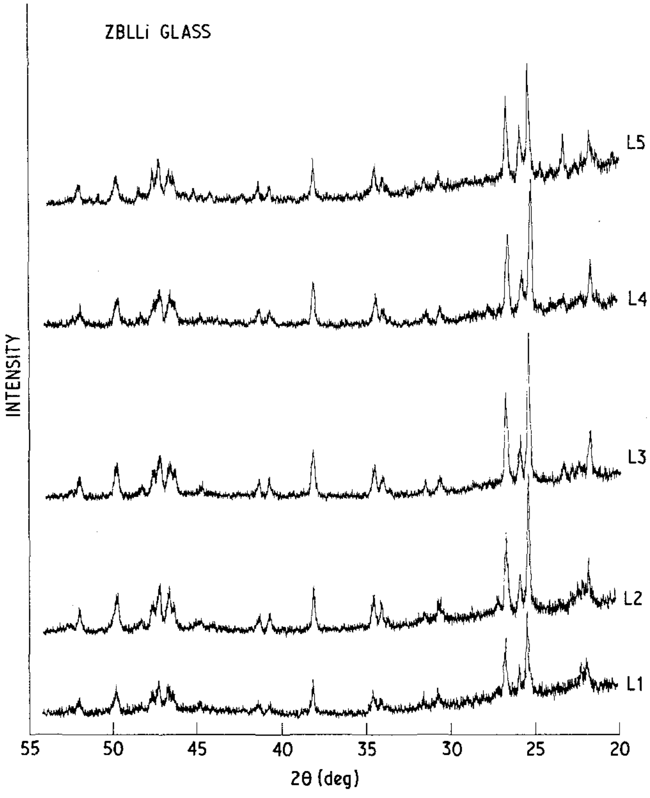

Figure 4 Powder X-ray diffraction patterns of ZrF_4–BaF_2–LaF_3–LiF glass after different heat treatments.

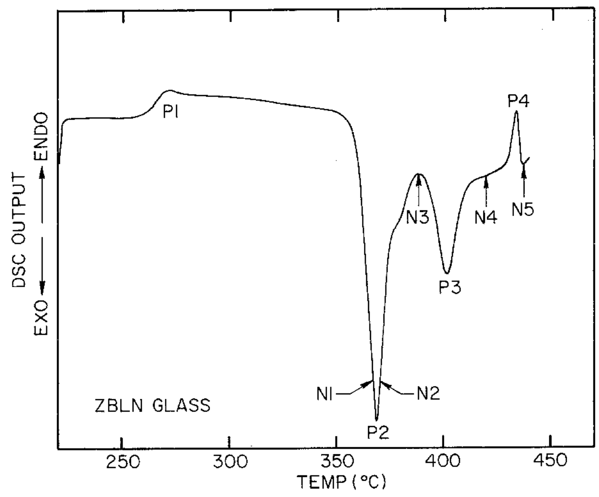

Figure 5 DSC output for ZrF_4–BaF_2–LaF_3–NaF glass at a heating rate of 10° C min^{-1}. N1, N2, etc. show the stages to which the glass samples were heated.

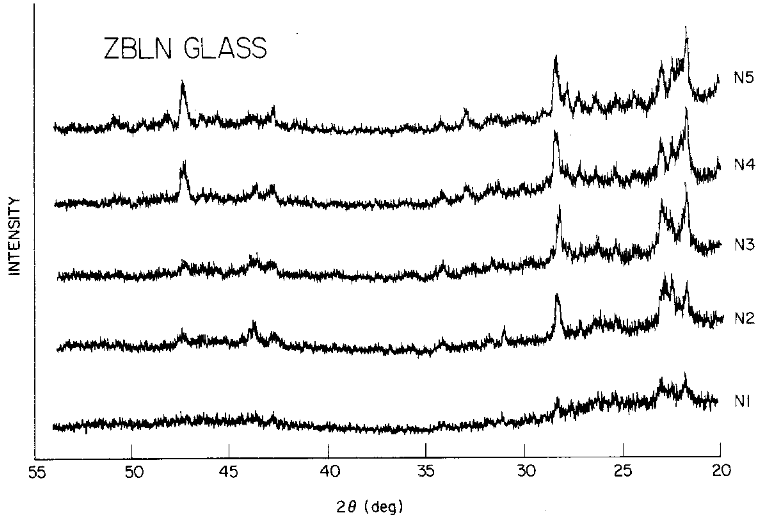

Figure 6 Powder X-ray diffraction patterns of ZrF_4–BaF_2–LaF_3–NaF glass with different thermal treatments.

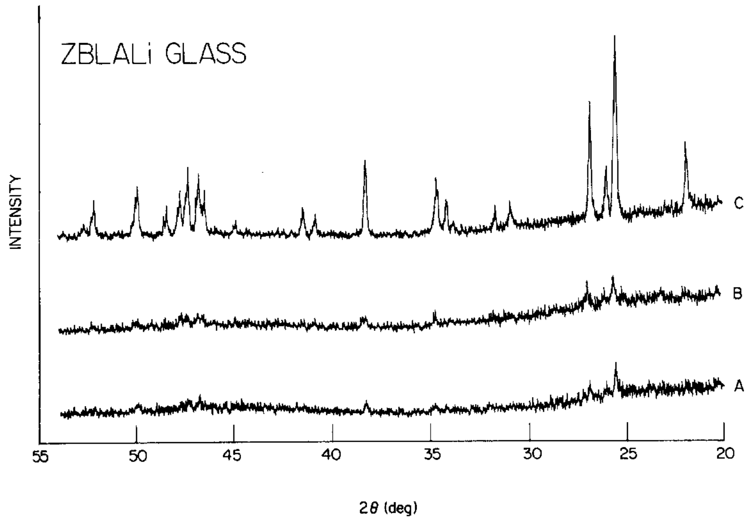

Figure 7 Powder X-ray diffraction patterns of ZrF_4–BaF_2–LaF_3–AlF_3–LiF glass after heating for (A) 30 min at 315° C; (B) 60 min at 315° C, and (C) 3 min at 380° C.

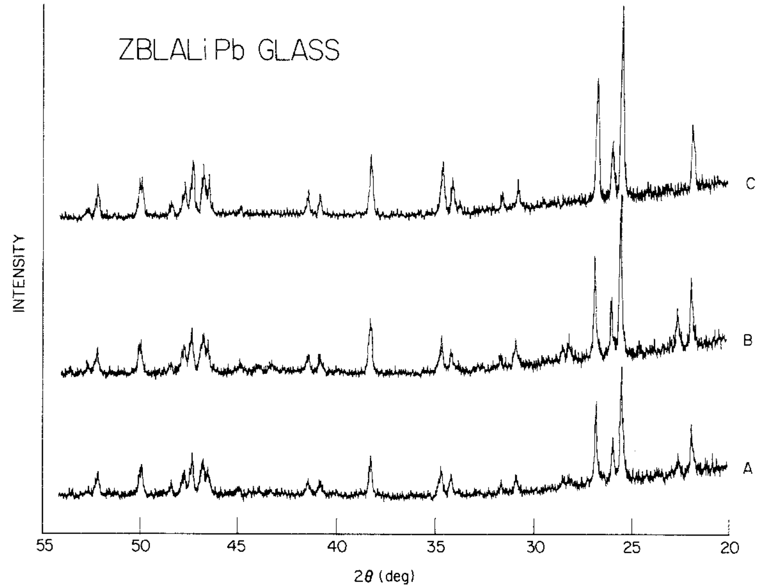

Figure 8 Powder X-ray diffraction patterns of ZrF_4–BaF_2–LaF_3–AlF_3–LiF–PbF_2 glass heated for (A) 30 min at 320° C; (B) 45 min at 320° C, and (C) 3 min at 360° C.

endotherm P4 is perhaps due to a reversible polymorphic phase transformation, $\alpha \rightleftharpoons \beta$, where a low-temperature phase α is changing into the high-temperature stable phase β. On cooling, the β phase reverts back to its α-analogue. Unfortunately none of these phases could be identified, as the relative intensities and positions of the peaks in the XRD patterns did not match with any of the Zr–Ba, Zr–Na, or other fluoride compounds for which information is available in the literature [11–15].

3.4. ZrF_4–BaF_2–LaF_3–AlF_3–LiF (ZBLALi) and ZrF_4–BaF_2–LaF_3–AlF_3–LiF–PbF_2 (ZBLALiPb) glasses

The crystallization kinetics of these two glasses have recently been reported by Bansal *et al.* [4] using isothermal and non-isothermal DSC. The DSC curves for these glasses are given in that paper. The powder X-ray diffractograms of ZBLALi and ZBLALiPb glasses after isothermal heat treatments at different temperatures are given in Figs. 7 and 8 respectively. The peak positions in the XRD of ZBLALi and ZBLALiPb glasses heated for 3 min at 380 and 360° C respectively are exactly the same. This shows that the same crystalline phase(s) separate out in both glasses, and that PbF_2 is not a constituent of the crystals. Additional peaks are present in ZBLALiPb glass samples heated for 30 and 45 min at 320° C, which implies that another crystal phase is present at this temperature. It was not possible to identify any of these phases. Lu *et al.* [17] have reported the presence of different morphologies of crystals of pure components ZrF_4, LaF_3 and AlF_3 in "quenched" ZBLALi glasses, i.e. glasses without any heat treatment.

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