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The influence of $Ba(PO_3)_2$ on the formation characteristics of fluorophosphate glasses

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Formation characteristics of glasses in the system AlF_3–MF_2–$Ba(PO_3)_2$ (M = Ca, Mg, Sr, Ba) have been studied as a function of $Ba(PO_3)_2$ content. Glass formation tendency increased with increasing $Ba(PO_3)_2$. The critical cooling rate, R_c, for glass formation decreased from 98 ± 7 to $2 \pm 0.5\,^\circ C\,s^{-1}$ when the $Ba(PO_3)_2$ content of the glass increased from 0 to 1.5 mol %. The improvement in glass formation caused by $Ba(PO_3)_2$ was due to linking of the broken chains present in the structure. The infrared transmission spectra of these glasses and their crystallization products suggested that the structure changed from short chains of AlF_6 groups to long chains of PO_3F and Ba(Ca, Mg, Sr)P_2O_7 groups with increasing $Ba(PO_3)_2$ content of the glass.

1. Introduction

Fluorophosphate glasses have received considerable interest as materials for optical applications because they offer improved optical properties, such as low refractive index with high Abbe number, large anomalous partial dispersion, low non-linear refractive index, and high transmittance in near ultraviolet (u.v.) and infrared (i.r.) regions [1–5]. The combination of these properties makes these glasses useful for special applications, such as components of high energy laser systems (undoped lenses, turning mirrors, filters, Faraday rotators, laser windows), i.r. domes, mid i.r. optical fibres and polarizing substrates [6–8].

Complex Ca–Mg–Sr–Ba–Al fluoride glasses are reported to possess superior optical characteristics for the construction of high efficiency optics [9–12]. However, these glasses are very hard to prepare. The main difficulties associated with the preparation of these glasses are the large crystallization tendency and phase separation on cooling, compositional change due to fluorine volatilization on melting fracture on casting and serious chemical corrosion of the crucible. These difficulties are minimized when small amounts of metaphosphate compounds are introduced into the glasses [2, 4, 13]. Therefore, fluorophosphate glasses possess improved glass forming characteristics and stability compared with fluoride glasses. However, the addition of phosphate deteriorates the optical properties of the glasses. In order to obtain a glass with desirable optical properties, the phosphate content of the glass has to be as low as possible. In spite of some investigations on the formation [1–6], properties [3–5, 7] and structure [8, 13–16] of fluorophosphate glasses the data are sparse compared with silicate, borate and phosphate glasses. Hence, studies on fluorophosphate glasses have both scientific and practical significance.

The fabrication of glass in bulk shapes for optical applications requires slow cooling to achieve suitable optical quality and convenient size. However, slow cooling rates promote devitrification. Therefore, the crystallization rate of a glass must be as low as possible; otherwise glassy preforms may crystallize during processing or service. The utilization of these glasses in critical applications requires complete understanding of their formation characteristics in order to provide the designer with sufficient information to make use of these glasses. An understanding of the correlation between the crystallization kinetics and glass formation characteristics of these glasses is also important.

The purpose of this study was to determine the influence of former glass concentrations, $Ba(PO_3)_2$, on the formation characteristics of fluorophosphate glasses. The critical cooling rate, R_c, for glass formation has been measured for each composition. The compositional dependence of R_c and the activation energy, E, for crystallization have been determined and evaluated.

2. Experimental procedure

On the basis of studies on the formation of fluorophosphate glasses containing $Ba(PO_3)_2$, eight different compositions of progressively higher $Ba(PO_3)_2$ content were prepared using certified reagent grade raw materials. Batch compositions of fluorophosphate glasses investigated in this study are given in Table 1. This work is a continuation of the investigation where the crystallization kinetics of fluorophosphate glasses was studied as a function of $Ba(PO_3)_2$ content. The reader is referred to [1] for details of the melting and forming procedures.

The critical cooling rate, R_c, for glass formation, the minimum rate at which a melt can be cooled without

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TABLE I Batch compositions of fluorophosphate glasses investigated in this study

Glass no.	Composition (mol %)					
	$Ba(PO_3)_2$	AlF_3	CaF_2	MgF_2	SrF_2	BaF_2
1	0.00	42.10	31.58	10.53	10.53	5.26
2	0.10	42.06	31.55	10.52	10.52	5.25
3	0.25	42.00	31.50	10.50	10.50	5.25
4	0.50	41.90	31.43	10.47	10.47	5.23
5	0.75	41.78	31.35	10.45	10.45	5.22
6	1.00	41.69	31.26	10.42	10.42	5.21
7	1.50	41.48	31.10	10.37	10.37	5.18
8	3.00	40.84	30.64	10.21	10.21	5.10

TABLE II The critical cooling rate, R_c, for glass formation and the activation energy, E, for crystallization for fluorophosphate compositions[a] of varying $Ba(PO_3)_2$ content

$Ba(PO_3)_2$ (mol %)	R_c (°C s^{-1})	$E \pm 10$, (kJ mol^{-1})
0.0	98 ± 7	377
0.1	80 ± 6	–
0.125	63 ± 5	365
0.5	43 ± 3	–
0.75	19 ± 2	352
1.0	4 ± 1	–
1.5	2 ± 0.5	303

[a] Mol % composition is given in Table I.

crystallizing, of selected compositions was determined by inserting a Pt–Pt–13% Rh thermocouple bead in the platinum boat during batch melting. The thermocouple bead was completely submerged in the melt without touching the boat. The thermocouple was connected to a chart recorder so as to obtain a record (cooling curve) of the temperature as a function of time. Cooling rates of $< 50\,°C\,s^{-1}$ were controlled by gradually decreasing the power to the strip furnace. Cooling rates from 50 to $100\,°C\,s^{-1}$ were produced by simultaneously turning the power off and blowing helium gas over the sample. The glass was recovered by unfolding the platinum boat. The glass formed in this way was examined by X-ray diffraction (XRD) and by scanning electron microscopy (SEM), and its composition was analysed by energy dispersive X-ray analysis (EDX) at three to five different locations. The compositions of the glasses as agreed with the starting batch compositions for all instances.

The kinetic parameters for crystallization were calculated from the change in the temperature at the crystallization peak, corresponding to the maximum rate of crystallization, for several heating rates using differential thermal analysis (DTA). For a more complete description of the experimental technique and the methods of determining the crystallization kinetic parameters the reader is referred to [1].

The i.r. spectra of glassy and devitrified samples were measured using the KBr pellet technique.

3. Results and discussion

As-quenched samples containing > 1.5 mole % $Ba(PO_3)_2$ yielded good glasses, but it was extremely difficult to obtain glass for compositions containing < 0.5 mol % $Ba(PO_3)_2$ when quenched in air. These compositions yielded a mixture of glass and crystalline phase(s) adjacent to the sides of the platinum boat, indicating heterogeneous crystallization. Approximately 20 vol % glass was obtained from the composition containing no $Ba(PO_3)_2$, when a 10 g batch was quenched on steel plates.

The variation of R_c as a function of $Ba(PO_3)_2$ for samples weighing ~ 0.5 g was determined for fluorophosphate compositions containing 0–1.5 mol % $Ba(PO_3)_2$. R_c for compositions containing greater amounts of $Ba(PO_3)_2$ was too small to be measured precisely. No exothermic peak, corresponding to crystallization of the melt, was observed on the cooling curve because the heat of crystallization of fluorophosphate glasses was apparently low. When the cooling rate, R, was less than R_c the sample crystallized or contained a trace of crystalline material. The melt was then cooled at slightly higher rates until it was free from crystallinity. The cooling curve for which the sample became completely free from crystals was used to calculate the cooling rate that was taken as R_c.

Results of R_c are presented in Table II along with the ± 1 standard deviation from the average values of each set of tests. The determination of the value for R_c is based on five to ten individual experiments. As seen by the results in Table II, R_c decreases, i.e. glass formation becomes easier, with increasing $Ba(PO_3)_2$ content. Values for the activation energy, E, for crystallization of these glasses are also listed in Table II, and the methodology for determining E is given in [1]. A plot of E and R_c as a function of $Ba(PO_3)_2$ content for fluorophosphate glasses is shown in Fig. 1. As seen in Fig. 1, E and R_c both decrease with increasing $Ba(PO_3)_2$ content, indicating that E is approximately proportional to R_c. The variation of E with R_c for these glasses is shown separately in Fig. 2, which suggests that there is a linear relationship between E and R_c. The tendency for glass formation obviously increases with increasing $Ba(PO_3)_2$ content; although the corresponding decrease in activation energy for crystallization could be interpreted to indicate that the crystallization becomes easier. Similar dependence of E on R_c has also been reported for selected oxide glasses [17–20] A considerable reduction (by more than two-thirds) in the activation energy for crystallization was reported for ZrF_4–BaF_2–LaF_3 (ZBL) glass when AlF_3, LiF and PbF_2 were added [21, 22].

The improvement in glass formation (decrease in R_c) with a small amount of $Ba(PO_3)_2$ incorporation is attributed to linking of the *broken chains* present in the structure of fluoride glasses. The structure of fluoride glasses containing AlF_3, CaF_2, MgF_2, SrF_2, and BaF_2 consists of a mixture of linear and branched AlF_6 octahedral chains of various lengths connected by Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} ions [9, 10]. The strongly charged Al^{3+} cation may link two or several chains, playing the role of a bridge [12]. Other cations (Ca, Mg, Sr and Ba) fill the interspace between

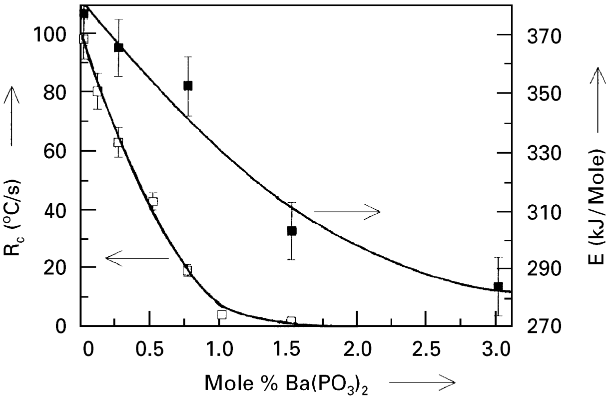

Figure 1 Variation of critical cooling rate, R_c (□), for glass formation and the activation energy, E (■), for crystallization as a function of $Ba(PO_3)_2$ content for fluorophosphate glasses.

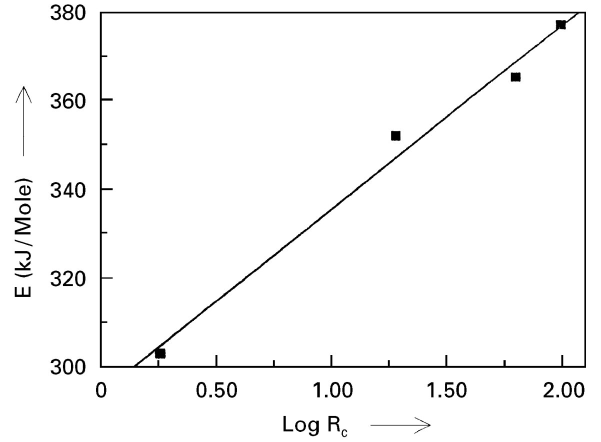

Figure 2 Variation of the activation energy, E, for crystallization as a function of critical cooling rate, R_c, for glass formation for fluorophosphate glasses.

the short chains and gather the short chains by electrostatic attraction between the cations and fluorine [12]. Al^{3+} and Mg^{2+} may also form AlF_4 and MgF_4 tetrahedra and then reconnect the chains to one another, so that the ease of glass formation increases [13].

The improvement in glass formation caused by $Ba(PO_3)_2$ may be explained by the formation of long PO_4 chains in the glass structure. When $Ba(PO_3)_2$, which has a structure of long chains of PO_4, is introduced into the glass, M–F bonds are disrupted and P–F bonds are formed as oxygen replaces fluorine. This results in the formation of PO_3F and the complex phosphate group Ba(Ca, Mg, Sr)P_2O_7. The formation of P–F bonds due to the formation of simple or complex fluorophosphates lengthens the chain. With increasing $Ba(PO_3)_2$ content the chains become increasingly longer forming P–O–P bonds gradually. The formation of long P–O–P bonds modifies the glass network structure. The structure changes gradually from short AlF_6 groups to long PO_3F and Ba(Ca, Mg, Sr)P_2O_7. As a result, direct bonding of PO_4 groupings with the AlF_6 octahedral chains impedes the crystallization process.

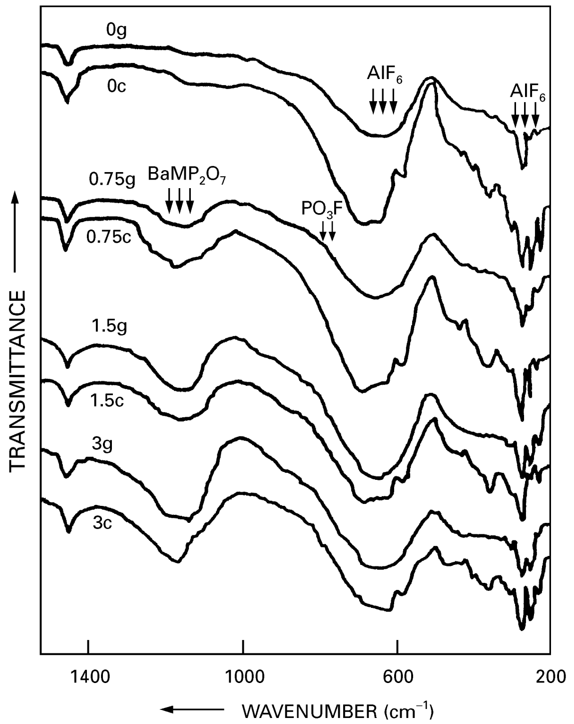

Figure 3 i.r. transmission spectra of selected fluorophosphate glasses (top curve) and their crystallization products (bottom curve) for (a) 0, (b) 0.75, (c) 1.5, and (d) 3 mol % $Ba(PO_3)_2$ content, respectively. The curves are arbitrarily displaced along the vertical axis for clarity.

A portion of the i.r. spectra of selected fluorophosphate glasses and their crystallization products are shown in Fig. 3. The high frequency i.r. bands correspond to stretching vibrations, while the low frequency bands correspond to deformation bands. As seen in Fig. 3, the i.r. curves of the glasses resemble those of the corresponding devitrified products although the absorption peaks for the glasses are not as sharp as those of crystallized products. The location of the bands in the glasses is essentially the same as for the crystals, which implies that the basic structural groups remain unchanged during crystallization. A comparison of the spectra for the crystallization products of the glasses containing 3 mol % $Ba(PO_3)_2$ and no $Ba(PO_3)_2$ reveals, that the i.r. spectra of the crystallization products change, i.e. the number of bands in the spectra increases, with increasing $Ba(PO_3)_2$ content of the glass. This is attributed to the formation of pyrophosphate structural groups, and gradual symmetricization of the structural units of the phosphates.

The i.r. spectra of the glass containing no $Ba(PO_3)_2$ and corresponding devitrification product have no absorption peak at the high frequency bands, but absorption peaks appear at 240, 260, 285, 320, 380, 410 cm^{-1}, and in the region of 520–780 cm^{-1}, which have been previously attributed to the vibration of $(AlF_6)^{3-}$ groups [13, 15]. With increasing $Ba(PO_3)_2$ content $(PO_3F)^{2-}$ and mixed pyrophosphates, BaMP_2O_7 (M = Ca, Mg, Sr) are known to be formed [13, 15, 16, 23]. However, the absorption peaks of $(PO_3F)^{2-}$, which is associated with the formation of P–F bonds, are overlapped with those of $(AlF_6)^{3-}$ and pyrophosphate groups [13, 23]. The formation of $(PO_3F)^{2-}$ and BaMP_2O_7 (M = Ca, Mg, Sr) groups confirms the effect of increasing $Ba(PO_3)_2$ on lengthening the PO_4 chains. In the region of the stretching vibrations, 800–1500 cm^{-1}, the spectra do not contain any other bands apart from those characteristic of pyrophosphates. The absorption peak appears at 1130 cm^{-1}, which is due to asymmetric stretching vibrations, characteristic of pyrophosphates [13, 15, 16, 23].

4. Conclusions

1. Incorporation of a small amount of $Ba(PO_3)_2$ improved the glass formation tendency of fluorophosphate glasses. The activation energy, E, for crystallization and the critical cooling rate, R_c, for glass formation decrease with increasing $Ba(PO_3)_2$ content. The tendency for glass formation obviously increases with increasing $Ba(PO_3)_2$ content, although the corresponding decrease in activation energy for crystallization could be interpreted to indicate that crystallization becomes easier.

2. A linear relationship between E and R_c suggests that glass formation depends on the cooling rates for fluorophosphate glasses.

3. The i.r. transmission analyses of selected fluorophosphate glasses and their crystallization products reveal that the basic structural groups remain unchanged during crystallization. The basic structural groups in these glasses are $(AlF_6)^{3-}$, $(PO_3F)^{2-}$ and mixed pyrophosphates, $BaMP_2O_7$ (M = Ca, Mg, Sr). The additions of $Ba(PO_3)_2$ change the network structure from short chains of AlF_6 octahedra to the long chains of PO_3F and $BaMP_2O_7$. The M–F bonds are disrupted and P–F and/or P–O–P bonds are formed gradually.

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