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STRUCTURE AND DEVITRIFICATION OF $Li_2O \cdot P_2O_5$–B_2O_3 AND $BaO \cdot P_2O_5$–B_2O_3 GLASSES

F. BRANDA, A. ARONNE, A. MAROTTA and A. BURI

Department of Materials and Production Engineering, University of Naples, Piazzale Tecchio, 80125 Naples (Italy)

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ABSTRACT

The effect of equimolar substitution of lithium or barium metaphosphate in boric oxide was studied on the glass transition temperature (T_g) and devitrification behaviour. Hypotheses on the structural units present were inferred from T_g vs. composition curves. The different thermal stabilities of the glasses were roughly evaluated. The devitrification kinetic parameters of $LiPO_3$ and $Ba(PO_3)_2$ glasses were evaluated by means of thermoanalytical methods.

INTRODUCTION

A recent paper [1] described the effect of the substitution of one network-former, B_2O_3, by another, P_2O_5, on the thermal properties and the devitrification behaviour of Na_2O–B_2O_3–P_2O_5 glasses. In this paper the study has been extended to the Li_2O–B_2O_3–P_2O_5 and BaO–B_2O_3–P_2O_5 systems.

EXPERIMENTAL

The compositions of the samples are expressed by the general formulas:

$$x\mathrm{Li_2O} \cdot x\mathrm{P_2O_5} \cdot (1-x)\mathrm{B_2O_3} \qquad \text{(i)}$$

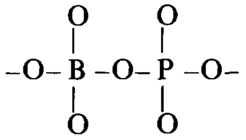
$$x\mathrm{BaO} \cdot x\mathrm{P_2O_5} \cdot (1-x)\mathrm{B_2O_3} \qquad \text{(ii)}$$

with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.

The glasses were prepared by melting analytical grade Li_2CO_3, $BaCO_3$, $NH_4H_2PO_4$ and H_3BO_3 in a platinum crucible, in an electric oven in the temperature range 700–1100°C. The samples were held at melting temperatures for 2–4 h, and the melts were cast by plunging the bottom of the crucible into cold water. It was not possible to prepare glasses with $x = 0.1$ and 0.2 in the lithium series. The as-quenched glasses were crushed or cut to obtain powdered ($-50+60$ mesh) or small bulk samples (suitable for the sample holder of the DTA apparatus). DTA and the first temperature derivative (DDTA) curves were recorded, using a Netzsch thermoanalyser (404 M) and powdered Al_2O_3 as reference material.

RESULTS AND DISCUSSION

Figure 1 gives the T_g values of the glasses studied as a function of composition. It can be seen that, as already obtained for the analogous B_2O_3–$Na_2O \cdot P_2O_5$ series [1], intermediate terms show much higher T_g values than either end member. According to Ray [2], and on the basis of NMR measurements [3], this trend for the sodium borophosphate series was linked to the increase in coordination number of the boron atoms. The similarity in the results for the lithium and barium borophosphate glasses suggests that some similar structural change must occur. When Li_2O or BaO and P_2O_5 are substituted for B_2O_3, the extra oxygen introduced by the modifying oxides must, at first, be taken up by the increasing coordination number of the boron atoms, so that BO_3 triangles are changed into tetrahedral BO_4 units, as in the binary alkali borate glasses [4]. The presence of P_2O_5, at higher percentages of modifying oxides, allows the formation of BPO_4 groups of the type



$$-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{B}}}-\mathrm{O}-\underset{\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{P}}}-\mathrm{O}-$$

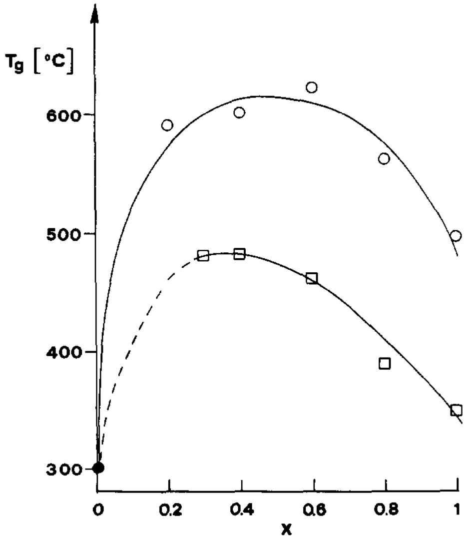


Fig. 1. Glass transition temperature vs. composition in (□) glass series (i) and (○) glass series (ii).

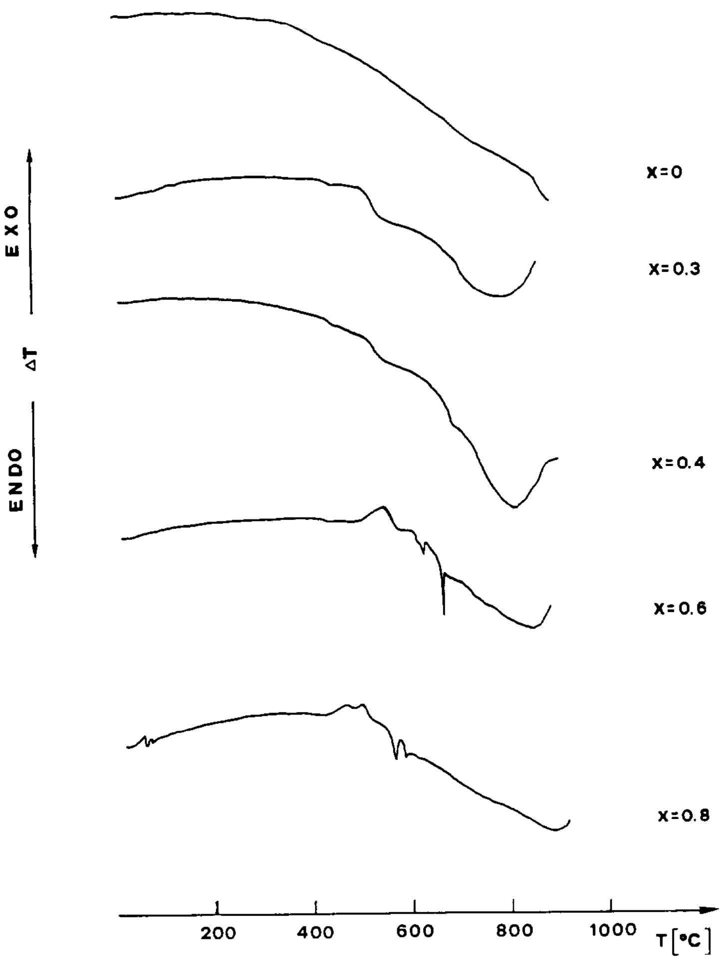


Fig. 2. DTA curves of glasses of series (i) at 1°C min^{-1}.

in which the negative charge of BO_4 is compensated by the positive charge of the PO_4 group. According to Ray [2], the greater covalent bond density could easily explain the higher T_g values of the intermediate glasses. The fact that T_g values strongly depend on the coordination of the modifying oxide must also be taken into account [2,5]; so higher T_g values of the barium metaphosphate glasses can be explained on the basis of the higher mean coordination number of the larger Ba^{2+} ion.

Intermediate terms of the series showed a high thermal stability. Devitrification only occurred easily for the $x = 0.1$ and 0.2 terms of the lithium series that could not be obtained as glasses, and in the $x = 1$ end members. As shown by the DTA curves reported in Figs. 2 and 3, only on very slow heating did devitrification occur in glasses near the end member compositions. Lithium glasses showed poorer thermal stability than the barium

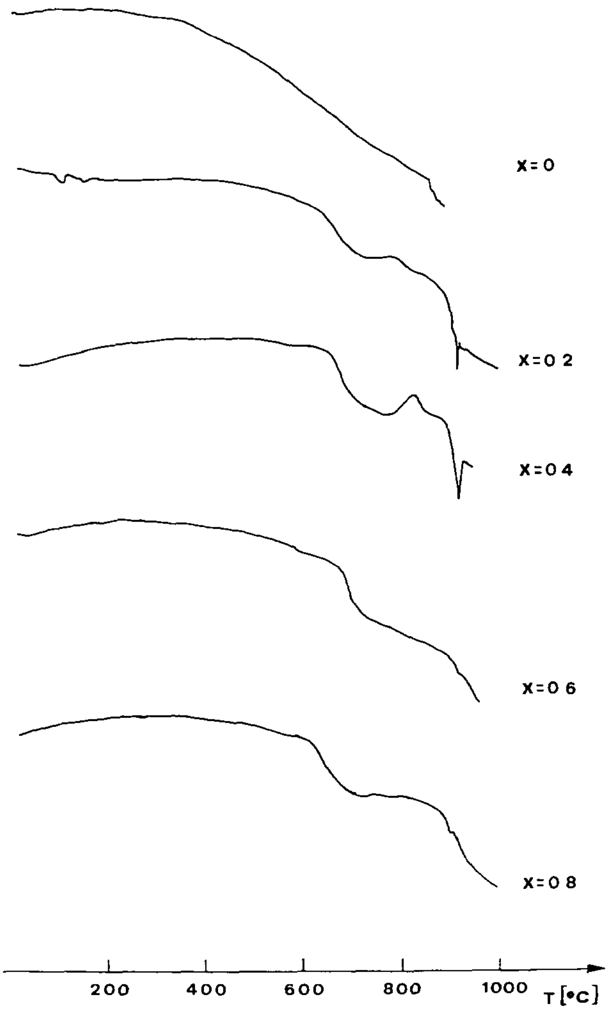


Fig. 3. DTA curves of glasses of series (ii) at 1°C min^{-1}.

glasses. The devitrification kinetic parameters of lithium and barium metaphosphate glasses were evaluated by means of thermoanalytical techniques.

The non-isothermal devitrification of glasses is well described by the following equation [6]:

$$-\ln(1-\alpha) = \left(A_1/\beta^{n+b}\right)\exp(-nE/RT) \tag{1}$$

where α is the crystallized fraction at temperature T, A_1 is a constant, β the heating rate and E the activation energy of the process. The Avrami parameter, n, is related to the devitrification mechanism. The parameter b assumes two values ($b=0$ and 1); it is zero when crystal growth occurs, at different heating rates, from a constant number of nuclei.

Taking into account that the crystallization degree [7] reaches the same specific value at peak temperature, independent of the heating rate, the following relation between the heating rate, β, and the peak temperature, T_p, is easily obtained:

$$\ln \beta = -(n/n+b)(E/R)(1/T_p) + \text{constant} \tag{2}$$

Moreover, the deflection from the baseline, ΔT, is proportional to the instantaneous reaction rate [8] and in the initial part of the DTA crystallization peak has a much larger effect than α on the deflection of ΔT [9]. Therefore, the following equation can be obtained:

$$\ln \Delta T = (nE/R)(1/T) + \text{constant} \tag{3}$$

Equations (2) and (3) were applied to evaluate the devitrification kinetic parameters of lithium and barium metaphosphate glasses. Figures 4 and 5 give plots of $\ln \beta$ vs. $1/T_p$ and $\ln \Delta T$ vs. $1/T$. The values of $(n/n+b)E$ and nE obtained from their slopes are reported in Table 1. If DTA runs at 20°C min^{-1} were performed after DTA runs at 1°C min^{-1}, stopped at the onset of crystal growth, no peak shift was observed with respect to an "as-quenched" sample, so a value of $b = 0$ was assumed. The value of E thus calculated for Li_2O–P_2O_5 glass is very close to that reported in the literature ($E = 33$ kcal mol^{-1} [10]). It is, however, considerably lower than the value of the activation energy for viscous flow ($E_\eta = 53$ kcal mol^{-1}), obtainable from literature data [10] in the temperature range $[(T_{\text{melt}}/T) = 1.09$–$1.31]$ of devitrification during DTA runs. In the more general case, however, it must be taken into account that the rate of crystal growth, V, is governed by the following equation [11]:

$$V = A_2 \exp(-\Delta G'/RT)[1 - \exp(-\Delta G/RT)] \tag{4}$$

where ΔG is the free energy of crystallization, $\Delta G'$ the activation energy,

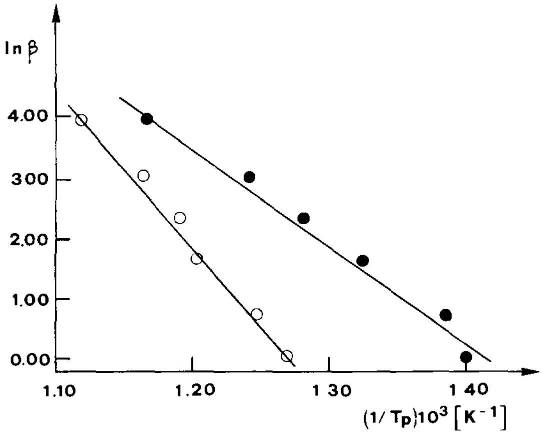


Fig. 4. Plot of $\ln \beta$ vs. $1/T_p$ for (●) $LiPO_3$ and (○) $Ba(PO_3)_2$ glasses.

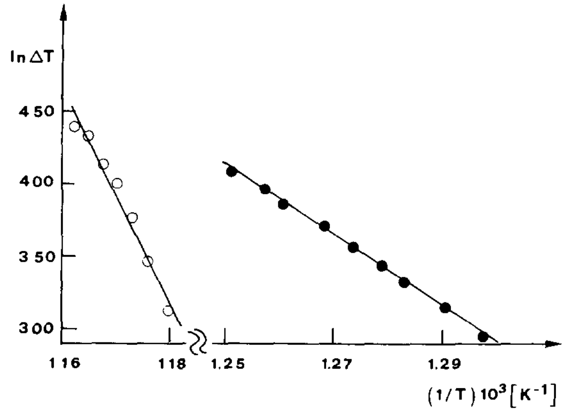


Fig. 5. Plot of ln ΔT vs. $1/T$ for (●) $LiPO_3$ and (○) $Ba(PO_3)_2$ glasses.

and A_2 a constant. For substances with high entropies of melting, the dependence of the crystallization rate constant on temperature can be approximated as follows [12,13]:

$$K = (A_3/\eta)(T_l - T)^{1.75} = A_4(T_l - T)^{1.75} \exp(-E_\eta/RT) \qquad (5)$$

where T_l is the liquidus temperature and A_3 and A_4 are constants. Therefore, the activation energy for crystal growth evaluated by means of eqns. (2) and (3), which are derived by assuming a dependence of the crystallization rate constant K on temperature:

$$K = A_4 \exp(-E/RT) \qquad (6)$$

differs from the activation energy for viscous flow. By comparing the first temperature derivatives of eqns. (5) and (6), the following relationship can be obtained:

$$E = E_\eta - 1.75RT^2/(T_l - T) \qquad (7)$$

Only when $(T_l - T)$ is sufficiently large $(E = E_\eta)$ is the process controlled by the kinetic factor. The value of E_η evaluated using $E = 32$ kcal mol^{-1}

TABLE 1

Devitrification kinetic parameters and activation energies (kcal mol^{-1}) of viscous flow [as reported in the literature (E_η) and as evaluated by means of eqn. (7) (E'_η)] of $LiPO_3$ and $Ba(PO_3)_2$ glasses

	$\frac{n}{n+b}E$	nE	E	n	E_η	E'_η
Li_2O glass	32	46	32	1.4	53	47
BaO glass	52	148	52	2.9	–	60

from eqn. (7) agrees well with that calculated from viscosity data in the same temperature range (Table 1). In the case of $BaO-P_2O_5$ glass, devitrification during DTA runs occurred at much higher undercoolings ($T_l - T \approx 300°C$) as compared to those of $Li_2O-P_2O_5$ glass ($T_l - T \approx 150°C$). It must be expected, therefore, that E in this case is very close to E_η. As the approximation of eqn. (5) depends on the entropy of fusion, eqn. (7) was also applied to the $BaO-P_2O_5$ glass data. As can be seen from Table 1, only minor differences between E and E_η were observed in this case.

CONCLUSIONS

(1) The presence of Li_2O or BaO and P_2O_5 allows a fourfold coordination for boron atoms.

(2) In the series studied, lithium-containing glasses with $0.3 \leqslant x < 1$ and barium-containing glasses with $0 < x < 1$ show a good thermal stability.

(3) The non-isothermal devitrification of $BaPO_3$ glass is essentially controlled by kinetic factors; on the contrary, the effect of undercooling cannot be neglected in the case of $LiPO_3$ glass.

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