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Nitrogen dissolution in alkali–barium–metaphosphate melts

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Phosphorus oxynitride glasses were prepared by remelting $30R_2O$–$20BaO$–$50P_2O_5$, (R = Li, Na or K) glasses in anhydrous ammonia. The nitrogen content of these metaphosphate melts decreased with increasing size of the alkali ion. The dissolution rate in water and thermal expansion coefficient of the base glasses increased with increasing alkali ion size. The dissolution rate of the oxynitride glasses was lower than that of the base glasses but was essentially independent of the alkali ion. The thermal expansion coefficient of the oxynitride glasses increased with increasing alkali size as observed in other glasses.

1. Introduction

Phosphate glasses have potential application in glass-to-metal seals because of their low melting temperature [1] and relatively high thermal expansion coefficient [2]. The commercial use of phosphate glasses is presently limited by their usually poor chemical durability in aqueous solutions or low weathering resistance [3, 4]. The addition of Al_2O_3 [5] or the substitution of nitrogen for oxygen [2, 6–8] in phosphate glasses has been found to increase their chemical durability to aqueous environments.

The properties of phosphate glasses such as chemical durability, thermal expansion and glass transition temperature are known [5] to depend on the type of alkali ion in the glass. The Raman spectra [9] of alkali–barium–metaphosphate glasses indicate that the P–O–P bond strength varies with the size of the alkali ion present in the glass. The present paper examines nitrogen dissolution in phosphate melts as a function of the alkali ion. The dissolution rate in water, thermal expansion coefficient, dilatometric softening temperature and refractive index were measured as a function of nitrogen content.

2. Experimental procedure

The $30R_2O$–$20BaO$–$50P_2O_5$, (R = Li, Na or K) base glasses were prepared from reagent-grade Li_2CO_3, $NaH_2PO_4 \cdot H_2O$, KH_2PO_4, $BaHPO_4$ (or $BaCO_3$), and $NH_4H_2PO_4$. The powdered batch materials were dry-mixed for about 15 min, calcined at about 650° C for 6 h in a platinum crucible, and then melted in air at 900 to 1000° C for 3 h. When all the batch had melted, the melt was stirred periodically and then quenched on steel plates. All the base glasses were colourless.

The oxynitride glasses (Table I) were prepared in a graphite crucible since the phosphorus oxynitride melt did not react or adhere to graphite. A 4 cm × 1.5 cm × 1 cm crucible was filled with ~10 g of the crushed base glass and inserted into a fused silica tube. The tube was sealed, flushed with dry nitrogen to remove any residual air, and then heated to one of the temperatures given in Table I, whereupon the nitrogen was replaced with anhydrous ammonia. Each melt was held for 5 h at the chosen temperature in dry ammonia flowing at a rate 300 $cm^3\,min^{-1}$. The silica tube was then flushed with nitrogen to remove the ammonia, whereupon the sample was removed from the furnace and placed in a preheated (~350° C) annealing furnace. The annealing furnace was turned off and the oxynitride glass cooled overnight to room temperature in air.

The nitrogen content of the phosphorus oxynitride glass was measured by inert gas fusion as reported elsewhere [8].

The dissolution rate in deionized water at 30° C was measured for each phosphorus oxynitride glass from its weight loss as described elsewhere [8]. The estimated error in the dissolution rate ($g\,cm^{-2}\,min^{-1}$) is ±20%.

The coefficient of thermal expansion (α) and the dilatometric softening temperature (T_d) were measured (equipment from Orton Foundation, Colombus, Ohio) on an annealed bar 5 cm in length. Each bar was heated in air at a rate of 5° C min^{-1}. The estimated error in α and T_d is ±5% and ±4%, respectively.

The refractive index was measured (±0.001) by the Becke line technique using calibrated refractive index liquids.

3. Results

The nitrogen content for the $30R_2O$–$20BaO$–$50P_2O_5$ glasses, melted at 750° C in dry ammonia for 5 h, is shown in Fig. 1. The alkali ion radius for the $15Li_2O$–$15Na_2O$–$20BaO$–$50P_2O_5$ glass was arbitrarily assumed equal to the mean value of the radius for Li^+ and Na^+ ions. The nitrogen content in alkali–barium–metaphosphate melts obviously decreases

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TABLE I Processing temperature, analysed nitrogen content, dissolution rate, thermal expansion coefficient, softening temperature, and refractive index of $30R_2O$–$20BaO$–$50P_2O_5$ glasses melted in ammonia (flow rate of $300\,cm^3\,min^{-1}$ for 5 h)

Starting composition (mol %)	Processing temperature (° C)	Analysed nitrogen (wt %)	Dissolution rate* ($g\,cm^{-2}\,min^{-1}$)	Thermal expansion coefficient†, $\alpha \times 10^7 (°C)^{-1}$	Softening temperature (° C)	Refractive index n_D
$30Li_2O$–$20BaO$–$50P_2O_5$	Base glass	0	3.1×10^{-7}	171	320	1.543
	650		Glass did not melt			
	700	2.39	1.3×10^{-7}	160	345	1.563
	750	8.24	1.2×10^{-7}	156	405	1.617
$15Li_2O$–$15Na_2O$–$20BaO$–$50P_2O_5$	Base glass	0	4.6×10^{-7}	187	290	1.535
	650	0.532	2.6×10^{-7}	187	285	1.539
	700	4.95	8.0×10^{-8}	180	330	1.573
	750	7.16	2.0×10^{-8}	162	360	1.597
$30Na_2O$–$20BaO$–$50P_2O_5$	Base glass	0	1.8×10^{-6}	210	330	1.527
	650	2.05	6.0×10^{-7}	207	335	1.542
	700	5.33	4.9×10^{-7}	190	350	1.580
	750	5.63	2.9×10^{-7}	185	375	1.580
$30K_2O$–$20BaO$–$50P_2O_5$	Base glass	0	3.4×10^{-4}	248	305	1.507
	650	‡	4.0×10^{-5}	226	350	1.535
	700	2.70	9.2×10^{-7}	218	365	1.551
	750	5.47	3.1×10^{-7}	215	390	1.562

*Measured at 30° C in deionized water.
†Averaged from 100 to 200° C.
‡Not measured.

with increasing alkali ion size up to Na^+ and then remains essentially constant.

The dissolution rate of the $30R_2O$–$20BaO$–$50P_2O_5$ base glasses in deionized water at 30° C increased with increasing size of the alkali ion as shown in Fig. 2. As can be seen in Fig. 3, the dissolution rate for these oxynitride glasses decreased with increasing nitrogen content, as similarly reported [2, 7, 8] for other phosphorus oxynitride glasses. It is interesting to note from Fig. 3 that these phosphorus oxynitride glasses have nearly the same dissolution rate when the nitrogen contents exceeds ~4 wt %, and this rate appears to be independent of the alkali cation size. A similar behaviour has been observed [10] for $30Na_2O$–$20MO$–$50P_2O_5$ glasses where M = Mg, Ca, Sr or Ba.

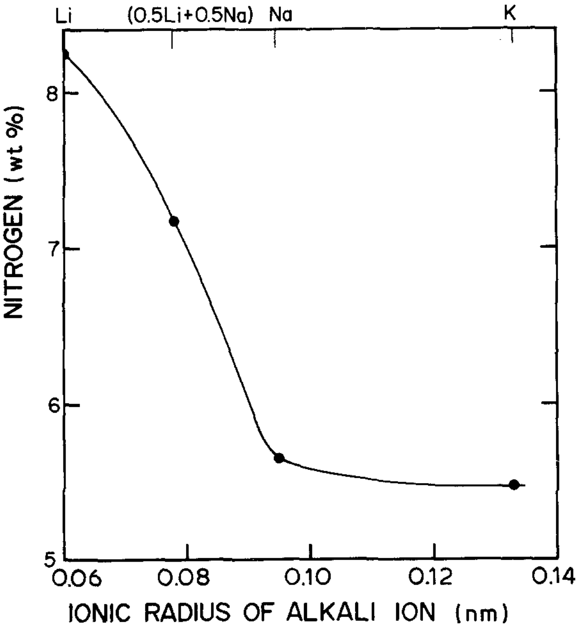

Figure 1 Nitrogen content of $30R_2O$–$20BaO$–$50P_2O_5$ glasses as a function of the alkali ion (R^+) radius. Glasses were remelted in dry ammonia (flow rate of $300\,cm^3\,min^{-1}$) for 5 h at 750° C.

The thermal expansion coefficient for the $30R_2O$–$20BaO$–$50P_2O_5$ base glasses increased with increasing size of the alkali ion as shown in Fig. 4. The thermal expansion coefficient of each base glass decreased with increasing nitrogen content (see Figs 4 and 5) as observed in other oxynitride glasses.

Nitriding each base glass increased its softening temperature (T_d) and refractive index (see Table I). Based on visual observation, nitriding also increased the

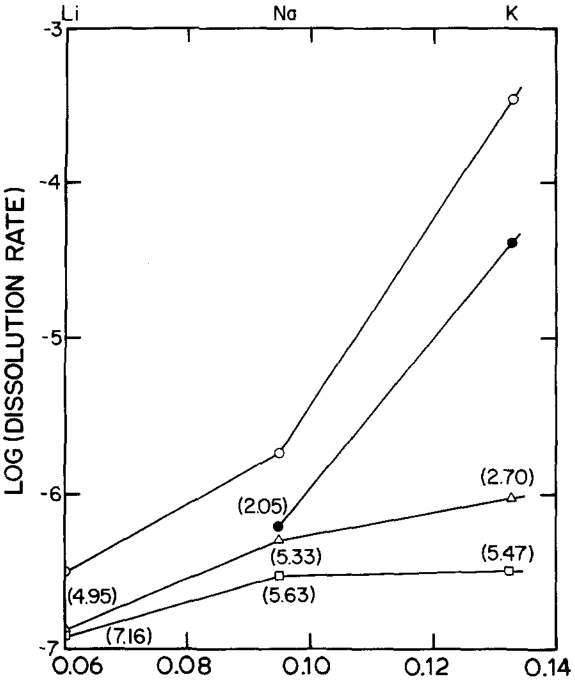

Figure 2 Dissolution rate in deionized water at 30° C (Table I) as a function of the alkali ion (R^+) radius for (○) $30R_2O$–$20BaO$–$50P_2O_5$ base glasses and oxynitride glasses made by remelting the base glasses in ammonia (flow rate of $300\,cm^3\,min^{-1}$) for 5 h at (●) 650, (△) 700 and (□) 750° C. Numbers in parantheses are nitrogen content (wt %).

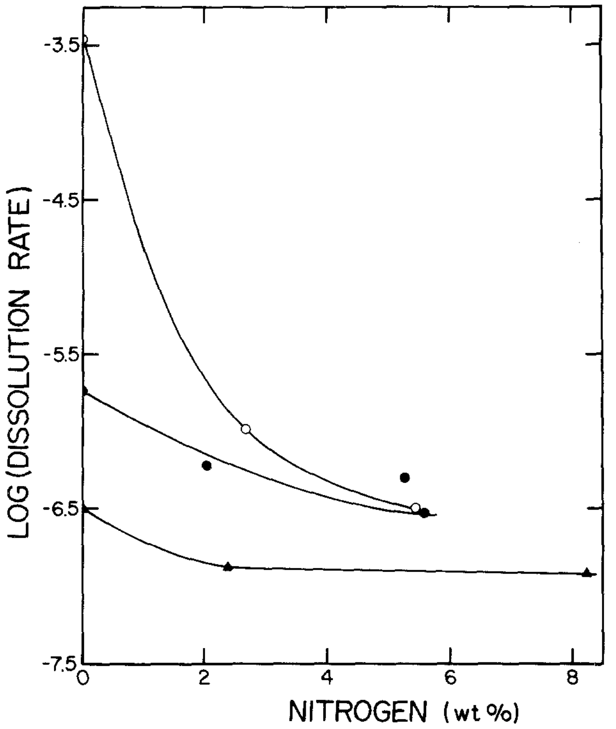

Figure 3 Dissolution rate of oxynitride glass in deionized water at 30° C made by remelting $30R_2O$–$20BaO$–$50P_2O_5$ glass in ammonia (flow rate of $300\,cm^3\,min^{-1}$) for 5 h at 650, 700 and 750° C; alkali ion (○) K, (●) Na, (○) Li.

viscosity of each melt and improved its glass-forming tendency, i.e. reduced the tendency to crystallize.

4. Discussion

From earlier studies [11–12] nitrogen is known to be present in phosphate melts as the nitride ion (N^{3-}) and to replace either the bridging oxygen or non-bridging, double-bonded oxygen in the PO_4 tetrahedral network of the glass. The Raman spectra of alkali barium metaphosphate glass [9] show that the addition of BaO to alkali metaphosphate melts tends to localize the electron density on the non-bridging oxygens which form ionic bonds with the Ba^{2+} ions. This leaves some non-bridging oxygen ions that are more weakly coordinated to Ba^{2+} ions with a relative deficiency in electron density. Thus, the non-bridging oxygens in the PO_4 chains are bonded to the Ba^{2+} ions, leaving only the bridging oxygens in the PO_4 chains to be replaced by nitrogen. Further, the Raman spectra of alkali–barium–metaphosphate glasses show [9] that the vibrational mode frequency for P–O–P bonds in $LiPO_3$ glass decreases with the substitution of BaO for Li_2O. In the case of sodium or potassium metaphosphate glasses, however, the substitution of Ba^{2+} ions (for Na^+ or K^+ ions) does not affect the orientation or strength of the bridging oxygen bond. The P–O–P bond strength is nearly the same in sodium or potassium glasses [9]. This may explain why the nitrogen content was highest in the lithium–barium–metaphosphate glass and decreased with increasing alkali size. As shown in Fig. 1, the nitrogen content was almost the same in the sodium and potassium glasses.

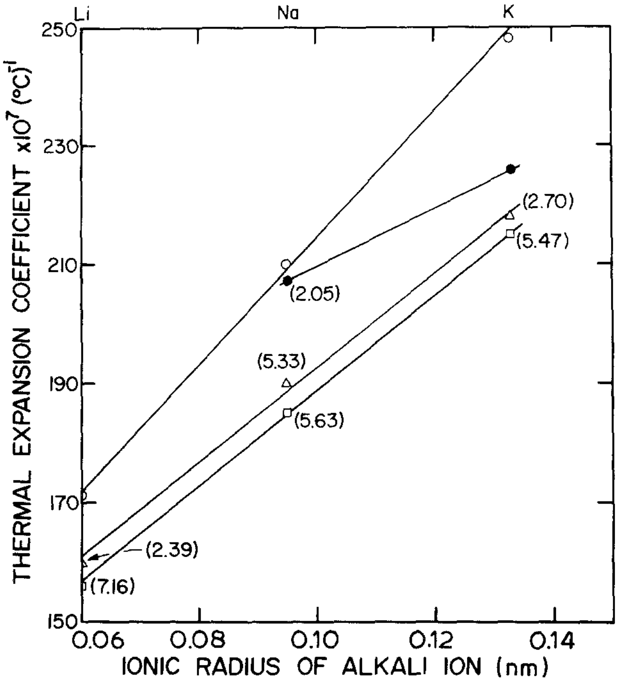

Figure 4 Average thermal expansion coefficient, between 100 and 200° C, of (○) $30R_2O$–$20BaO$–$50P_2O_5$ base glass, and oxynitride glasses made by remelting in ammonia (flow rate of $300\,cm^3\,min^{-1}$) for 5 h at (●) 650, (△) 700 and (□) 750° C, as a function of the alkali ion radius (R^+). Numbers in parentheses are nitrogen content (wt %).

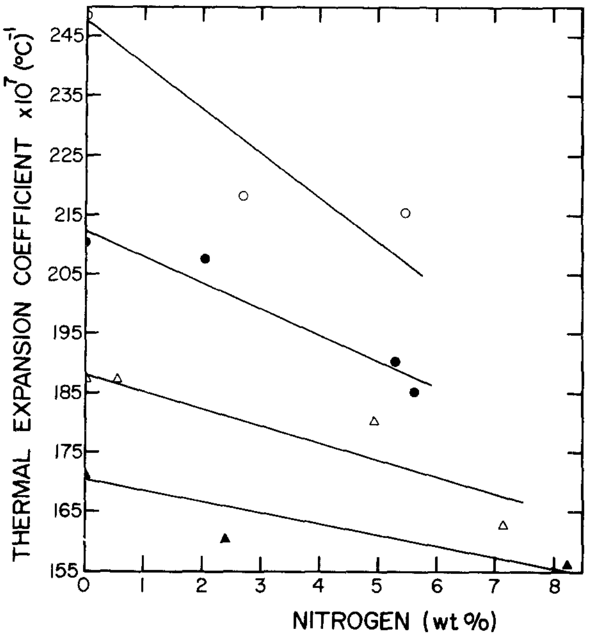

Figure 5 Average thermal expansion coefficient, between 100 and 200° C, of oxynitride glasses made by remelting $30R_2O$–$20BaO$–$50P_2O_5$ glass in ammonia (flow rate of $300\,cm^3\,min^{-1}$) for 5 h at 650, 700 and 750° C; alkali ion (○) K, (●) Na, (△) 0.5Li + 0.5Na, (▲) Li.

The mechanism by which alkali metaphosphate glasses [3, 14] dissolve in water consists of the diffusion of water molecules into the PO_4 network. This produces a swelling of the network and weakens the Van der Waals forces between the phosphate chains. Continued hydrolysis eventually causes an entire segment of the PO_4 chain to be released to the aqueous solution. In alkali–barium–metaphosphate glasses, the Ba^{2+} ions are located in interstitial positions within the PO_4 network and tend to block other diffusing molecules [5]. Because of the small size of the Li^+ ion, the available interstitial sites in the lithium glass could be completely occupied by the Ba^{2+} ions, thereby blocking the diffusion of water molecules. Conversely K^+, being a larger ion, could cause larger interstitial sites in the phosphate network which the Ba^{2+} ions might not fully fill when Ba^{2+} ions are substituted for the K^+ ions in the KPO_3 glass. The diffusion of water molecules in these glasses is expected to increase with increasing alkali ion size, which is consistent with the increasing dissolution rate shown in Fig. 2 with increasing alkali size.

Since water and ammonia molecules have nearly the same size, one might expect higher nitrogen contents in the potassium glasses compared to the lithium glasses. However, the experimental results show just the opposite (see Fig. 1). This may be due to differences in the chemical reactions involving water or ammonia. The dissolution of phosphate glass in water at room temperature is via a chain hydrolysis reaction whereby secondary bonds such as the weak Van der Waals bonds between the PO_4 chains are gradually broken. In the case of nitrogen dissolution, the reaction occurs at ~ 700° C and appears to involve P–O bonds being broken and replaced by new P–N bonds [8]. The P–O bonds are slightly weaker in the lithium glasses compared to those in the potassium glass [9], which could explain why the nitrogen content is highest for the lithium glass and decreases with increasing alkali ion size, for a constant nitriding temperature.

The decrease in dissolution rate for the phosphorus oxynitride glasses with increasing nitrogen content, along with the tendency for all the glasses to have nearly the same dissolution rate at higher nitrogen content, may be explained by the cross-linking of the PO_4 network by the nitrogen ions. Earlier work [10] shows that a nitrogen content of ~4.5 wt % is adequate for one of the two bridging oxygens in each PO_4 tetrahedron to be replaced by nitrogen in the $30R_2O$–$20BaO$–$50P_2O_5$ glass and corresponds to a glass composition (mol %) of $75(RPO_{2.5}N_{0.33})$–$25(Ba(PO_{2.5}N_{0.33})_2)$. All the phosphorus oxynitride glasses, except those prepared at 650° C (see Table I), have a nitrogen content of more than 5 wt %, so more than 50% of the PO_4 groups should be cross-linked by nitrogen in these glasses. Since phosphorus oxynitride glasses appear to dissolve via network hydrolysis [14], rather than by chain hydrolysis, as is the case of the non-nitrided phosphate glasses, the additional cross-linking provided by nitrogen may explain why the dissolution rate of the oxynitride glasses eventually becomes independent of cation size (see Fig. 3). A similar behaviour has been observed [10] in alkaline earth phosphorus oxynitride glasses.

The increase in thermal expansion coefficient with increasing alkali size is attributed to the decreasing field strength [5] of the alkali ion and to weaker ionic bonds between the PO_4 chains. This is consistent with the concept that a higher field-strength cation creates a more tightly bonded glass structure. The incorporation of nitrogen in these glasses increases the cross-link density between the PO_4 chains, thereby tightening the glass structure and reducing the thermal expansion coefficient with increasing nitrogen content (Fig. 5).

5. Conclusion

The nitrogen content of the alkali barium metaphosphate glasses remelted in ammonia depends on the size of the alkali ion since the substitution of Ba^{2+} for alkali in the glass alters the orientation and strength of the bridging oxygen bond in the PO_4 chains in the starting glass. The dissolution rate of the base glasses in deionized water depended upon the size of the alkali ion, but was essentially independent of the alkali ion present in oxynitride glasses when the nitrogen content exceeded ~4.5 wt % since nearly 50% of PO_4 groups in the oxynitride glasses were cross-linked by nitrogen. The lower thermal expansion coefficient and higher softening temperature for the lithium-base glasses and the oxynitride glasses are consistent with the concept that a higher field-strength ion, either alkali or nitrogen, creates a more tightly bonded cross-linked network structure.

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