Surface degradation behaviour of sodium borophosphate glass in aqueous media: Some studies

K V SHAH[†], M GOSWAMI, S MANIKANDAN, V K SHRIKHANDE and
G P KOTHIYAL*

Technical Physics & Prototype Engineering Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

[†]Present address: Department of Condensed Matter Physics & Materials Science,

Tata Institute of Fundamental Research, Mumbai 400 005, India

Abstract. The degradation behaviour of phosphate glass with nominal composition, $40\text{Na}_2\text{O}-10\text{BaO}-x\text{B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$, where $0 \leq x \leq 20$ mol%, was studied in water, HCl and NaOH solutions at room temperature to 60°C for different periods extending up to 300 h. These glasses were synthesized by conventional melt-quench technique. Dissolution rates were found to increase with B_2O_3 content in the glass. The dissolution rates for the glass having 10 mol% B_2O_3 were found to be 0.002 g/cm^2 and 0.015 g/cm^2 in distilled water and 5% NaOH solution, respectively, at room temperature after 225 h of total immersion period, whereas it increased considerably to 0.32 g/cm^2 in 5% NaOH at 60°C after 225 h. However, glass samples with $x = 15$ and 20 mol% B_2O_3 were dissolved in 5% HCl solution after 5 h immersion. The degradation behaviour has been correlated with the structural features present in the glass. The optical microscopy of the corroded surface revealed that the corrosion mechanism were different in acid and alkali media.

Keywords. Borophosphate glass; surface degradation; aqueous media.

1. Introduction

Phosphate glasses and glass–ceramics are useful for applications such as bone transplantation, glass–to–metal seals, containment of radioactive wastes, fast ion conductors, laser host materials etc (Brow 2000). They have a comparatively high transmission in the ultraviolet region compared to silicate and borate glasses (Brow 1996). They also have low glass transition and melting temperatures compared to silicate glasses (Brow and Tallant 1997). The network structure of simple phosphate glass consists of P tetrahedra linked to neighbouring tetrahedra through bridging oxygen (BOs). Addition of Al^{3+} , B^{3+} , Bi^{3+} , etc has been found to improve the chemical durability because of the formation and relative stability of $\text{M}^{3+}\text{--O--P}$ bond (Tsuchiya and Moriya 1980). These ions modify various physical properties including thermo-mechanical and optical behaviour basically due to change in glass structural network through formation of cross-linked bonds.

Borophosphate glasses having improved durability are among the multi component glasses studied for various interesting applications. Alkali and silver borophosphate glasses have been developed for fast ion conducting applications (Kaushik and Hariharan 1987; Coppo *et al* 1996); zinc–calcium borophosphate glasses were studied as candidates for applications as low-melting glass sol-

ders and glass–to–metal (GM) seals (Ma *et al* 1993; Harish Bhat *et al* 2001). The structure of borophosphate glasses was studied by NMR spectroscopy (Yun and Bray 1978) and it was found that both BO_3 and BO_4 structural units were present in the glass structure. The fraction of BO_4 units in the glasses was also found out in this study, which is an important parameter in the context of improvement of durability of these glasses. The presence of BO_3 and BO_4 structural units affects the chemical bonding with the phosphate tetrahedra, which becomes important in determining the chemical durability of these glasses.

The corrosion studies on alkali alkaline earth phosphate glasses (Wilder 1980) revealed that corrosion resistance of these glasses to water attack was improved by small addition of Al_2O_3 and glasses with thermal expansion coefficients (TEC) greater than $200 \times 10^{-7}/^\circ\text{C}$ and glass transition temperatures, T_g , below 400°C and melting points, below 600°C which could be hermetically sealed to aluminium alloys. Sodium borophosphate glass studies show an increase in T_g and decrease in TEC for $y = \text{B}/(\text{B} + \text{P}) = 0\text{--}0.5$ ($\text{B} = \text{B}_2\text{O}_3$ content in mol%, $\text{P} = \text{P}_2\text{O}_5$ content in mol%) where BO_4 units dominate over BO_3 units. The maximum TEC reported for sodium borophosphate glasses is 199×10^{-7} for $y < 0.5$. Therefore, it seems interesting to study the effect of B_2O_3 addition in sodium barium phosphate glass since the addition of boron oxide tends to improve the durability of sodium phosphate glass without any major change in the TEC of these glasses. In this work we report the degradation behaviour of sodium barium borophosphate glasses in water,

*Author for correspondence (gpkoth@barc.gov.in)

acid and alkali media at room temperature and at 60°C. To the best of our knowledge this data is new for phosphate glasses and the structural and physico-mechanical properties for these glasses are reported elsewhere (Shah *et al* 2006). We have prepared a vacuum seal using glass composition, $x = 10$ mol% with Al metal, withstanding 10^{-6} Torr pressure and also carried out glass to metal interface study.

2. Experimental

Sodium borophosphate glasses having composition, $40\text{Na}_2\text{O}-10\text{BaO}-x\text{B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$, where $x = 0-20$ mol% were prepared by conventional melt-quench technique as reported earlier (Shah *et al* 2006). Analytical grade reagents with no water of crystallization, NaNO_3 , $\text{Ba}(\text{NO}_3)_2$, B_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ were used as starting materials in such proportions that the O/P ratio changed from 3.0–4.33. The initial charge (30–40 g) was thoroughly mixed and ground for 30–40 min in a mortar pestle and then calcined in an alumina crucible for 18–20 h by heating in a predetermined manner considering the decomposition temperatures of individual compounds at the maximum temperature of 600°C. This charge was reground and calcined again at 600°C for 4 h in the same manner. The calcined charge was then melted in a platinum crucible using lowering and raising hearth furnace (Model OKAY 70R 10, M/s Bysakh and Co., Kolkata) and held at temperatures ranging from 750–800°C depending on the composition for 2 h for thorough mixing in air ambient. When the melt was thoroughly homogenized and attained the desirable viscosity, it was poured either onto a metal plate and pressed by a graphite disc or into graphite moulds. The glass was then annealed at appropriate temperatures (between 350 and 400°C) for 3 h and stored in a desiccator prior to evaluation.

Powder XRD patterns of the glasses were recorded on JEOL 3080 Diffractometer using $\text{Cu-K}\alpha$ radiation to ascertain the glassy nature of the samples. The weight loss of well-polished glass samples (degradation) was measured in distilled water, 5% HCl and 5% sodium hydroxide (NaOH) solution at room temperature and 60°C. Separate samples were used for each medium. The samples were removed, dried and weighed after immersion time of 5 h or 24 h depending on the weight loss. The glass surfaces were also examined under microscope at 25 and 50X magnification to study the degradation if any at the surface of the glass samples. The weight loss was then calculated and dissolution rate was calculated using the following formula

$$D = \frac{W_0 - W_t}{At},$$

where W_0 is the initial weight of glass sample in air, W_t the weight of glass sample after time t , A the surface area and t the time of measurement.

3. Results and discussion

XRD patterns for different glass samples are presented in figure 1. These patterns confirm the glassy nature of the samples with broad peaks around 20–30° and 40–50° (2θ values). Figure 2 shows the plot of dissolution rates of glass samples of different contents of $x = 5-20$ mol% in distilled water as a function of immersion time. It is evident from figure 2 that for glass with $x = 5$ mol% the dissolution rate (degradation) is nearly constant throughout immersion for 260 h whereas, the glass with $x = 10$ mol%, shows similar dissolution rate up to 110 h which substantially increases with further immersion. The dissolution rates for glasses with $x = 15$ and 20 mol% start showing increase even after 30–40 h but the rate for glass with

Figure 1. XRD plots of the different glass samples having nominal composition, $40\text{Na}_2\text{O}-10\text{BaO}-x\text{B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$, where $x = 0-20$ mol%.

Figure 2. Dissolution of glass samples having composition $x = 5-20$ mol% in distilled water at room temperature and at 25X magnification.

Figure 3. A. Morphology of the surface of the sample with $x = 5$ mol% after different immersion times in distilled water and at 25X magnification, B. morphology of the surface of the sample with $x = 10$ mol% after different immersion times in distilled water and at 25X magnification, C. morphology of the surface of the sample with $x = 15$ mol% after different immersion times in distilled water and at 25X magnification and D. morphology of the surface of the sample with $x = 20$ mol% after different immersion times in distilled water and at 25X magnification.

$x = 20$ mol% increases to at least two orders of magnitude. This shows that glass samples having lower B_2O_3 content are not greatly attacked by distilled water. Possible dissolution reactions in the aqueous medium are given in following equations (Gao *et al* 2004)

or

As B_2O_3 content in the glass increases, the metaphosphate chains are converted into orthophosphate structural units with the formation of P-OH and Na^+OH^- bonds, which are relatively weak in nature, resulting in increase in the dissolution rate. B_2O_3 reacts with water and forms boric acid, which readily dissolves in water. It is also observed that with increase in B_2O_3 content, BO_4 units are increased. BO_4 structural units exist as $BO_4^-Na^+$ units, which readily react with aqueous medium to form sodium borate, which is soluble in water or acidic medium. Thereby it increases the dissolution rate.

It is believed that Na^+ ions get dissolved in water solution and the solution becomes alkaline in nature due to increase in the pH value with increase in time of expo-

sure. The alkaline nature of the solution breaks the glass network leading to pronounced leaching of the sample, thereby increasing the weight loss after immersion time of 140 h, as seen in figure 2.

It is seen that in general, dissolution rate increases with increase in B_2O_3 content as well as immersion time.

Figures 3A–D show the morphology of the surface of corroded glass samples of different compositions and different immersion period in distilled water.

The glass sample with $x = 5$ mol% does not show any change in the surface morphology up to 116 h at room temperature (figures 3A.a and 3A.b). However, only small degradation is seen on prolonged immersion, after 140 and 260 h (figures 3A.c and 3A.d) at room temperature. In the case of glass sample with $x = 10$ mol%, there is a negligible change in the surface morphology up to 20 h immersion (figures 3B.a and 3B.b). But after 140 and 260 h of exposure it seems that thin layers are leached out (figures 3B.c and 3B.d).

The optical micrograph of the glass sample with $x = 15$ mol% also shows that there is a negligible change in the surface morphology up to 20 h immersion, whereas, the glass surface is corroded considerably after 140 h (figure 3C.c) and a thin layer seems to be leached out after 260 h (figure 3C.d).

In the case of glass sample, $x = 20$ mol%, the surface starts corroding even after 10 h of exposure (figure 3D.b). A large number of pits are formed as seen in figures 3D.c and 3D.d after 15 h immersion. The size of pits and in turn the corrosion increases with further increase in immersion time (figures 3D.e and 3D.f). A thicker layer appears to be leached out after 116 h, which is evident from the increased weight loss.

Figure 4 shows the dissolution rate for glass samples with $x = 5$ and 10 mol% in 5% HCl solution, as a function of immersion time at room temperature. It is seen that the

Figure 4. Dissolution rate as a function of TIT of glass samples ($x = 5$ and 10 mol%) at room temperature in acid medium.

weight loss increases with increase in immersion. Glass samples with $x = 15$ and 20 mol% were dissolved in 5% HCl after 5 h of exposure.

Figures 5A and B show the optical micrographs of glass samples with $x = 5$ and 10 mol%, respectively immersed in 5% HCl at room temperature for different periods. Figure 5A (a, b and c) for glass sample with $x = 5$ mol% shows that the ditches on the surface go on increasing with immersion time due to attack of H^+ ions on the network. It appears that a new surface layer is formed due to the diffusion of H^+ ions after 20 h of exposure and dissolution of original layer (figure 5A.d). It is seen from figure 5B (a and b) that, for glass sample with $x = 10$ mol%, there is a rapid increase in dissolution of the surface layer with few ditches forming on the surface. As regards the dissolution in acid medium, as B_2O_3 content in the glass increases, the O/P ratio also increases and the bridging oxygens are converted into non-bridging oxygens. The dissolution rates increase as the phosphate chains get converted from meta phosphate (O/P = 3) to orthophosphate (O/P = 4.0) structural units by hydration mechanism. Possible dissolution reactions are given in the following equations (Wen and Jijian 2001)

Therefore, for $x = 5$ mole% sample the metaphosphate chains containing less non-bridging oxygens are less corroded with HCl, whereas the $x = 10, 15$ and 20 mol% samples contain more non-bridging oxygens and are more corroded with HCl. The phosphate chains are leached by hydration mechanism.

Figure 6 shows the weight loss (dissolution rate) of glass samples of various compositions in 5% NaOH solution, at room temperature, as a function of immersion time.

It is evident that the dissolution rate initially decreases from 27.6 mg/cm² to 17.4 mg/cm² as B_2O_3 content is increased from 5 mole% to 10 mole%. However, with further increase in B_2O_3 content to 15 mole%, it increases substantially from 17.4 mg/cm² to 58 mg/cm² after 205 h immersion time.

Figures 7A–D show photographs of the surface of various glass samples exposed to 5% NaOH solution, at room temperature, for different periods.

As regards the dissolution in alkaline medium, in the glass sample with $x = 5$ mol%, OH^- ions modify the meta-

Figure 5. A. Photographs of $x = 5$ mol% sample exposed to 5% HCl solution at room temperature and at 25X magnification, and B. photographs of $x = 10$ mol% sample exposed to 5% HCl solution at room temperature and at 25X magnification.

Figure 6. Dissolution of glass samples ($x = 5$ – 15 mol%) in 5% NaOH at room temperature.

phosphate network, as confirmed by ^{31}P MAS NMR¹² (Shah *et al* 2005). The presence of less BO_4 structural units and more P–O–P linkages results in the increase of weight loss. Whereas, for glass sample with $x = 10$ mol%, as BO_4 structural units increase, more and more P–O–B bonds are formed at the cost of P–O–P bonds. Since P–O–B bonds are stronger as compared to P–O–P bonds, there is a decrease in the dissolution rate of the glass sample. It may be mentioned that although O/P ratio is higher for the sample with $x = 10\%$, compared to that with $x = 5\%$, the dissolution rate is reduced, which may

be attributed to the increase in the formation of P–O–B bonds. When B_2O_3 content further increases, i.e. $x = 15$ and 20 mol%, BO_3 structural units as well as the O/P ratio increases. As BO_3 units are moisture sensitive, the dissolution rate increases with increase in BO_3 units. Also O/P ratio reaches to that of the orthophosphate structure, with a low P_2O_5 content dispersed in disordered borate network. These orthophosphate units readily dissolve in NaOH solution due to increase in non-bridging oxygen atoms and thereby increasing the dissolution rate as compared to glass samples with $x = 5$ and 10 mol%. The possible reactions for the dissolution in alkali medium for orthophosphate glasses are as follows

The formation of ortho phosphoric acid and sodium borate also suggests increase in dissolution rates with exposure to alkali medium for higher B_2O_3 content samples ($x = 15$ and 20 mol% glass samples).

The surface of as polished glass sample with $x = 5$ mol% is smooth (figure 7A.a). As the immersion time increases from 3 h to 205 h, the size of ditches formed on the surface increases, resulting in the increase in weight loss (figures 7A.b–7A.e). Whereas, the surface of the glass sample with $x = 10$ mol% shows that the chemical attack is much less even after immersing for 205 h (figures 7B.b–B.g), which is consistent with weight loss observed (figure 6). The glass sample, $x = 15$ mol%, shows that

Figure 7. A. Photographs of sample with $x = 5$ mol% exposed to 5% NaOH solution at room temperature and at 25X magnification, B. photographs of sample with $x = 10$ mol% exposed to 5% NaOH solution at room temperature and at 25X magnification, C. photographs of sample with $x = 15$ mol% exposed to 5% NaOH solution at room temperature and at 25X magnification and D. photographs of sample with $x = 20$ mol% exposed to 5% NaOH solution at room temperature and at 25X magnification.

Figure 8. Dissolution of $x = 10$ mol% glass sample in alkali medium at 60°C .

Figure 9. a–g. Photographs of continuous degradation of the surface of sample with $x = 10$ mol%, in 5% NaOH at 60°C for different periods.

there is a continuous degradation (increases in the size of ditches) of the surface with increase in immersion time (figures 7C.b–7C.g). As B_2O_3 content is further increased to 20 mol%, there is a fast degradation of the surface and the sample is completely dissolved after 9 h immersion (figure 7D).

Figure 8 shows the dissolution rate (weight loss) of a glass sample of $x = 10$ mol% in 5% NaOH solution at 60°C as a function of immersion time. The dissolution rate increases linearly with immersion time. It is nearly twice compared to the weight loss at room temperature after 205 h immersion.

Figure 9 shows the photographs of the surface of the glass sample with $x = 10$ mol% glass sample exposed to 5% NaOH solution at 60°C for different periods. Figures 9a–e show continuous degradation of the surface and the weight loss with the formation and growth of ditches on the surface in between 24 and 97 h of exposure. Figure 9f shows the total leaching of the surface layer, which is consistent with significant increase in weight loss between 121 and 193 h of exposure. The surface is further degraded after 217 h with the increase in diffusion rate at 60°C .

The dissolution rates are controlled by diffusion process, which is affected remarkably by temperature. With the increase in temperature, the effect of diffusion rate on dissolution rate is significant as seen in figure 8. Similar abnormal and complicated trend of change of dissolution rates in borophosphate glasses with relatively higher sodium content has been observed by Gao *et al* (2004).

4. Conclusions

Bubble free glasses of sodium barium borophosphate, $40\text{Na}_2\text{O}-10\text{BaO}-x\text{B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$ ($0 \leq x \leq 20$ mol%), were prepared. At low B_2O_3 content, the durability (degradation behaviour) of these glasses in water, acid and alkali medium is improved. However, at higher B_2O_3 content, the dissolution rates are increased. All the glasses were found to be fairly stable in alkali and water medium than acid medium. However, the glass sample, $x = 10$ mol%, was found to be more stable than the other glasses in all media at room temperature and at 60°C .

Acknowledgements

The authors would like to thank Drs V C Sahni and J V Yakhmi for their constant support and encouragement to this work. They acknowledge the useful technical discussions with Dr Sudarsan. The authors would also like to acknowledge Mr Arjun Sarkar, Mr Rakesh Kumar and Mr P A Wagh for technical assistance. One of the authors (KVS) would like to thank DAE for giving him a fellowship.

References

- Brow R K 1996 *J. Non-Cryst. Solids* **194** 267
- Brow R K 2000 *J. Non-Cryst. Solids* **263 & 264** 1
- Brow R K and Tallant D R 1997 *J. Non-Cryst. Solids* **222** 396
- Coppo D, Duclot M J and Souquet J L 1996 *Solid State Ionics* **90** 111
- Gao H, Tan T and Wang D 2004 *J. Controlled Release* **9** 21
- Harish Bhat M, Berry M J, Jiang J Z and Rao K J 2001 *J. Non-Cryst. Solids* **291** 93
- Kaushik R and Hariharan K 1987 *Solid State Commun.* **63** 925
- Ma Y, Deoff M M, Visco M J and Jonghe De L C 1993 *J. Electrochem. Soc.* **140** 2726
- Shah K V, Goswami M, Patil A S, Manikandan Shobha, Shrikhande V K and Kothiyal G P 2005 *Solid State Phys.* **50** 359
- Shah K V, Goswami M, Deo M N, Sarkar A, Manikandan Shobha, Shrikhande V K and Kothiyal G P 2006 *Bull. Mater. Sci.* **29** 43
- Tsuchiya T and Moriya T 1980 *J. Non-Cryst. Solids* **38–39** 323
- Wen L and Jijian C 2001 *Glass Technol.* **42** 153
- Wilder J A 1980 *J. Non-Cryst. Solids* **3–39** 879
- Yun Y H and Bray P J 1978 *J. Non-Cryst. Solids* **30** 45