

## Effect of hydroxyl content on the physical properties of calcium metaphosphate glasses

B KARMAKAR\*, P KUNDU, ANUP K CHAUDHURI, K ANNAPURNA, A KUMAR and R N DWIVEDI

Glass Technology Section, Central Glass and Ceramic Research Institute, Calcutta 700 032, India

MS received 7 October 1998; revised 9 February 1999

**Abstract.** The hydroxyl (OH) content of calcium metaphosphate glasses has been controlled in the range 50–800 ppm by melting calcium dihydrogen phosphate in air, under vacuum and with fluoride addition. Density, refractive index and glass transition temperature of the glasses increase with decrease in OH content while the coefficient of thermal expansion remains almost unchanged. With gradual decrease in OH, the UV cutoff initially shifts towards shorter and finally towards longer wavelengths. IR spectroscopic study shows that the OH groups exist exclusively in the hydrogen bonded states. Correlations of the glass properties with OH content have been explained in terms of structural rearrangement leading to the change in P–O bond length and O–P–O/P–O–P bond angles of the  $\text{PO}_4$  tetrahedral units of  $(\text{PO}_3)_n$  chains. These changes are caused due to conversion of non-bridging oxygens (NBOs) of the H-bonded OH groups into bridging oxygens (BOs) during progress of dehydroxylation.

**Keywords.** Phosphate glass; hydroxyl content; glass properties; IR spectra; hydrogen bond.

### 1. Introduction

Unintentional water enters into the glasses as impurity during melting from the raw materials and surrounding humid atmospheres. In oxide glasses, low residual water ( $< 2 \times 10^3$  ppm) exists entirely in the form of hydroxyl (OH) groups (Davis and Tomozawa 1996). This OH group behaves as modifier like alkali and alkaline earth metal ions by terminating the polymeric chains of the glass network (Shelby and McVay 1976; Bartholomew 1982; Brow *et al* 1990; Gomez *et al* 1997). In presence of nonbridging oxygens (NBOs), it exists both as un-bonded (i. e. free OH) and hydrogen bonded (H-bonded OH) states (Scholze 1959, 1966; Adams 1961). Alteration of glass structure by various types and concentrations of OH group is well established (Davis and Tomozawa 1995; Jewell and Aggarwal 1995; Mercier *et al* 1998). Physical properties of a glass are governed by its structure (Gaskell 1997). Thus, variation of glass properties is expected with structural modifications imparted by the OH groups. Several studies have been published on the effects of high OH content on the physical properties of oxide glasses (Shelby and McVay 1976; Bartholomew 1982; Abe 1983; Tomozawa 1985; Toratani *et al* 1987), but only a few concern about their low OH content (Arriagada *et al* 1987). In this paper, we report the influence of low OH content (50–800 ppm) on the optical and thermal properties of calcium metaphosphate glasses.

### 2. Experimental

#### 2.1 Preparation of glass

Calcium metaphosphate glasses with varying OH content were prepared by melting calcium dihydrogen phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (Alfa) at  $1100^\circ\text{C}$  in a platinum crucible in air, under vacuum ( $4 \times 10^{-3}$  mm Hg) and by adding calcium fluoride,  $\text{CaF}_2$ . Molten glasses were cast in preheated graphite moulds and quenched in air. All the glasses were annealed at about  $20^\circ\text{C}$  below the glass transition temperature.

#### 2.2 Measurement of glass properties

Infrared (IR) absorption spectra in the range  $1500\text{--}4000\text{ cm}^{-1}$  of the glasses were recorded on a Perkin-Elmer 1615 FTIR spectrometer at  $4\text{ cm}^{-1}$  resolution. The OH content of the glasses was calculated from the IR spectra following the method described in Ebendorff-Heidepriem *et al* (1993). The ultraviolet (UV) spectra of the samples were examined utilizing a Hitachi (Model U 3210) double beam UV–VIS spectrophotometer. Optically polished glass samples of  $1.0 \pm 0.02$  mm thickness were used in these measurements.

Density ( $d$ ) of the glasses was measured by the Archimedes method at  $25 \pm 0.5^\circ\text{C}$  using kerosene as the immersion liquid. The refractive index ( $n_D$ , at  $\lambda = 587.6$  nm) was measured with the Pulfrich-Refractometer (Model

\*Author for correspondence

PR2). Glass transition temperature ( $T_g$ ) and coefficient of linear thermal expansion ( $\alpha$ ) of the glasses were determined from the dilatometric thermogram recorded with an Orton Automatic Recording Dilatometer.

### 3. Results and discussion

#### 3.1 IR spectra

The IR spectra of some representative calcium metaphosphate glasses with OH content has been shown in figure 1. It can be seen that there are three distinct bands at around 2900, 2340 and 1750  $\text{cm}^{-1}$  which gradually decrease in intensity with the progress of dehydroxylation. They are thought to be OH group related bands. In silicate glasses, the band due to free OH group has been observed at about 3570  $\text{cm}^{-1}$ . The bands due to weakly associated H-bond of middle OH and strongly bound H-bond of isolated or end  $\text{SiO}_4$  tetrahedral OH with NBOs have been observed at around 3000 and 2350  $\text{cm}^{-1}$ , respectively (Scholze 1959, 1966). A very strong H-bonded band in the range 1650–1750  $\text{cm}^{-1}$  has also been found to develop in the cases of organophosphonic and phosphonous acids ending with  $>\text{P}(=\text{O})\text{OH}$  group (Braunholtz *et al* 1959). It is known that metaphosphate glasses consist of mainly linear chains of polyphosphate anions which are connected to one another by the ionic bonds to the modifier cations (Van Wazer 1950). Thus, all of the OH groups of the calcium metaphosphate glasses are thought to be due to H-bonded states. The bands at around 2900, 2340 and 1750  $\text{cm}^{-1}$  have been assigned to O–H stretching vibration of weakly H-bonded middle OH groups with middle NBOs of the phosphate chains, strongly H-bonded isolated and/or end  $\text{PO}_4$  tetrahedral OH groups with middle NBOs (of an another chain), and very strongly H-bonded end OH groups with end NBOs, respectively.

A band at around 2170  $\text{cm}^{-1}$  not observed in high OH containing glasses rather has been found to develop with the progress of dehydroxylation (figure 1). Perhaps, it was hidden in the tail of strong absorption band at around 2340  $\text{cm}^{-1}$  of strongly H-bonded OH group. This band has been assigned to the first overtone of  $\nu_{\text{as}}(\text{OPO})$  and/or combinational band of  $\nu_{\text{as}}(\text{OPO}) + \nu_{\text{as}}(\text{POP})$  fundamentals of  $\text{PO}_4$  tetrahedra; the fundamental band of  $\nu_{\text{as}}(\text{OPO})$ ,  $\nu_{\text{ss}}(\text{OPO})$  and  $\nu_{\text{as}}(\text{POP})$  develops at around 1280, 1100 and 900  $\text{cm}^{-1}$ , respectively. Development of the 2170  $\text{cm}^{-1}$  band with dehydroxylation is brought about by structural rearrangement leading to the change in P–O bond distance and O–P–O or P–O–P bond angles. Brow *et al* (1990) showed by MAS NMR study of sodium phosphate glasses that decrease in NBOs (i.e.  $\text{Na}_2\text{O} + \text{H}_2\text{O}$ ) causes increase in average  $\pi$ -character of the P–O bonds which results in decrease in P–O bond distance due to  $\pi$ -bond shortening.

#### 3.2 UV cutoff

Dependence of UV cutoff on the OH content of the glasses has been shown in figure 2. It shows two distinct regions. In region I, between 110 and 720 ppm OH content, the UV cutoff shifts towards shorter wavelength. This is caused due to removal of weakly associated H-bonded chain middle OH groups which is supported by the decrease in intensity of the 2900  $\text{cm}^{-1}$  band with dehydroxylation (see figure 1). In region II, between 60 and 110 ppm OH content, the UV cutoff shifts towards longer wavelength. This effect has been brought about by the removal of very strongly H-bonded chain end and isolated  $\text{PO}_4$  tetrahedral OH groups as evident from the intensity decrease of the bands at 2340 and 1750  $\text{cm}^{-1}$  (see figure 1). These results are in accordance with those obtained in calcium metaphosphate glasses

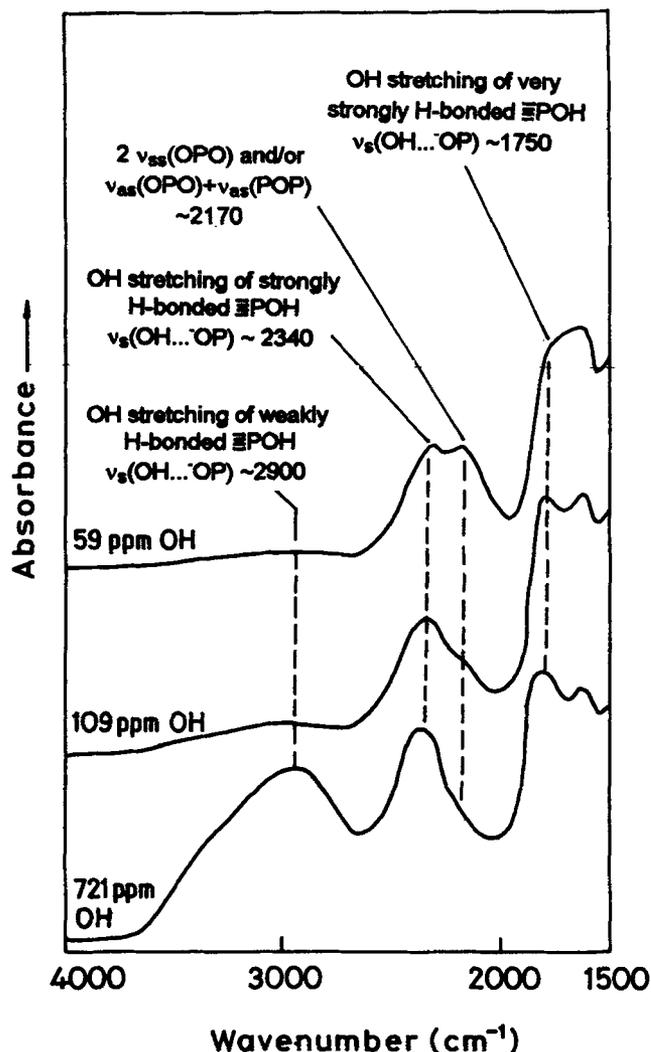


Figure 1. Infrared absorbance spectra of calcium metaphosphate glasses with varying OH content.

(Arriagada *et al* 1987). Similar effect has also been observed when network modifying cations are added to vitreous  $P_2O_5$  (Kordes and Worster 1959; Kordes 1965). In these glasses, with addition of  $Na^+$  or  $Ba^{2+}$  the UV absorption edge shifts towards shorter wavelengths for low concentrations (up to around 25 mol%) and for high concentrations (above around 25 mol%), it shifts towards longer wavelengths.

Further, in region I, it is assumed that more P–O–P bonds, i.e. bridging oxygens (BOs), are generated with the removal of middle OH groups (Gomez *et al* 1997) and due to lower microscopic basicity,  $\lambda$  (Duffy and Ingram 1976), of the P–O–P bond ( $\lambda = 0.25$ ) than that of P–O–H bond ( $\lambda = 0.32$ ), the UV cutoff shifts towards shorter wavelengths. Whereas in region II, the average  $\pi$ -character of the P–O bonds increases as the end OH group decreases (Brow *et al* 1990), thereby increasing the optical basicity (Duffy and Grant 1975) which causes the shift of the UV cutoff towards longer wavelengths. The increase in intensity of the IR band at around  $2170\text{ cm}^{-1}$  supports the formation of P–O–P and O–P=O bonds with dehydroxylation (§ 3.1).

### 3.3 Density and refractive index

The influence of OH content on density and refractive index has been shown in figures 3 and 4, respectively. It is seen that both these properties increase simultaneously as the OH content decreases and clearly exhibit two regions. In the region between 0 and 200 ppm OH content they increase rapidly due to the removal of end group OH whereas in the region between 200 and 800 ppm OH content they increase slowly due to the

removal of middle group OH. These simultaneous variations of density and refractive index with OH content agree well with the direct variation relationship of density and refractive index of a glass (Cohen and Roy 1965). IR spectra depict that all of the OH groups are in the H-bonded states (figure 1) and the glasses attain the denser structures with dehydroxylation through the formation of bridging oxygens (BOs) of the P–O–P bonds as concluded due to increase in intensity of the IR bands at around  $2170\text{ cm}^{-1}$  (§ 3.1).

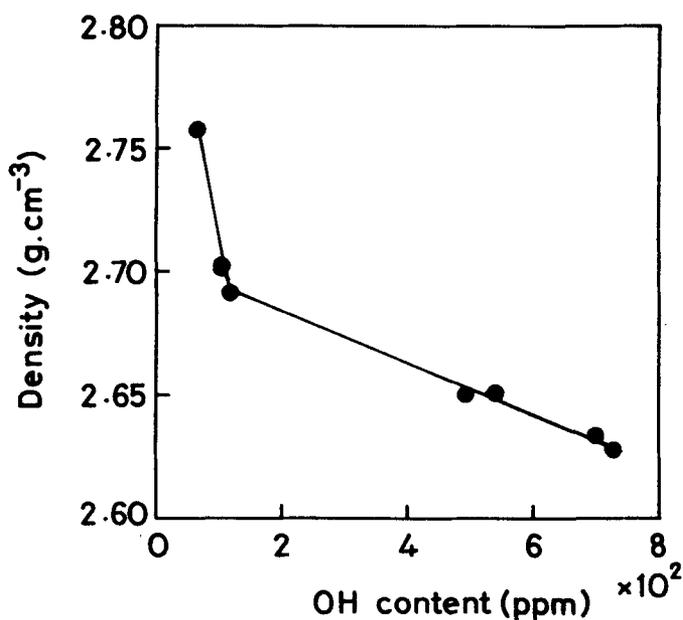


Figure 3. Dependence of density ( $d$ ) of the glasses on OH content.

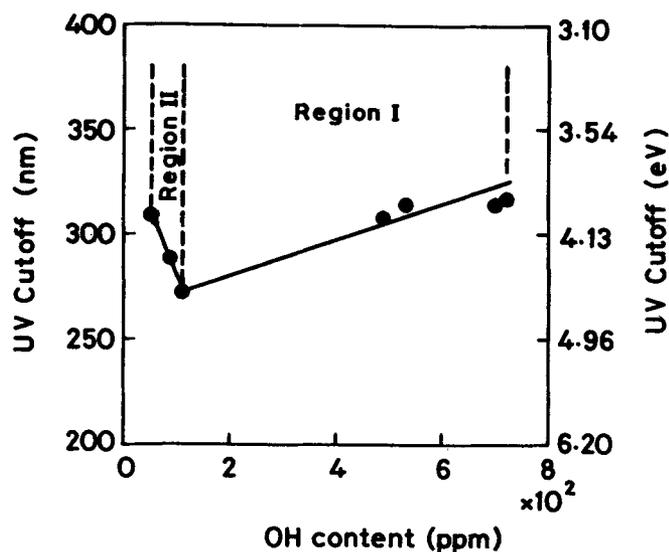


Figure 2. Dependence of UV cutoff of the glasses on OH content.

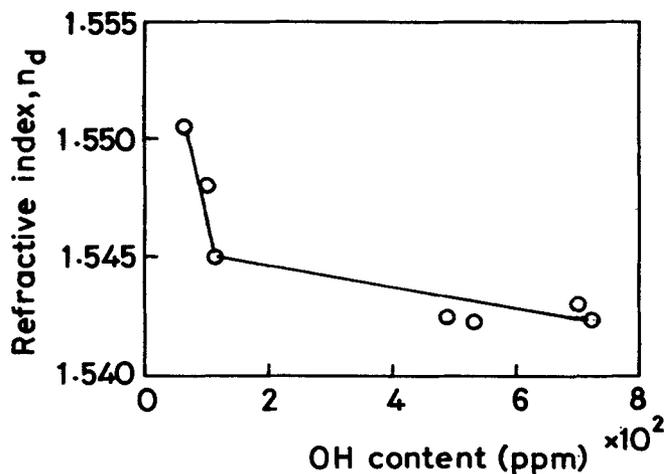


Figure 4. Dependence of refractive index ( $n_d$ ) of the glasses on OH content.

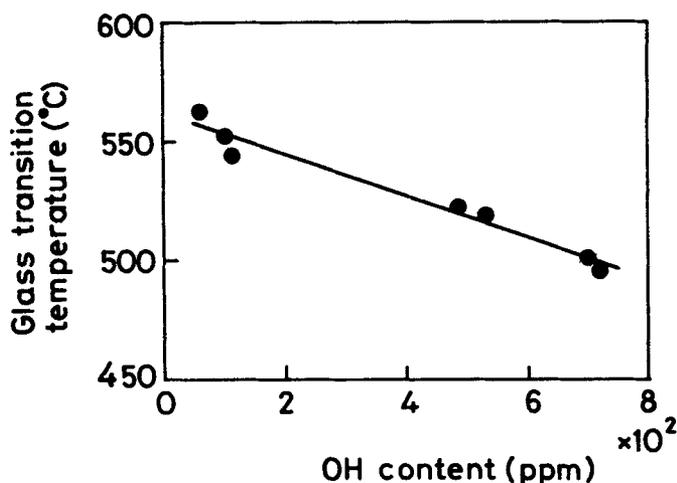


Figure 5. Dependence of glass transition temperature ( $T_g$ ) on OH content.

### 3.4 Glass transition temperature and coefficient of linear thermal expansion

Dependence of glass transition temperature,  $T_g$ , on the OH content has been shown in figure 5. It is seen that the glass transition temperature increases with decrease in OH content which is caused due to strengthening of the glass structure. This tightening of structure is also reflected by the increase in intensity of the IR band at  $2170\text{ cm}^{-1}$  (§ 3.1). The effect is analogous to the alkali effect on the glass properties which has been explained with the concept of NBO formation on alkali oxide addition (Brow *et al* 1990). Results of this study agree well with those obtained with decrease in OH content in calcium metaphosphate (Abe 1983; Arriagada *et al* 1987) and sodium trisilicate (Shelby and McVay 1976; Tomozawa *et al* 1983) glasses.

The effect of OH content on the coefficient of linear thermal expansion,  $\alpha$  ( $30\text{--}300^\circ\text{C}$ ), has been shown in figure 6. Expansivity of the glasses is virtually unaffected by the presence of negligible amount of OH groups or to a small extent to be measured by the standard dilatometer used in this investigation. However, there is a good agreement of these results with those obtained in calcium metaphosphate (Abe 1983) and sodium trisilicate (Shelby and McVay 1976) glasses.

## 4. Conclusions

Calcium metaphosphate glasses with varying OH contents have been obtained by melting in air, vacuum and with fluoride addition. Density, refractive index and glass transition temperature have been found to increase with decrease in OH content while the coefficient of linear

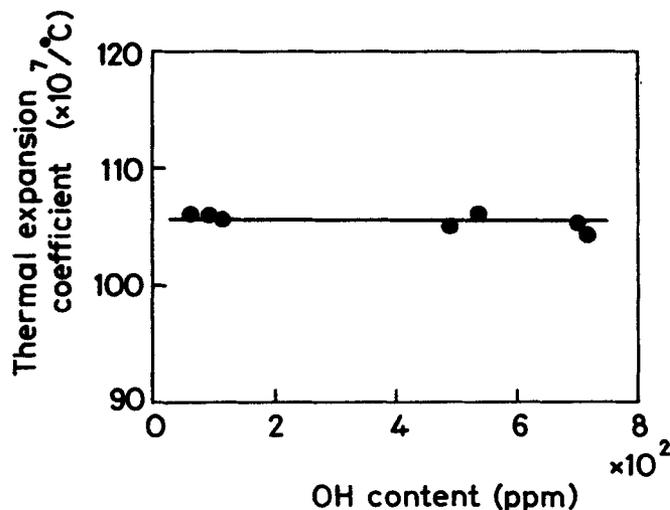


Figure 6. Dependence of coefficient of linear thermal expansion ( $\alpha$ ) of the glasses on OH content.

thermal expansion remains almost unaffected. The UV cutoff, with decrease in OH content, shifts initially to the shorter wavelength and then towards longer wavelengths. IR spectroscopic study show the presence of exclusively H-bonded states of the OH groups and the formation of O–P=O and P–O–P bonds with the progress of dehydroxylation. Variation of glass properties with OH content is brought about by structural rearrangement leading to the change in P–O bond length and O–P–O/P–O–P bond angles during dehydroxylation.

## References

- Abe Y 1983 in *Topics in phosphorous chemistry* (eds) M Grayson and E J Griffith (New York: John Wiley) Vol. 11, p. 20
- Adams R V 1961 *Phys. Chem. Glasses* **2** 39
- Arriagada J C, Burckhardt W and Feltz A 1987 *J. Non-Cryst. Solids* **91** 375
- Bartholomew R F 1982 in *Treatise on materials science and technology* (eds) M Tomozawa and R H Doremus (New York: Academic Press) Vol. 22, p. 75
- Braunholtz J T, Hall G E, Mann F G and Shepard N 1959 *J. Chem. Soc.* 868
- Brow R K, Kirkpatrick R J and Turner G L 1990 *J. Non-Cryst. Solids* **116** 39
- Cohen H M and Roy R 1965 *Phys. Chem. Glasses* **6** 149
- Davis K M and Tomozawa M 1995 *J. Non-Cryst. Solids* **185** 203
- Davis K M and Tomozawa M 1996 *J. Non-Cryst. Solids* **201** 177
- Duffy J A and Ingram M D 1976 *J. Non-Cryst. Solids* **21** 373
- Duffy J A and Grant R J 1975 *Phys. Chem. Glasses* **16** 124
- Ebendorff-Heidepriem H, Seeber W and Ehrh D 1993 *J. Non-Cryst. Solids* **163** 74
- Gaskell P H 1997 *J. Non-Cryst. Solids* **222** 1
- Gomez F, Vast P, Llewellyn Ph. and Rouquerol F 1997 *J. Non-Cryst. Solids* **222** 415

- Jewell J M and Aggarwal I D 1995 *J. Non-Cryst. Solids* **181** 189
- Kordes E 1965 *Glastechn. Ber.* **38** 242
- Kordes E and Worster E 1959 *Glastechn. Ber.* **32** 267
- Mercier C, Montagne L, Sfihi H, Palavit G, Boivin J C and Legrand A P 1998 *J. Non-Cryst. Solids* **224** 163
- Scholze H 1959 *Glastechn. Ber.* **32** 142
- Scholze H 1966 *Glass Ind.* **47** 622
- Shelby J E and McVay G L 1976 *J. Non-Cryst. Solids* **20** 439
- Tomozawa M 1985 *J. Non-Cryst. Solids* **73** 197
- Tomozawa M, Takata M, Acocella J, Watson E B and Takamori T 1983 *J. Non-Cryst. Solids* **56** 343
- Toratani H, Meissner H E and Izumitani T 1987 *J. Non-Cryst. Solids* **95 & 96** 701
- Van Wazer J R 1950 *J. Am. Chem. Soc.* **72** 644