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Preparation and studies of some thermal, mechanical and optical properties of $xAl_2O_3(1 - x)NaPO_3$ glass system

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Abstract. Sodium aluminophosphate glasses having compositions of $xAl_2O_3(1 - x)NaPO_3$ (x = 0·05–0·2) were prepared using conventional melt-quench technique. Density, glass transition temperature, microhardness (MH), thermal expansion coefficient (TEC) and transmission characteristics were measured as a function of alumina content for different samples. They were found to depend on O/P ratio with pronounced changes taking place for O/P ratio ≥ 3·5. Density, glass transition temperature and microhardness were found to increase up to 15 mol% of alumina and then they showed a decreasing trend. Thermal expansion coefficient decreased continuously with alumina content. Optical gaps for different glass samples as measured from transmission characteristics were found to be in the range 3·13–3·51 eV. It initially decreased with alumina content up to 15 mol% and then increased. The behaviour was explained on the basis of change in the average aluminum coordination number from six Al(6) to four Al(4) (i.e. $Al(OP)_6/Al(OP)_4$ ratio) along with the changes in polyhedra linkages in the glass network due to change in O/P ratio.

Keywords. Phosphate glass; thermal expansion coefficient; microhardness; optical gap.

1. Introduction

Pure phosphate glasses, due to their hygroscopic nature and volatility were not considered to have industrial and technological applications. But the recent developments of novel compositions of superior physical and chemical properties of these glasses have revived interest in phosphate glasses and glass ceramics. These glasses and glass ceramics are used in various applications such as bone transplantation (Oliveira *et al* 2000), glass to metal seals (Wilder 1980; Peng and Day 1991; Donald 1993; Brow and Tallant 1997; Brow *et al* 1998; Wei *et al* 2001), containment of radioactive wastes (Sales and Boatner 1986), fast ion conductors (Kokubo *et al* 1986; Hench 1991), laser host materials (Weber 1990), etc. The network structure of simple phosphate glass consists of P tetrahedra linked to neighbouring tetrahedra through bridging oxygens (BOs). Addition of Al^{3+}, B^{3+}, Bi^{3+}, etc has been found to improve the chemical stability because of the formation and relative stability of M^{3+}–O–P bond (Minami and Mackenzie 1997). 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.

Sodium aluminophosphate (NAP) glasses have been the subject of various investigations (Tallant and Nelson 1986; Brow *et al* 1990, 1993; Inoue *et al* 1995; Hudgens *et al* 1998). Addition of Al depolymerizes the glass network, replacing Na–O bands with Al–O bands and also some P–O bands (Yan *et al* 1996; Egan *et al* 2000). It is seen that many of the glass properties are dependent on O/P ratio and the average Al coordination number (Al–CN) and the latter changes from Al(6) to Al(4) for Al between 10 and 12·5 mol%. Also the structure of glass is a combination of coordination polyhedra and linkages among them. The investigations of Brow *et al* (1990, 1991, 1993) as regards ^{31}P MAS–NMR spectra of NAP glasses exhibited low frequency shoulder near – 8 to – 10 ppm in chemical shifts spectra with increasing Al content. This shoulder appears to merge with Q^2 peak to form a single peak in higher Al contents. The frequency shoulder near – 8 to – 10 ppm is assigned to Q^1 aluminophosphate groups that form when P–O–Al linkages replace P–O–P linkages. Further, chemical shifts of + 40, + 15, – 10 ppm in ^{27}Al MAS–NMR are related to $Al(OP)_4$, $Al(OP)_5$, $Al(OP)_6$ sites, respectively. The structure has also been analysed using combination of X-ray diffraction and molecular dynamics by Inoue *et al* (1995) and noted that oxygen coordination number around Al atoms decreased with increasing Al_2O_3 content. Raman data of Tallant and Nelson (1986) provided evidence of the presence of mixed networks of linked Al^{3+} polyhedra and

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phosphate tetrahedra. Recent $^{31}P/^{23}Na$ and $^{31}P/^{27}Al$ 'TRAPDOR' experiments of Lang and Alam (2003) in which a pulse sequence is applied under MAS conditions during the rotational period have shown the proximity of ^{23}Na and ^{27}Al nuclei, respectively with each of the ^{31}P environments.

Sodium aluminophosphate glass system, in particular, is important not only because of its improved chemical durability but also because of its potential use in glass to metal seals with Cu and Al. General procedure for making the glass is available in the literature, but information available with regard to the effects of processing parameters and the usefulness of particular glass composition for a specific end use is rather vague. It seems the study of microhardness (MH) of these glasses has not received much attention but is important for determining the mechanical strength of seal. In addition, thermal expansion coefficient of glass is another important parameter determining its suitability for applications in glass to metal seals. In this work we report on the preparation of sodium aluminophosphate glasses having compositions $x\mathrm{Al_2O_3}$ $(1-x)$ $\mathrm{NaPO_3}$ ($x = 0{\cdot}05$–$0{\cdot}2$) and a systematic study of the microhardness, thermal expansion coefficient (TEC), and optical transmission. Optical gap has been determined using transmission characteristics. The properties of the glasses were seen to be governed by the changes in the average Al–CN along with polyhedra linkages in the glass network as a result of increase in the content of alumina.

2. Experimental

2.1 *Glass preparation*

Sodium aluminophosphate glass was prepared by conventional melt-quench technique. Glasses with compositions, $x\mathrm{Al_2O_3}(1-x)\mathrm{NaPO_3}$ ($x = 0{\cdot}05$–$0{\cdot}20$), were prepared using analytical grade compounds of $\mathrm{NaNO_3}$, $\mathrm{Al_2O_3}$ and $\mathrm{NH_4H_2PO_4}$ as the starting materials. The content of $\mathrm{Al_2O_3}$ was varied from 5–20 mol%. These chemicals were thoroughly mixed and ground for 30–40 min in a planetary ball mill and then the charge (30–40g) was calcined in alumina crucible for 18–20 h by heating in predetermined manner considering the decomposition temperatures of initial compounds. This charge was reground and calcined again as before. The calcined charge was then melted using lowering and raising furnace (Model OKAY 70R 10, M/s Byshakh and Co., Kolkata) and held for 2 h for thorough mixing in platinum crucible in air ambient at temperatures ranging from 800–1300°C depending on composition. When the melt was thoroughly homogenized and attained desirable viscosity it was poured either onto metal plate and pressed by graphite disc or into graphite moulds. The glass was then annealed at appropriate temperatures (between 300 and 425°C) for 2 h and stored in desiccator prior to evaluation.

2.2 *Glass characterization*

Powder XRD patterns of the glasses were taken using Cu–Kα radiation to ascertain the glassy nature of the samples. Density (r) of bubble free glass samples was measured at room temperature using Archimedes principle with an accuracy of $\pm\ 0{\cdot}03$ g/cc. The molar volume was also calculated. Microhardness of bubble free glass samples was measured by indentation technique using Vickers indenter on the microhardness tester (Leica model VMHT30M). Before measurements, the sample was polished with $0{\cdot}3$ μm alumina powder to get good reflective surface. Indentation was obtained by applying a 50 g load for 10 s. From the measurements of the diagonals of Vickers impressions on the sample surface, microhardness was found out by using the standard formula. An average of 10 readings was taken. The thermal expansion coefficient measurements were carried out in a dilatometer (model TMA-92 Setaram, France) using a silica probe. The heating rate was kept to 10°C/min for all measurements. The size of the sample was about 1–3 mm thickness (maximum acceptable size is 20 mm height and 10 mm diameter) with both ends flat. The samples were kept in a quartz sample holder with a constant load of 5 g for all measurements. Before starting the experiment the chamber was evacuated up to 10^{-2} mbar pressure and then the chamber was flushed with high purity (IOLAR grade) Ar gas. All the measurements were carried out in flowing Ar atmosphere with a constant flow rate of 40–50 l/h. The temperature was varied in the range 30–450°C for measurement of TEC. The expansion coefficient being reported is the average in the temperature range 30–300°C. Transmission characteristics in the wavelength range 320–3200 nm were measured on well-polished glass samples in a spectrophotometer (Shimadzu model UV-3101PC). Optical gap was determined by plotting $(ahn)^{1/2}$ as a function of photon energy. FT–IR spectra were recorded on samples dispersed in KBr pellets.

3. Results and discussion

We have obtained in all the cases bubble free glass samples. XRD patterns confirm the glassy nature of the samples with broad peaks around 20–30° and 40–50° ($2q$ values). The densities for glass samples of different batches were found to be in the range $2{\cdot}49$–$2{\cdot}69$ g/cc. Figure 1 shows the variation of density with $\mathrm{Al_2O_3}$ content. Density increases monotonically up to 15 mol% alumina and slightly decreases at 20 mol% alumina. Correspondingly molar volume first decreases and then increases slightly. Similar trend has been reported by Brow *et al* (1993). Change in density/molar volume affects microhardness as well as TEC being discussed later. Figure 2 shows the variation of glass transition temperature (T_g) as obtained from dilatometric measurement (change in length vs tem-

perature plots) with Al_2O_3 content. T_g also shows an increasing trend up to 15 mol% alumina and then shows a slight decrease at 20 mol% alumina. It is believed that the properties are related to the linkages present in the glassy network as well as the relative proportion of $Al(OP)_6$ and $Al(OP)_4$ units. As mentioned earlier, the average Al coordination number (Al–CN) is not simply a function of alumina content but also O/P ratio. Thus properties of this glass system depend in somewhat complex manner near and beyond O/P ratio of 3·5. The increase is attributed to progressive increase in the formation of stronger $Al(OP)_6$ groups which cross-link sections of phosphate chains. The decrease at higher alumina (20 mol%) content in r, T_g is consistent with the replacement of $Al(OP)_6$ with more open $Al(OP)_4$ structures which in turn makes the glass network somewhat less rigid.

A typical Vickers impression obtained on the surface of glass sample is shown in figure 3. Figure 4 shows variation of microhardness with alumina content. The depen-

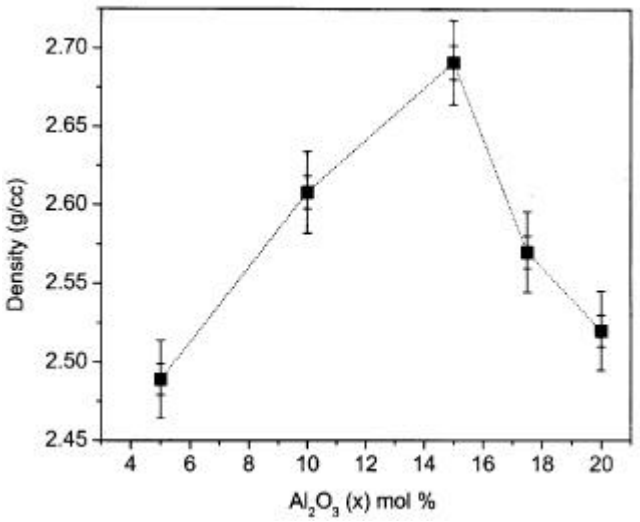

Figure 1. Density as a function of composition (x) for the glass samples, $xAl_2O_3(1-x)NaPO_3$.

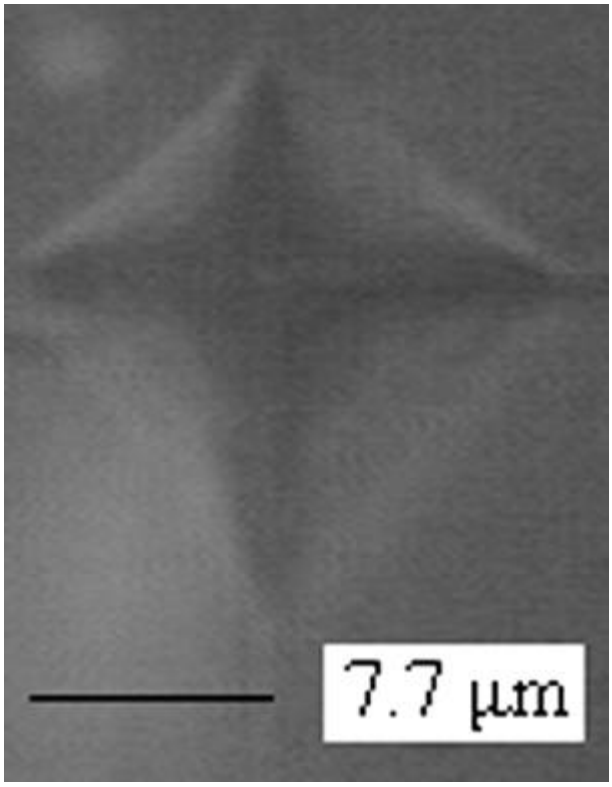

Figure 3. Optical micrograph of Vickers impression on the surface of glass sample having nominal composition, x = 17·5 mol%.

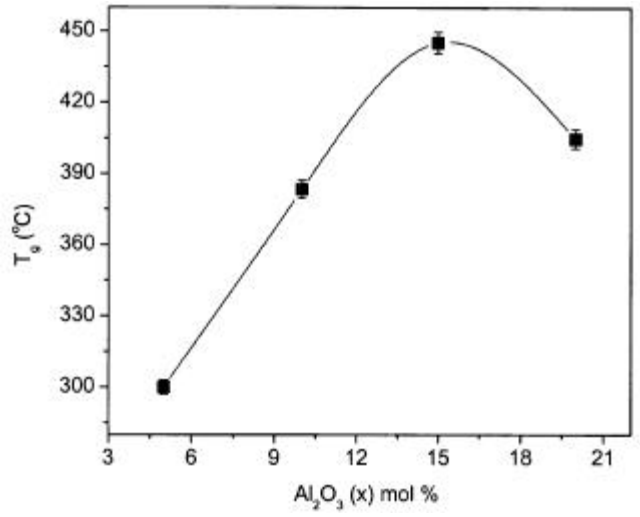

Figure 2. Dependence of glass transition temperature (T_g) on the composition of $xAl_2O_3(1-x)NaPO_3$ glasses.

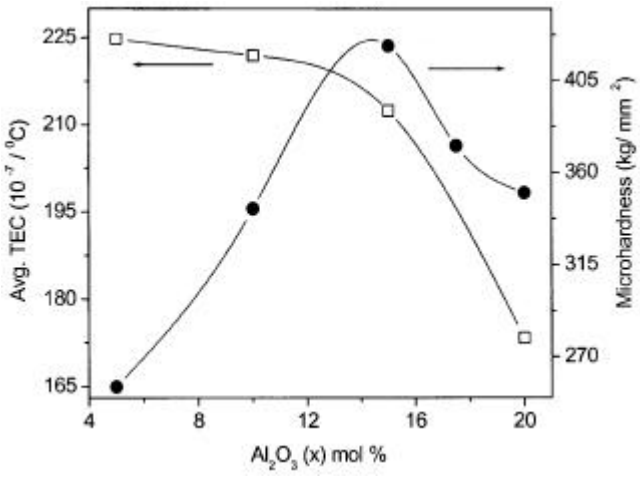

Figure 4. Dependence of average thermal expansion coefficient (TEC) and microhardness on composition of $xAl_2O_3(1-x)NaPO_3$ glasses.

dence of TEC on alumina content is also shown in figure 4. Microhardness increases up to 15 mol% alumina content. Both the microhardness and TEC are seen to decrease with alumina content rather sharply beyond 15 mol% of alumina. The decrease of TEC is rather unusual because normally it should increase when microhardness decreases. However, other workers have also observed the decrease of TEC. We think this is due to change in Al coordination and polyhedra linkages in somewhat complex manner in this glass system above O/P ratio of 3·5. It may be noted that at low alumina content the preferred coordination of aluminium is 6. Initial increase in microhardness and decrease in TEC are thought to be due to increase in rigidity (strength) of the glassy network up to 15 mol% alumina as mentioned above. At alumina content more than 15 mol% (where O/P ratio becomes > 3·5) due to the competition in the formation process between $Al(OP)_6$ and $Al(OP)_4$ there is reduction in the number of strong P–O–Al cross linkages and the number of relatively weak $PO^- Na^+$ bonds, thereby decreasing the average Al coordination(Al–CN) number from six-Al(6) to four-Al(4). Further, it is known that Al(6) provides more P–O–Al cross links per Al than Al(4). Consequently decrease of microhardness is consistent with the weakening of glass network (figure 5). These results are summarized in table 1.

Transmission characteristics for different glass compositions having different thicknesses are shown in figure 6. Transmission in the range 400–2800 nm is found to be 65–85% in these glasses having thickness of 0·8–3·5 mm. Addition of Al_2O_3 does not appear to change the transmission characteristics significantly in this wavelength range. However, the short wavelength (high energy) absorption edge is affected by alumina content as seen in figure 7 which shows plots of $(ahn)^{1/2}$ as a function of photon energy (hn). Optical absorption coefficient was calculated using the formula (Liu *et al* 1996),

$$a = -\ln T/x.$$

The optical energy gap in these glasses is found to fit the Tauc's equation,

$$(ahn)^{1/2} = k(hn - E_{opt}),$$

assuming a parabolic density of states. E_{opt} follows a decreasing trend up to 15 mol% Al_2O_3 and increases at 20 mol% Al_2O_3. As pointed out by Dayanand *et al* (1994) in their studies on lead phosphate glasses that in the glassy materials the absence of long range order and contribution from local inhomogeneities related to bridging/non bridging oxygen (BO/NBO) play important role in deciding the absorption edge. In the present system due to addition of alumina there is a progressive increase in NBO (P–O–Al) leading to a decrease in optical gap up to 15 mol%. Above this concentration of alumina due to dominance of Al(4) coordination, the optical gap shows an increasing trend.

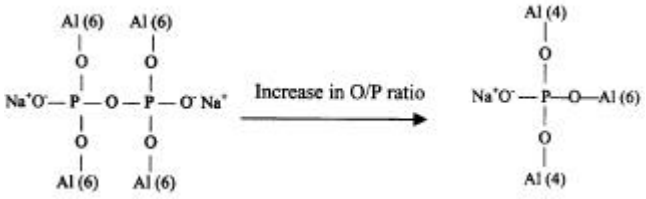

Figure 5. Schematic of NAP structure showing the change in Al coordination number with increase in O/P ratio.

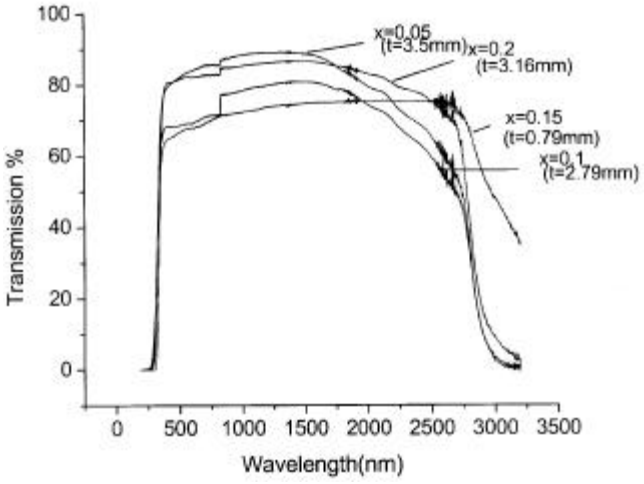

Figure 6. Transmission characteristics of different glass samples having compositions of $xAl_2O_3(1 - x)NaPO_3$.

Table 1. Density, molar volume, glass transition temperature, microhardness, thermal expansion coefficient and optical gap for different NAP glass samples.

Composition (nominal) Na_2O–Al_2O_3–P_2O_5 (mol%)	Density ± 0·03 (g/cm^3)	V_M (cm^3)	T_g (± 3°C)	MH (kg/mm^2)	TEC 10^{-7}/°C (30–300°C)	E_{opt} (eV)	O/P ratio
47·5–5–47·5	2·49	40·96	300	255	224·79	3·45	3·15
45–10–45	2·61	39·09	383	342	221·98	3·32	3·33
42·5–15–42·5	2·69	37·89	445	422	212·41	3·13	3·52
41·25–17·5–41·25	2·57	39·71	–	373	203·35	–	3·63
40–20–40	2·52	40·46	405	350	173·29	3·51	3·75

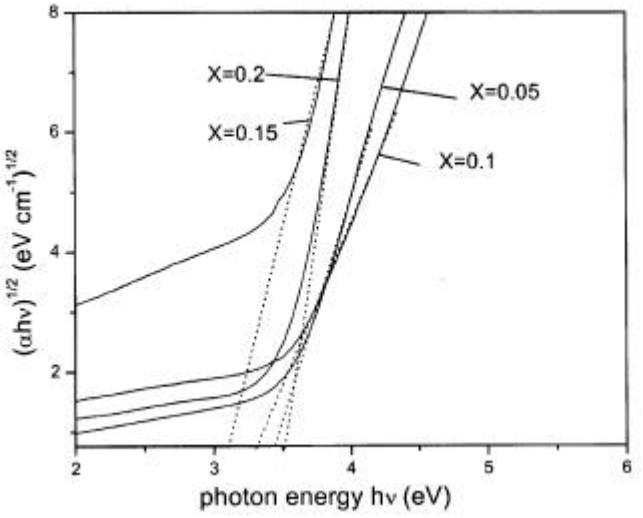

Figure 7. Plots of $(ahn)^{1/2}$ as a function of photon energy (hn) for different glass samples.

Infrared transmission characteristics of NAP samples with different Al_2O_3 contents are shown in figure 8. It is observed that symmetric and anti-symmetric stretching vibrations of PO_2 groups (around 1100 cm^{-1} and 1280 cm^{-1}, respectively) reduce with the addition of alumina. These frequencies are characteristics of PO_2 groups in chain phosphates (equivalent to Q^2 sites for ^{31}P NMR). It was pointed out by Montagne *et al* (1997) that the absorption bands around 1200 and 1115 cm^{-1} sample are assigned to antisymmetric stretching of PO_3 groups (chain end groups equivalent to Q^1 sites). The bands around 1115 cm^{-1} are attributed to PO_3 groups with less aluminium neighbours than those vibrating at 1200 cm^{-1} (Q_2^1, where 1 is BO per PO_4 tetrahedron, and 2 is aluminium neighbours) because of lowering of P–O bond constant due to lower frequency of 1115 cm^{-1} band compared to 1200 cm^{-1} band and the non bridging oxygens of PO_3 groups are bonded to cation (Na^+ or Al^{3+}) via a more ionic bond than those associated with 1200 cm^{-1} band. The bands at around 760 and 730 cm^{-1} are due to symmetric stretching of P–O–P bridges.

When the Al content increases the 1280 cm^{-1} band disappears progressively and 1200 cm^{-1} band intensity increases indicating that depolymerization (decreasing average chain length) occurs and Q^2 sites are replaced by chain end groups, Q^1 sites. The frequency of P–O–P shifts from 886 cm^{-1} to 921 cm^{-1} which is the characteristic of transition from chains to pyrophosphates. The increase of 1200 cm^{-1} band intensity compared to 1115 cm^{-1} shows that decondensation first occurs with formation of Q^1 sites bonded to 1 Al^{3+} (Q_1^1) and then to 2 Al^{3+}(Q_2^1). The weak absorption band around 745 cm^{-1} in $x = 0{\cdot}2$ sample is attributed to more Al neighbours having mixed structural units (Q^2, Q^1). The changes in the structural units have been confirmed by ^{27}Al, ^{31}P MAS NMR spectra, which are being reported elsewhere.

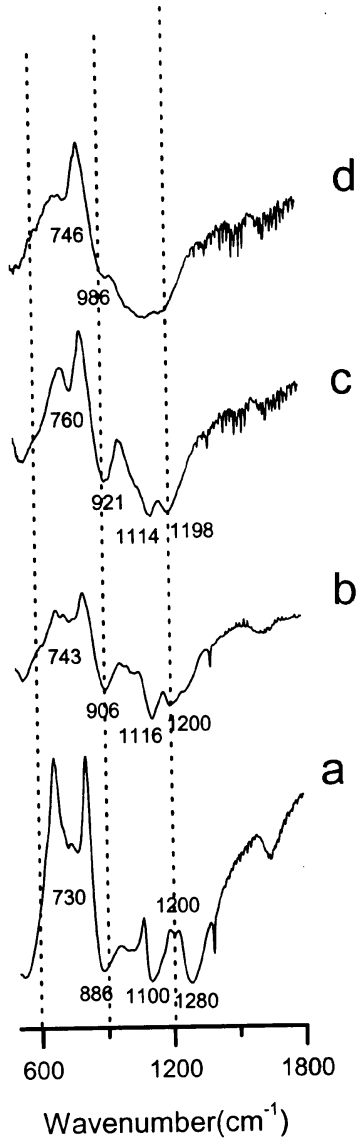

Figure 8. Infrared spectra of different glass samples having composition of $xAl_2O_3(1-x)NaPO_3$: a. $x = 5$, b. $x = 10$, c. $x = 15$, and d. $x = 20$ mol%.

4. Conclusions

Small size bubble free sodium aluminophosphate glasses with different compositions, $xAl_2O_3(1-x)NaPO_3$ ($x = 0{\cdot}05$–$0{\cdot}20$), have been prepared. A pronounced effect on the composition dependence behaviour in density, glass transition temperature, microhardness, TEC and optical gap was seen for O/P ratio ≥ 3·5. This is due to change in Al-coordination number from six to four with increase in alumina content beyond 15 mol%. In view of the lower values of microhardness and higher TEC of these glasses compared to silicate glasses we are exploring the possibility to prepare glass to metal seals with metals like copper.

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