Journal of Thermal Analysis and Calorimetry, Vol. 89 (2007) 1, 153–157

EFFECT OF Na_2O/K_2O SUBSTITUTION ON THERMOPHYSICAL PROPERTIES OF PbO BASED PHOSPHATE GLASSES

K. V. Shah, M. Goswami, D. K. Aswal, V. K. Shrikhande, S. K. Gupta and G. P. Kothiyal[*]

Technical Physics and Prototype Engineering Division, Bhabha Atomic Research Center, Mumbai 400 085, India

PbO based phosphate glasses having composition $40P_2O_5{\cdot}12Al_2O_3{\cdot}6B_2O_3{\cdot}9PbO{\cdot}xNa_2O{\cdot}(33–x)K_2O$ (x=0–33) [F=Na/(Na+K)] have been prepared using conventional melt quench technique. Density, morphology, thermal expansion coefficient (α) and glass transition temperature (T_g) were studied as a function of Na/(Na+K) ratio. Formation of transparent, bubble free and clear glass was observed up to x=18 mol%. Density was found to vary from 2.70 to 3.69 g cm^{-3}. The significant changes were noticed in external morphologies at temperatures corresponding to softening, half ball and melting points under high temperature microscope for three compositions (x=0, 10 and 15 mol%). These glasses recorded the softening and half ball temperatures in the range 454–470°C and 523–576°C respectively and melting temperatures agree well with DTA studies within the experimental limits. Glass transition temperature showed a broad maxima while thermal expansion coefficient (TEC) a broad minima around Na/(Na+K)=0.54. This behaviour is explained on the basis of bond formation/phase separation.

Keywords: *glass transition, high temperature microscopy, phosphate glasses, thermal expansion coefficient*

Introduction

Phosphate glasses have been the subject of recent investigations because of their important applications such as bone transplantation [1], glass-to-metal seals (GM), [2, 3], containment of radioactive wastes [4], fast ion conductors [5], laser host materials [6], solid-state batteries [7], etc. The structure of phosphate glass is formed by PO_4 tetrahedra connected by corners. They have comparatively high transmission in the ultraviolet region compared to silicate and borate glasses. They also have low glass transition and melting temperatures compared to silicate glasses.

For achieving desired characteristics for an application the properties of materials are tailored with careful combination of modifiers such as alkali oxides or rare earth oxides in the glass network. High quality Na phosphate glasses with a concentration of Gd as high as possible are prepared for exhibiting maximum radio-luminescence intensity [8]. Various properties of sodium aluminophosphate glasses depend on O/P ratio and the significant changes take place above the pyrophosphate limit at O/P=3.5 [9]. Associated with the property changes, there is a change in the aluminium co-ordination from six to four for O/P>3.5. Al_2O_3, in tetrahedral co-ordination improves the chemical durability of the glass by cross-linking the phosphate chains. B_2O_3, like Al_2O_3 in tetrahedral co-ordination also behaves as a network former and helps in improving the durability of the glass. PbO is known to play a dual role both as a network modifier [10] and as a network former [11]. Lead when increased up to 40 mol% increases the glass transition temperature close to 400°C in the sodium phosphate glass [12]. It acts like a modifier as well as network former in phosphate glass when P_2O_5 content is more than 50 mol% [12].

Normally a single alkali glass system behaves in a linear manner with additivity. However, many physical properties measured in mixed alkali systems show non-linear growth and subsequent reversal in trends leading to maxima or minima as a function of modifier fraction [13]. This phenomenon is known as mixed alkali effect and therefore there exists both technological and theoretical interests in studying the physics and chemistry of mixed alkali glasses. Among various sodium aluminum phosphate glasses, $40P_2O_5{\cdot}12Al_2O_3{\cdot}6B_2O_3{\cdot}9PbO{\cdot}xNa_2O{\cdot}(33–x)K_2O$ series is a potential glass for making glass-to-metal seals at relatively lower temperatures with Cu–Be alloys, Al-alloys, etc. and are quite durable. In the design of glass-to-metal seals, among other parameters, thermal expansion, softening point, wettability, viscosity, etc. are important parameters. Since the real intimate contact of glass with metal begins at the melting point, the high temperature microscopy helps in understanding the melt behaviour at the interface. To the best of our knowledge, this is the first reported data on these glasses.

---

[*] Author for correspondence: gpkoth@apsara.barc.ernet.in

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

In this communication we report on the preparation of $40P_2O_5\cdot12Al_2O_3\cdot6B_2O_3\cdot9PbO\cdot xNa_2O\cdot(33-x)K_2O$ (x=0–33 mol%) glasses and effect on Na/(Na+K) ratio on some physical parameters such as density, morphology, T_g and TEC. We have also studied the macroscopic changes at softening, half ball and melting points using a high temperature microscope for three selected compositions. Melting temperatures as observed on high temperature microscope match with those obtained from DTA measurements. Glass transition temperature increases giving a broad maxima around F=Na/(Na+K)= 0.54 whereas TEC shows initial decrease and then increase with increase in Na_2O content with minima around F=0.54.

Experimental

Glass preparation

Glasses were prepared by conventional melt-quench technique following the procedure reported earlier [14]. Glasses with compositions $40P_2O_5\cdot12Al_2O_3\cdot6B_2O_3\cdot9PbO\cdot xNa_2O\cdot(33-x)K_2O$, $0\leq x\leq33$, were prepared. Analytical grade compounds of $NaNO_3$, KNO_3, Al_2O_3, B_2O_3, PbO and $NH_4H_2PO_4$ were used as starting materials. Na_2O content was varied from 0 to 33 mol% [Na/(Na+K)=0–1] keeping the O/P ratio=3.7 constant. The initial charge (30–40 g) was thoroughly mixed and ground for 30–40 min in a planetary ball mill and then calcined in an alumina crucible for 18–20 h by heating in a programmed manner considering the decomposition temperatures of individual compounds. Accordingly the heating schedule followed was as follows: heating rate of 15°C h^{-1} and dwell time of 15 h each at 200, 330 and 410°C and cooling rate of 90°C h^{-1} up to room temperature. This charge was reground and calcined again for 4 h. The calcined charge was then melted using lowering and raising furnace (Model OKAY 70R 10, M/s Bysakh and Co., Kolkata) and held for 2 h for thorough mixing in a platinum crucible in air ambient at temperatures ranging from 825–1300°C depending on the composition. The temperature more than 1000°C was used only for compositions $\geq x$=20 mol%. 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. It may be noted that with increase in Na_2O content pouring temperature also increased indicating increase in viscosity. The glass was then annealed at appropriate temperatures (between 350 and 400°C) for 3 h and stored in a desiccator prior to evaluation.

Instrumental methods

Powder XRD patterns of the glasses were recorded on JEOL 3080 Diffractometer using CuK_α radiation to ascertain the glassy nature of the samples. Density (ρ) of bubble free glass samples was measured at room temperature using Archimedes principle with an accuracy of ±0.03 g cc^{-1} in toluene.

High temperature optical microscopy is a powerful characterization technique in broad areas of materials science and engineering [15]. The physical and chemical phenomena occurring in materials at high temperatures can be observed in situ with the aid of heating devices attached or surrounding the stage of a microscope [16]. This heating device provides the necessary temperature and thermal environment during the observation of the specimen. The change in the surface morphology of the sample during heating is an interesting observation, which can be made by such a hot stage microscopy setup. Thus, the process investigated resembles the real situation of sintering or melting of glass samples. Moreover, the parameters of interest in these investigations are macroscopic dimensions and shape of the glass samples are in the range of hundreds of microns to millimeters, so the microscopes of relatively low magnification are required (of the order of 5X). Application areas of such hot stage microscopy include determination of fusion, transition temperatures of different substances, softening of glasses, chemical reactions at elevated temperatures, etc. [17]. The external change in the morphology of the glass while heating was observed with BX60M Olympus optical microscope associated with hot stage. The experimental setup incorporates a CCD camera and a self-developed software package (GLPL), which supports sample image analysis, tracing protocol and evaluation of the temperature dependent sample image. Hot stage consists of a platinum resistor of resistance 0.4 ohms and the temperature is raised by passing a small current through an externally connected Eurotherm temperature controller circuit with an accuracy of control temperature ±0.1°C. Glass samples of ~2–3 mg were placed on a thin sapphire disc and securely placed inside the hot stage ceramic cup, then were heated at β=5 K min^{-1} and cooled at 20 K min^{-1}. The hot stage setup was calibrated using high purity indium and aluminum. It was found that the observed melting temperature deviated with 3–4°C from the literature value. The temperature is monitored by another CCD camera. Both the cameras supported by the software allowing us to collect simultaneously the images on the sample and the corresponding temperature.

TG-DTA system (Setaram 92-18 model) was employed for recording glass transition, crystallization and melting temperatures of the glass samples.

The instrument was calibrated using high purity indium and zinc. The experiment was performed with ~30 mg finely powdered and sieved glass powder taken in a platinum crucible under continuous argon purging. The TG-DTA curve was recorded over a temperature range of 30 to 700°C at heating rate of 10 K min^{-1}.

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 K min^{-1} for all measurements. The size of the sample was about 1–3 mm thick with 10 mm diameter, besides both ends were 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^{-1}. The temperature was varied in the range of 30–450°C for measurement of TEC. The expansion coefficient being reported is the average in the temperature range of 30–300°C.

Results and discussion

Bubble free and clear glass samples were obtained up to Na fraction F=0.54 and above this the glasses were found to be milky and opaque in appearance if poured at temperature below 1000°C. Density was found to vary from 2.703 to 3.69 g cc^{-1} as recorded in Table 1. Figure 1 shows the XRD plots of as prepared glass samples. XRD patterns confirm the glassy nature of the samples with broad peaks around 20–30° (2θ values). Opalescent glass formation for higher sodium oxide content i.e. for x≥20 mol% was observed, which seems to be due to lower pouring temperature used ≤(1000°C). However, the glass obtained for x=33 mol% was not so homogeneous, even when poured at 1200°C. The opacity in lead based phosphate glass has been reported to be due to many reasons such as presence of minute glass droplets, undissolved constituents, fine gas bubbles, etc. [18]. In the present case we feel the opacity might be due to the combined effect of both, phase separation and devitrification as confirmed by XRD patterns.

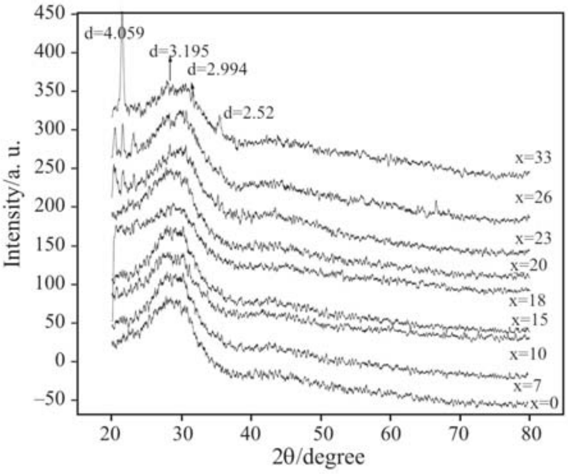

Fig. 1 XRD plots of $40P_2O_5·12Al_2O_3·6B_2O_3·9PbO·xNa_2O·(33–x)K_2O$ series of glasses

The ‘d’ values along with 2θ for higher Na_2O content (x≥20 mol%) correspond to the formation of $AlPO_4$ [ASTM card index=CAS#: 7784-30-7]. The glasses with x≥20 mol% when poured at the temperatures 1250–1300°C, turned out to be clear. However, some loss of P_2O_5 is expected at such higher temperatures.

Figure 2 shows images at softening, half ball and flow points of the above-mentioned samples. The corresponding temperatures are given in Table 2. Softening temperature increased from 454–470°C whereas the melting temperature increased from 665–680°C as sodium oxide content was varied from 0–15 mol%. Half ball points were recorded in the temperature range 523–576°C. The present glass system has low melting temperatures; hence the shrinkage points become difficult for observation under hot stage optical microscope. However, the softening and half ball-points were determined within an acceptable level of error. The melting points of these glasses agree with the melting points obtained from DTA. It was quite interesting to see the melting patterns of the glass at the melting stage. This type of information is quite

Table 1 Some physical properties of different glass samples. T_g obtained from DTA is given in the bracket

Comp. x/mol%	F=Na/(Na+K)	Density/g cm^{-3}	T_g(±3)/°C	TEC/·10^{-7} K^{-1}
0	0	2.70	387 (380)	186
7	0.212	2.78	398	156
10	0.3	2.98	412 (390)	154
15	0.45	3.03	410 (395)	142
18	0.54	3.37	400	140
20	0.606	3.35	413	167
23	0.69	3.66	390	185
26	0.78	3.69	370	182

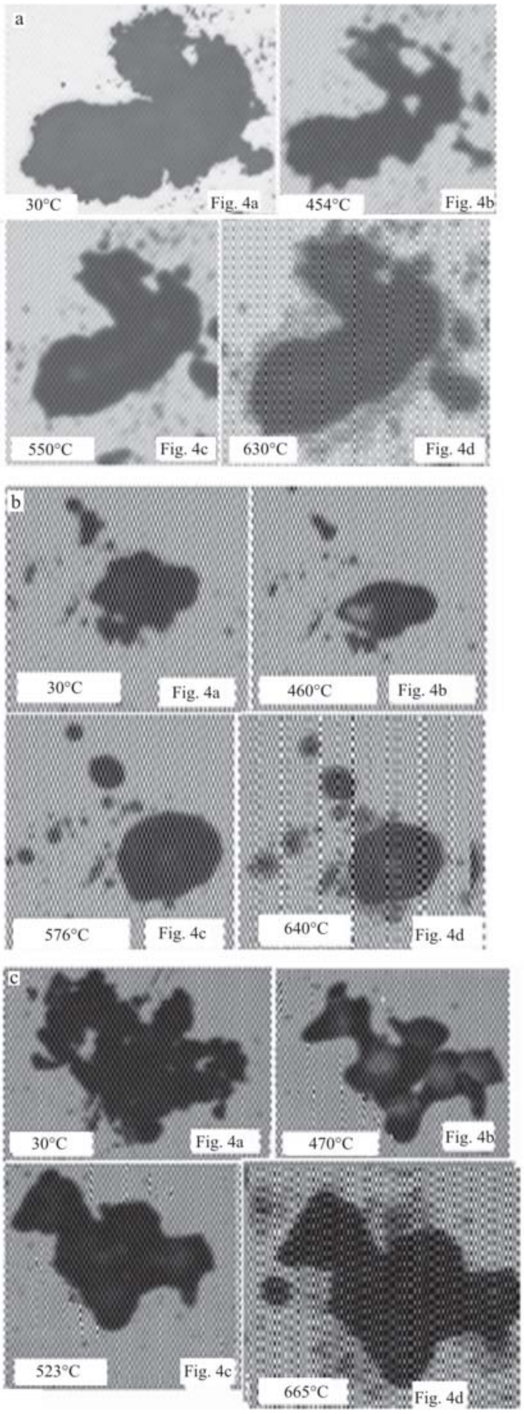

Fig. 2 Photographs obtained from high temperature optical microscope for the above glass samples; a – x=0, b – x=10 and c – x=15 mol%

Table 2 Softening, half ball and melting temperatures recorded from high temperature microscope. Melting temperatures as measured by DTA studies is given in bracket

Sample	x	$T_{\text{softening}}$/°C	$T_{\text{half ball}}$/°C	T_{melting}/°C
PH-03-01	15	470	523	665 (–)
PH-03-2	10	460	576	640 (620)
PH-03-3	0	454	550	630 (613)

important in deciding about the intimate contact with metal for fabrication of seal. As the dwell time and glass melting temperatures are vital for controlled interdiffusion at the interface these results are of lot of significance to us for seal fabrication.

Figure 3 shows the DTA data for three different samples namely x=0, 10 and 15 mol%. The endothermic baseline shifts give the glass transition temperatures, the sharp exothermic peaks show the crystallization temperatures whereas the weak endothermic peaks indicate the melting or flow points in the DTA results of these three samples. The samples show glass transition temperatures in the range 380–395°C, crystallization in the range 525–541°C and melting in the range 613–665°C. T_g values are given in Table 1. The glass transition temperatures determined from TMA differ within ±5% of T_g obtained from DTA. DTA measurements on x=0 sample shows a broad crystallization peak whereas sharper crystallization peaks are obtained for higher x values. Broader crystallization peaks imply surface crystallization and sharper peaks the bulk crystallization [18]. As the glass powder is finely ground and sieved, the particle size is assumed to be constant. Also, the crystallization peak temperature shifts towards the lower temperatures thereby increasing the possibility of devitrification at higher Na_2O contents.

Figure 4 shows the variation of glass transition temperature and TEC with Na/(Na +K) ratio. The values of T_g and TEC are given in Table 1. As mentioned earlier, the properties of phosphate glasses are influenced greatly on the O/P ratio. In the present series we have fixed the O/P ratio to 3.7 (intermediate between pyrophosphate and orthophosphate structure). The content of the constituents such as P_2O_5, PbO, Al_2O_3, B_2O_3 and total alkali are kept constant. We have investigated the dependence of physical properties as a function of relative content of Na_2O and K_2O and we expect the structural variations at the microscopic

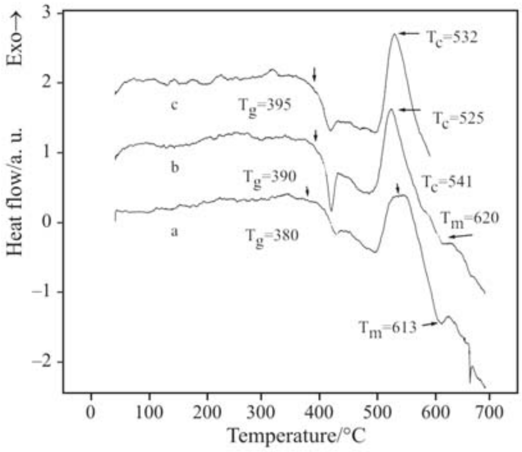

Fig. 3 DTA results for the following samples; a – x=0, b – x=10 and c – x=15 mol%

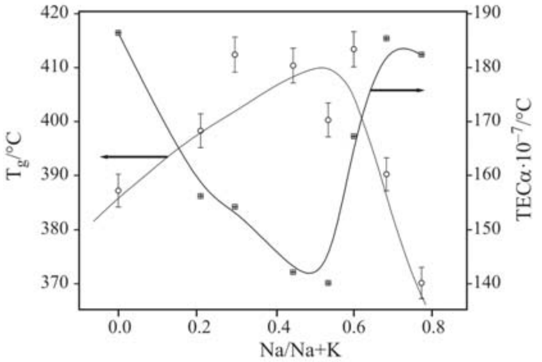

Fig. 4 Dependence of glass transition temperature (T_g) and TEC on Na/(Na+K) ratio

level to arise from their different ionic radii (ionic radius of Na^+<ionic radius of K^+). Glass transition temperature was found to increase with Na_2O content giving a broad maxima around F=0.54 whereas TEC shows initial decrease and then increase with increase in Na_2O content with minima around F=0.54. When Na_2O is added, Na^+ ions would replace the K^+ sites forming stronger P–O–Na^+ bonds. Since the ionic radius of Na^+<K^+ ion and the field strength of Na^+>K^+, thus increasing the Na_2O content increases the overall strength of the phosphate glass network through the formation of stronger P–O–Na^+ bonds resulting in some increase of viscosity. Formation of stronger bonds (i.e. making structure somewhat more rigid) leads to increase in T_g and decrease in TEC. It appears that at higher Na_2O content i.e. F>0.54 the viscosity increases significantly so as to enhance the possibility of phase separation through the formation of polycrystalline $AlPO_4$. This effect of phase separation/devitrification seems to weaken the bonding thereby decreasing T_g and increasing TEC.

Conclusions

Bubble free glasses were obtained for $40P_2O_5\cdot12Al_2O_3\cdot6B_2O_3\cdot9PbO\cdot xNa_2O\cdot(33-x)K_2O$, glasses up to x=18 mol% only. Above x=18 mol% the glasses turned out to be opaque if poured at lower temperatures ≤1000°C possibly due to some phase separation or devitrification. Formation of $AlPO_4$ phase [ASTM card index=CAS#: 7784-30-7] is identified from XRD at higher Na_2O content (x>20 mol%). These glasses show low T_g and higher TEC ($142–186\cdot10^{-7}$ K^{-1}). The results also indicate that low Na_2O content glass may be suitable for GM seal with Cu–Be alloys. For the three glass compositions (i.e. x=0, 10, 15 mol%) the values of softening and half ball temperatures are in the temperature range 454–470 and 523–576°C, respectively. Melting temperatures as observed on high temperature microscope were found to be matching with those of DTA studies within acceptable limits. This type of information is quite important for deciding intimate contact with metal and the dwell time for fabrication of seal, which in turn controls the inter-diffusion at the interface.

Acknowledgements

The authors would like to thank Drs V. C. Sahni and J. V. Yakhmi for their constant support and encouragement to this work. The authors would also like to thank Mr. Nilesh Kulkarni and Mr. R. K. Mishra for XRD and DTA measurements. Technical assistance of Smt A. S. Patil, Shri Arjun Sarkar and Shri P. A. Wagh is gratefully acknowledged. One of the authors (KVS) would like to thank DAE for giving him fellowship.

References

1 J. M. Oliveira, R. N. Correia and M. H. Fernandes, J. Non-Cryst. Solids, 273 (2000) 59.
2 R. K. Brow and D. R. Tallant, J. Non-Cryst. Solids, 222 (1997) 396.
3 Y. B. Peng and D. E. Day, Glass Technol., 32 (1991) 166.
4 B. C. Sales and L. A. Boatner, J. Non-Cryst. Solids, 79 (1986) 83.
5 J. Kincs and S. W. Martin, Phys. Rev. Lett., 76 (1996) 70.
6 M. Boudubala, H. Mohmoh, M. Bahtat, M. Ouchetto, M. Druetta and B. Elouadi, J. Non-Cryst. Solids, 259 (1999) 23.
7 F. Branda, A. Constantini, R. Fresa and A. Buri, Phys. Chem. Glasses, 36 (1995) 272.
8 K. Nitsch, A. Cihlar, D. Klimm, M. Nikl and M. Rodova, J. Therm. Anal. Cal., 80 (2005) 735.
9 K. V. Shah, V. Sudarsan, M. Goswami, A. Sarkar, S. Manikandan, R. Kumar, B. I. Sharma, V. K. Shrikhande and G. P. Kothiyal, Bull. Mater. Sci., 26 (2003) 715.
10 U. Selvaraj and K. Rao, J. Non-Cryst. Solids, 104 (1988) 300.
11 M. Abid, M. Et-Tabirou and M. Taibi, Mater. Sci. Eng. B, 97 (2003) 20.
12 Y. Dimitriev and V. Dimitrov, J. Non-Cryst. Solids, 122 (1990) 133.
13 D. E. Day, J. Non-Cryst. Solids, 21 (1976) 343.
14 K. V. Shah, M. Goswami, R. Kumar, S. Manikandan, V. K. Shrikhande and G. P. Kothiyal, Phys. Chem. Glasses, 46 (2005) 274.
15 M. J. Pascual, L. Pascual and A. Duran, Phys. Chem. Glasses, 42 (2001) 61.
16 W. Radmacher, Brensstoff-Chemie, 30 (1949) 377.
17 B. Boccaccini and B. Hamann, J. Mater. Sci., 34 (1999) 5419.
18 J. Edward, G. Grayson and M. Grayson, Topics in Phosphorus Chemistry, 9 (1977) 309.

Received: January 26, 2006
Accepted: February 3, 2006
OnlineFirst: August 11, 2006

DOI: 10.1007/s10973-006-7517-2