Characterization and structural studies of lithium doped lead zinc phosphate glass system

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ABSTRACT

Glasses in the system $(PbO)_{30}(P_2O_5)_{40}(ZnO)_{30-x}(Li_2O)_x$ (where $x = 0$, 15, 20, 25, 30 mol%) and $(PbO)_{30}(P_2O_5)_{50}(ZnO)_{20-x}(Li_2O)_x$ (where $x = 0$, 5, 10, 15, 20 mol%) were prepared by conventional melt quenching technique. XRD and DSC measurements were performed to confirm their amorphous nature. Thermal stability factor (S) has been evaluated using the values of T_g and T_c. The refractive indices of these glasses lie in the range of 1.40–1.45. IR spectra of these glasses show absorption peaks in the range 1233–1247 cm^{-1}, 1076–1087 cm^{-1}, 905–894 cm^{-1}, 735–731 cm^{-1} and 531–556 cm^{-1} corresponding to P=O, P—O$^-$, (P—O—P)$_{AS}$, (P—O—P)$_S$ and O—P—O vibrations respectively. The peak corresponding to P=O, shows red shift with increasing Li$_2$O content indicating depolymerization of phosphate network.

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1. Introduction

Recently, phosphate glasses have been extensively investigated due to their transparency in a wide spectral range from UV to IR, which makes them suitable for the fabrication of optical fibers, detection, sensing and laser technologies (laser host glasses). Further, phosphate glasses have their unique characteristics that include; low melting point, high thermal stability, high gain density, low refractive index and low dispersive power [1–7]. Phosphate glasses formed with heavy metal oxides such as lead, zinc and bismuth have varieties of applications [8]. For example, alkali aluminophosphate compositions have glass transition temperatures below 400 °C and thermal expansion coefficient values greater than 150×10^{-7} °C^{-1}. Thus, these glasses offer a greater advantage in many applications, such as hermetic sealing technology [9,10]. Zinc phosphate compositions are chemically durable, have processing temperatures under 400 °C and can be co-formed with high temperature polymers to produce unusual organic/inorganic composites [11]. The chemical durability and low processing temperature of iron phosphate glasses have been used for nuclear waste

hosts [12]. Biocompatible phosphate glasses and glass-ceramics have also medical applications [13]. Amorphous lithium phosphate and phosphorus oxynitride glasses have fast ion conductivity [14,15]. Thus, these glasses are potential candidate for solid state electrolytes.

The basic building blocks of crystalline and amorphous phosphates are the P-tetrahedra that result from the formation of sp^3 hybrid orbitals by the p outer electrons ($3s^2 3p^3$) [16]. The fifth electron is promoted to a 3d orbital where strong π-bonding molecular orbitals are formed with oxygen 2p electrons [17,18]. These tetrahedra link through covalent bridging oxygens to form various phosphate anions. The tetrahedra are classified using the Q^i terminology [19], where 'i' represents the number of bridging oxygens per tetrahedron. The networks of phosphate glasses can be classified by the oxygen-to-phosphorus ratio, which sets the number of tetrahedral linkages, through bridging oxygens between neighboring P-tetrahedra [20]. Vitreous P$_2$O$_5$ is one of the prototypical 'random network' glass formers [21]. Recent neutron diffraction studies confirm that Q^3 P-tetrahedra are the basic building blocks of v-P$_2$O$_5$. Long-range information about how the Q^3 tetrahedra are linked can also be obtained from diffraction studies [22]. These tetrahedra are linked to form a three-dimensional network being similar to the structure of P$_4$O$_{10}$ molecules found in crystalline H-P$_2$O$_5$. However, there seem to be uncertainties as to the details of such large range ordering. The density of v-P$_2$O$_5$ is intermediate to

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those of the H- and O-forms of crystalline P_2O_5 indicating that the glass under study likely contains long-range structural similarities to both forms. The addition of a modifying oxide to v-P_2O_5 results in the creation of non-bridging oxygens at the expense of bridging oxygens.

The reactivity of Q^3 sites to water limits the technological usefulness of ultraphosphate glasses even though they possess UV edges at wavelengths shorter than those found for silicate glasses [23]. An interesting feature of zinc-phosphate glass is that the addition of an alkali oxide (replacing ZnO) increases its aqueous corrosion resistance [24]. On the other hand lithium ion conducting glasses have enormous potential for utilization in electrochemical devices, such as solid-state batteries, sensors, electrochemical capacitors, electro-chromic displays and analog memory devices [25]. Depolymerization is known to occur in phosphate glasses with the addition of alkali oxides, alkaline earth oxides and many other divalent metal oxides, such as ZnO and PbO [26].

In this paper, we report the characterization and structural studies of the $(PbO)_{30}(P_2O_5)_{40}(ZnO)_{30-x}(Li_2O)_x$ and $(PbO)_{30}(P_2O_5)_{50}(ZnO)_{20-x}(Li_2O)_x$ glasses. Analysis of DSC and refractive index studies indicate that inter-substitution of Li_2O and ZnO show Li^{2+} ions act like a conventional glass modifier, while Zn^{2+} ions have the tendency of network former.

2. Experimental

The glasses with compositions $(PbO)_{30}(P_2O_5)_{40}(ZnO)_{30-x}(Li_2O)_x$ (where $x = 0$, 15, 20, 25, 30 mol%) (L series) and $(PbO)_{30}(P_2O_5)_{50}(ZnO)_{20-x}(Li_2O)_x$ (where $x = 0$, 5, 10, 15, 20 mol%) (Z series) were chosen for the studies. Analytical grade compounds of PbO, $NH_4H_2PO_4$, ZnO and Li_2CO_3 were used as starting materials. All these chemicals were screened into fine powder in a ceramic mortar and pestle. The homogeneously mixed powder was then heated up to $1000\,°C$ in a porcelain crucible for 30 min. The melt was constantly stirred for homogeneous mixing and then quickly poured on a brass block kept at $250\,°C$, and then pressed with a flat brass disc to get flat glass pieces of thickness about 0.1 cm. The samples were then polished before use. XRD measurements were carried out by Philips diffractometer with Ni filter and Cu Kα radiation. DSC measurements were carried out by Mettler Toledo DSC Star^e System. The IR spectra of the glasses were recorded at room temperature using PERKIN ELMER Spectrum GX. The refractive index of glass samples has been measured using Portable Jewel Refractometer, Chlight Corporation China (Model CL – 1.30–1.80) source of radiation of sodium D-Line (589 nm).

3. Results and discussion

3.1. XRD and DSC

X-ray diffractogram (XRD) of PbO—P_2O_5—ZnO—Li_2O glass is shown in Fig. 1. It can be seen from the figure that there are no sharp peaks which indicates the amorphous nature of the glass. The variation of glass transition temperature (T_g) and stability factor in L-series and Z-series of glasses are given in Figs. 2 and 3. Generally, the difference between crystallization temperature (T_c) and transition temperature (T_g), gives a measure of stability of a supercooled liquid (glass) i.e., stability factor S. The larger value of S, the stronger is the inhibition to nucleation and crystallization processes, and consequently, the better thermal stability of supercooled liquids (glass) [27]. As can be seen in Fig. 2 that, in general, T_g decreases with an increase in Li_2O content. However, it may be noted that with an addition of Li_2O content, T_g steeply decreases from $348\,°C$ to $287\,°C$ and further addition of the Li_2O content decrease in T_g is marginal. Whereas, in the case of Z-series of glasses, with the
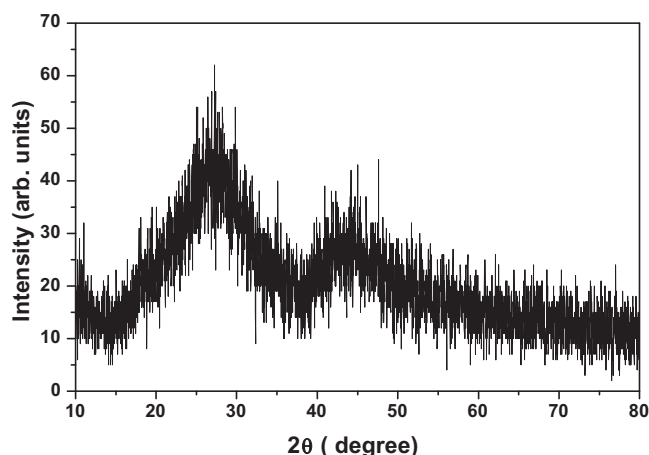

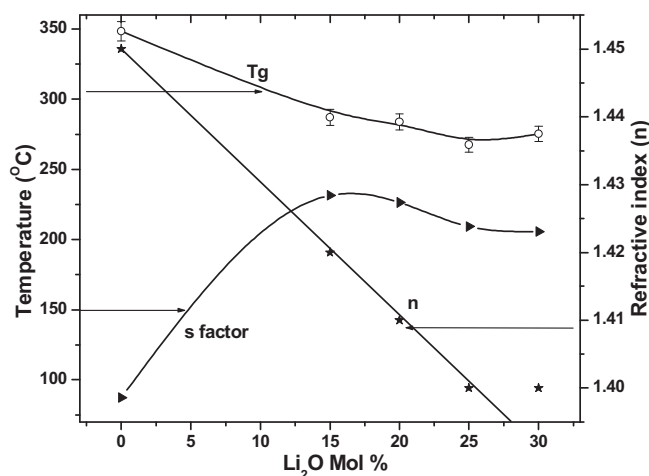**Fig. 1.** A typical XRD pattern of a glass.

Fig. 2. Glass transition temperature, thermal stability factor and refractive index v/s mol% of Li_2O contents for L-series.

increase in ZnO concentration the variation of T_g is insensitive up to 15 mol%. Then, there is steep increase in T_g when ZnO is 20 mol%. This observation indicates that the structural rearrangement of the phosphate glass network has been modified. It is well known that the addition of Li_2O shortens the phosphate chains by disrupting
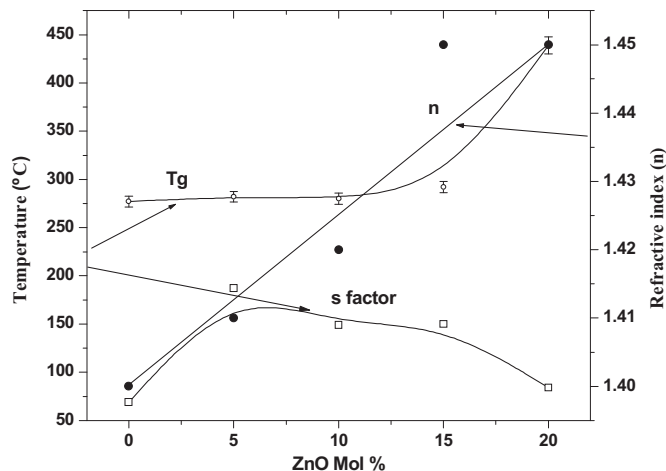

Fig. 3. Glass transition temperature, thermal stability factor and refractive index v/s mol% of ZnO contents for Z-series.
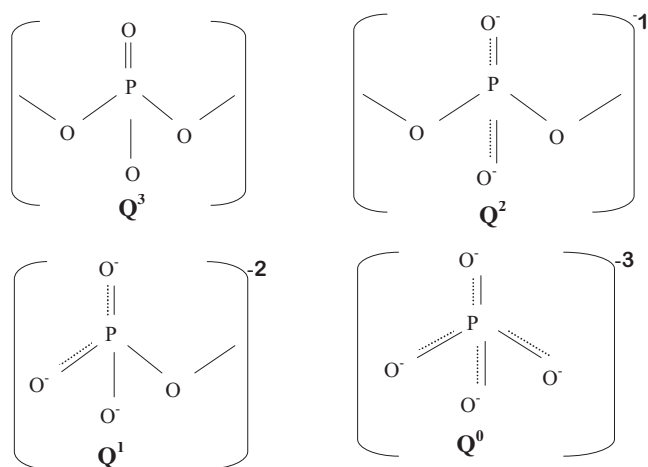
Fig. 4. Phosphate tetrahedral sites that can exist in phosphate glass system.

Table 1
Glass sample code and concentration of Q_3 and Q_2.

Sample code	[POO$_{3/2}$] group	[POO$_{2/2}$]$^-$ group
L1	80	0
L2	65	15
L3	60	20
L4	55	25
L5	50	30
Z1	80	20
Z2	85	15
Z3	90	10
Z4	95	5
Z5	100	0

the P—O—P bond and forms ionic cross-bonding between the broken chains and thus, creating non-bridging oxygens [28]. This reduces the connectivity of the network, and leads to a low glass transition temperature. Fig. 4 shows the different kind of polyhedra in phosphate glasses. In Table 1 we have shown the $Q^3 = [POO_{3/2}]$ concentration at 0 mol% Li_2O which is 100 and Q^2 concentration is zero. As the concentration of Li_2O content increases from 0 to 30 mol% one may note that the concentration of Q^2 species also increases (see Table 1) leading to an increase of non-bridging oxygens. In Z-series of glasses, with the increase in ZnO one may note that the concentration of Q^2 decreases. This indicates that the oxygen supplied by ZnO is not been utilized for the conversion of $Q^3 \rightarrow Q^2$. Therefore, in the case of Z-series of glasses, the structural role of ZnO appears to be a glass former. The field strength of Zn^{2+}
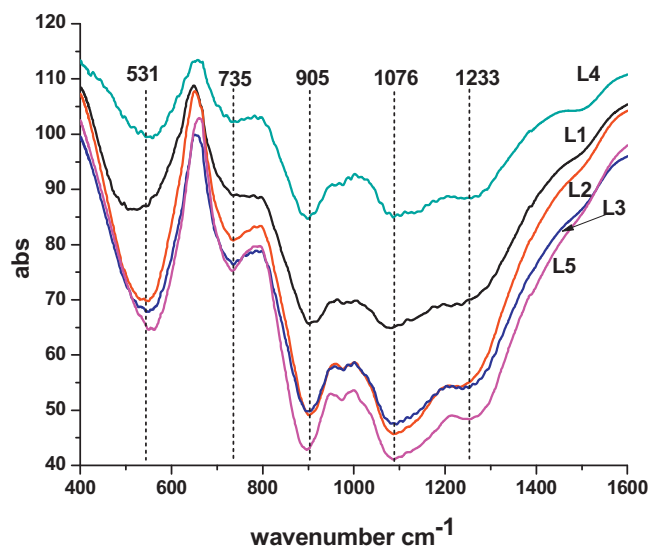

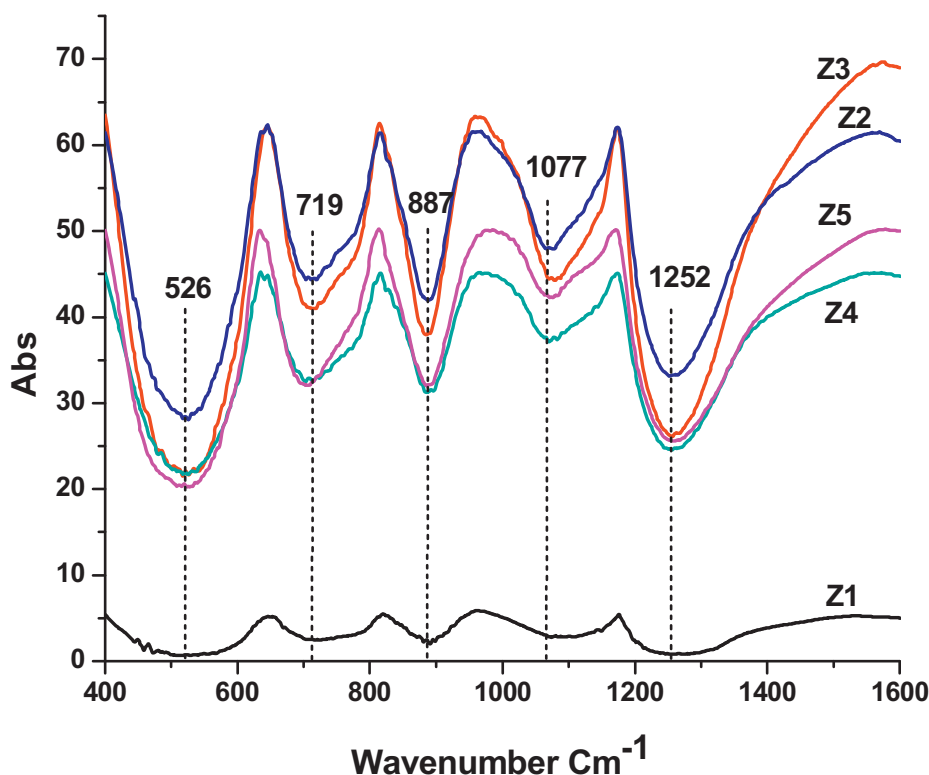**Fig. 5.** IR spectra of L-series glass system.

Fig. 6. IR spectra of Z-series glass system.

ion i.e., e/r is approximately 2.77 therefore, it likely acts as a former. And hence, one would expect that T_g is insensitive to ZnO content.

3.2. Refractive index

The values of refractive index (RI) lie in the range of 1.40–1.45, and are comparable with values reported in the literature on phosphate glasses [29]. Figs. 2 and 3 indicate the variation of refractive index with Li$_2$O and ZnO contents. As can be seen from the figures, the variation of refractive index with Li$_2$O/ZnO content is interestingly similar as that observed in the variation of T_g. It is evident that inter-substitution of ZnO to Li$_2$O has the similar consequence on the phosphate network as discussed in Section 3.1. The values of RI decrease with increase in Li$_2$O content because of the depolymarization of the phosphate network leading to creation of non-bridging oxygen. The process of creation of non-bridging oxygen causes easy vibrational oscillations in the network. An increase in RI with the increase in ZnO content (Fig. 3) is due to high polarizability of the Zn^{2+} ion. It is well known fact that the addition of highly polarizable ions such as Pb^{2+} or Zn^{2+} retards the light propagation through the phosphate network. Thus, this leads to an increase in the refractive index [30]. We may also note that the concentration of non-bridging oxygens (see Table 1) in L-series higher than Z-series of glasses.

3.3. IR spectra

Infrared spectra of L-series and Z-series glasses are shown in Figs. 5 and 6 respectively. The spectra show characteristic peaks originating from phosphate network. In L-series of glasses the peaks in the region of 1233–1247 cm^{-1} are due to the symmetric stretching vibration mode of P=O double bond in [POO$_{3/2}$]. The V_{as} (PO$_2$) and V_s (PO$_2$) vibrations of the P—O—P linkage of Q^1 and Q^2 tetrahedra with non-bridging oxygen (O$_{NB}$) are observed around 905–894 cm^{-1} and 735–731 cm^{-1} respectively [31–33]. The spectra exhibit a strong broad absorption peak in the region of 504–554 cm^{-1}, which is attributed to the O—P—O bending of [POO$_{3/2}$] and also the intensity increases with the increase in Li$_2$O content. By increasing Li$_2$O content the absorption peak exhibits red shift indicating weakening of the network. Further, it may also noted that in the region of 800–1300 cm^{-1}, the spectra show split peak suggesting structural modification as discussed in Section 1. In the case of Z-series of glasses the IR spectra are identical to those of L-series. However, we note that with increasing ZnO content, the peaks are rather sharper and their positions are almost independent of ZnO concentration indicating low degree of modification. This is consistent with the role of Zn^{2+} in this glass system as discussed above.

4. Conclusion

The stability factor of glasses investigated is in the range of 180–220 °C indicates glasses are stable. Li$_2$O addition causes structural degradation of phosphate network while ZnO causes least degradation. The role of ZnO appears to be like a glass former. These glasses exhibit low refractive index and decreases with the increase in Li$_2$O content. IR spectra reveal characteristic peaks originating from various vibrations in phosphate network. Low values of refractive index (1.40 ≤ n ≤ 1.45) of the glasses indicate that they are suitable for optical applications.

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