Electronic absorption studies on CO$^{2+}$ doped lithium phosphate glasses

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The optical absorption studies on cobalt doped binary lithium phosphate glasses $y$Li$_2$O-(100-y)P$_2$O$_5$ reveal a mixed octahedral and tetrahedral coordination for the cation sites through the characteristic bands $4T_1$ (F) $\rightarrow$ $4T_1$ (P) at $\sim$530 nm and $4A_2$ (F) $\rightarrow$ $4T_1$ (P) at $\sim$580 nm. The glasses show an increase in the number of tetrahedral sites as the modifier concentration increases which may be attributed to the increased optical basicity of the glasses. An enhancement in the ionic conductivity with increase in the dopant (Co$^{2+}$) concentration is observed in the glasses which may be due to Co$^{2+}$ entering Li$^+$ sites resulting in the generation of cation vacancies.

Keywords: Glass, Non-bridging oxygens, Optical absorption, Optical basicity

1 Introduction

Binary lithium phosphate glasses (Li$_2$O-P$_2$O$_5$) have been a subject matter of recent interest due to their low melting temperatures, strong glass forming character and potential use as solid electrolytes. In addition, phosphate glasses have a range of compositional and structural possibilities (ultra, meta, pyro, and ortho) that facilitate tailoring chemical and physical properties for various applications. There are several reports available discussing the structural aspects of these glasses using Raman, FT-IR and Radial density function (RDF) studies$^{1,2,3}$. The purpose of present study is to emphasize the under utilized experimental technique of optical absorption/visible spectroscopy for superionic glasses.

Visible spectroscopy originates from the electronic excitations and serves as a widely used tool for the structural investigations of glasses.$^{6}$ Transition metal (TM) ions can exist in different valence or coordination states when incorporated in the glass structure. The absorption bands originating from the d-d transitions of transition metal ions give a signature of their coordination environment. The various oxidation states of all the transition metal ions are listed in Table 1. In order to select a TM to be used as a probe ion to investigate the structure of the glass, two factors have to be taken into consideration; it should have (i) low octahedral site preference energy (OSPE), and (ii) less number of oxidation states. Cobalt possesses low OSPE $\sim$0.27$\Delta_0$ (1 kcal/mol)$^7$. A low value of OSPE allows the ion to adopt a coordination governed by the glass structure rather than that preferred according to the high crystal field stabilization energy. Cobalt is considered as a good probe ion owing to its low OSPE and less number of oxidation states$^{8}$ (+2 and +3).

Although cobalt can exhibit different oxidation states in many inorganic complexes but in glasses melted under normal atmospheric conditions, cobalt ion exists in the divalent state$^{9,11}$. Absorption spectra of cobalt in lithium phosphate glasses can provide valuable information about its coordination environment. The present work reports the optical absorption spectra of cobalt doped (mol% 0.005) binary lithium phosphate glasses in the composition range mol% $y$Li$_2$O-(100-$y$)P$_2$O$_5$, 30 $\leq y \leq$ 66.7.

2 Experimental Details

As the glass modifier (Li$_2$O) concentration increases in the glass the tendency for the nucleation and growth of the crystallites increases and hence higher quenching rates are required for glass formation. Lithium carbonate (Li$_2$CO$_3$), ammonium di-hydrogen phosphate (NH$_4$H$_2$PO$_4$) and cobalt oxide (CoO) were taken in stoichiometric amounts and pre-heated at 600$^\circ$C in a porcelain crucible for 5 h to ensure the removal of NH$_4$, H$_2$O and CO$_2$ and then the samples were melted at 850-1050$^\circ$C depending on the composition for 30 minutes before quenching the melts. Cobalt doped glasses with 0.005 mol% CoO in the glasses $y$Li$_2$O-(100-$y$)P$_2$O$_5$, 30 $\leq y \leq$ 60, were prepared by the usual melt-quench technique, while the doped mol% 66.7Li$_2$O-33.3P$_2$O$_5$ glass was prepared by using a home built twin roller rapid quenching set-up. Cooling rates as high as $10^5$-$10^6$ K/s can be achieved in such a setup while in the usual
melt-quench technique cooling rates of the order of $10^2-10^3$ K/s only are possible. Glass prepared by the rapid quenching set-up was in the form of thin flakes of thickness ~1 micron. As-prepared samples were used for recording the optical absorption spectra. The optical absorption spectra of Co$^{2+}$ doped lithium phosphate glasses were recorded on JASCO V570 UV-Visible-IR spectrophotometer. The spectrophotometer is a computer controlled double beam, direct ratio measuring system. To confirm the glassy nature of the sample, the X-ray diffraction studies were performed using Cu K$_\alpha$ (λ=1.5418 Å) while the DSC measurements were done using DSC 200 PC-PHOX (NETZSCH). Impedance data were collected using HP 4192A impedance analyzer.

### Results and Discussion

Figure 1 shows the XRD and the DSC plot for one of the Co$^{2+}$ doped (mol% 0.005) glass composition (mol% 30Li$_2$O-70P$_2$O$_5$) as a representative plot for the full glass composition. All the samples prepared were found to be X-ray amorphous and depicted characteristic glass transitions confirming the glassy nature of the samples (Table 2). The assignment of glass transition temperature ($T_g$) is depicted in inset of Fig. 1. The values of $T_g$ quoted in Table 2 for the doped glasses are in tune with $T_g$ values reported for the undoped glasses$^{13}$. Doped glasses were light blue in colour but as the modifier concentration increases, the glasses were found to have a darker shade.

#### 3.1 Ligand field theory (relevance for glasses)

The characteristic property of TM ions is their partially filled 3$d$ electronic orbitals. The 3$d$ orbitals are peculiar due to the spatial distribution of the electron densities. The $d$ orbitals $d_{xy}$ and $d_{z^2}$ have the electron density lobes pointing along the Cartesian axes while the lobes of $d_{x^2-y^2}$ and $d_{3z^2}$ point between the axes (Fig. 2). For an isolated atom, the $d$ orbitals are degenerate. However, when the TM ion is present at a particular coordination site, the electron clouds of the nearest neighbours (ligands) and TM ion interact Coulombically resulting in the splitting of the $d$ orbitals. The strength of the field produced by ligands decides the measure of splitting$^{13}$. As the $d$ orbitals are no longer degenerate, $d$-$d$ transitions are possible causing emission/absorption of light in the visible spectrum. In a typical octahedral coordination, it can be shown by simple symmetry arguments that the $d_{xy}$ and $d_{x^2}$ are repelled more strongly by the ligands as compared to the $d_{z^2}$ and $d_{yz}$, resulting into the splitting of the $d$ orbitals as shown in Fig. 2. Similar arguments can be used to decide the splitting of the $d$ orbitals in tetrahedral coordination (Fig. 2).

The ideal situations discussed above are seldom encountered in practical systems and the situation is further complex in disordered systems like glasses. Most of the TM sites will be distorted and will have lower symmetry than an ideal octahedral or tetrahedral geometry resulting in further splitting of the $d$ orbitals. In oxide glasses, the oxygen anions act as ligands and the geometry of these oxygen atoms around the TM site decides the extent of splitting in the $d$ orbitals.
two to as many as five degenerate levels which result in an increase in the number of possible d-d transitions.$^6$

3.2 Optical absorption spectra

The optical absorption spectra of Co$^{2+}$ doped lithium phosphate glasses are shown in Fig. 3. The bands between 400-600 nm correspond to octahedral coordination while the bands between 600-750 nm represent tetrahedral coordination in glasses.$^7,8$ Thus, it can be concluded that Co$^{2+}$ exists in a mixed octahedral and tetrahedral coordination for all the glass compositions.

The main octahedral band at ~530 nm corresponds to the transition $4T_1$ (F) $\rightarrow$ $4T_1$ (P) while the band at ~580 nm corresponding to $4A_2$ (F) $\rightarrow$ $4T_1$ (P) represents the prominent tetrahedral band. The evolution of a shoulder at ~620 nm (marked in Fig. 3) for the mol% 60Li$_2$O-40P$_2$O$_5$ and mol% 66.7Li$_2$O-33.3P$_2$O$_5$ glass indicates an increase in the number to tetrahedral sites.$^7,8$ To further investigate the reason behind the mixed coordination of the cobalt ion, the doped glass samples (y=50, 60 and 66.7) were heated for short duration of time (~1-5 min) at the peak crystallization temperature ($T_c$) obtained from the DSC measurements. Nucleation and growth of crystallites begin in the sample due to the thermal energy provided. It is assumed that the initial phases which crystallize in the doped glass samples will mimic the pre-existing coordination of cobalt in the glasses. The XRD patterns for these partially crystallized samples (Fig. 4) reveal the crystallized products indicated in the associated Table 3.

It is to be noted that in all the three crystalline phosphate (LiPO$_3$, Li$_3$P$_2$O$_7$ and Li$_3$PO$_x$), the coordination of lithium ion is four$^{16}$ while in lithium cobalt phosphate (LiCo$_2$(P$_3$O$_{10}$)) and lithium cobalt...
oxide (LiCoO$_2$), the coordination of both lithium and cobalt is octahedral$^{17,18}$. The presence of octahedral bands in the optical absorption spectra is clear from the octahedral coordination of cobalt in LiCo$_2$(PO$_{10}$) and LiCoO$_2$. The reason for the presence of tetrahedral bands may be due to the doping of Co$^{2+}$ ions at the Li$^+$ sites in the lithium phosphates.

To further probe this probable substitution of cobalt at lithium sites in the glass samples, ionic conductivity measurements were performed by varying the concentration of cobalt oxide from 0.005 to 0.1 in the y=60 glass. It is evident from Fig. 5 that the ionic conductivity increases with increase in the cobalt content in sample while there is no appreciable variation in the activation energy (Fig. 5). This enhancement in ionic conductivity points towards the creation of cation vacancies in the samples which further supports the doping of Co$^{2+}$ at Li$^+$ sites.

### 3.3 Optical basicity

The addition of a modifier (Li$_2$O) to v-P$_2$O$_5$ leads to the creation of non-bridging oxygen (NBO) at the expense of bridging oxygen (BO). For binary glasses, the bridging to non-bridging oxygen ratio (BO/NBO) depends on the composition$^5$ according to:

$$\text{BO} = \frac{0.5(3-0.04y)}{\text{NBO}}$$

Further, the optical basicity ($\Lambda$) of binary alkali phosphate is given by the relation:

$$\Lambda = \frac{y}{(500-4y)} + \frac{5(100-y)}{2.5(500-4y)}$$

The BO/NBO ratio and the optical basicity for all the composition are given in Table 4. As the modifier concentration increases the number of BO’s decreases (NBO’s increases) and correspondingly the optical basicity of the glass increases$^5$ resulting in the increase of the number of tetrahedrally coordinated cations.

### 4 Conclusions

Cobalt doped glasses have been prepared and characterized by XRD and DSC. Optical absorption spectra of these glasses reveal that cobalt (Co$^{2+}$) ions exist at octahedral and tetrahedral sites in the glass matrix depicting a mixed coordination environment. The similar ionic size of Co$^{2+}$ and Li$^+$ as well as the enhancement in the ionic conductivity with the increase of Co$^{2+}$ ion concentration indicates that Co$^{2+}$ may be occupying Li$^+$ sites in the glass matrix. In such a case, the optical absorption spectra of Co$^{2+}$ provide information about the coordination environment of Li$^+$. Further, the deconvolution of the optical absorption spectra divulges the increase in the number of tetrahedral sites with increase in the modifier concentration which has been correlated with the optical basicity of the glass. In view of above findings, optical absorption spectroscopy proves to be an effective tool to probe the coordination environment of cations in the glass matrix. Experimental techniques such as temperature variation of optical absorption spectra, ESR and EXAFS can be used to further probe the local structure of these glasses.

### References