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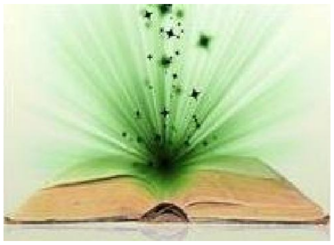

Structural Study of PbO-PbF_2-B_2O_3 Glasses Doped with CoO through Optical and Magnetic properties

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ABSTRACT

PbO-PbF_2-B_2O_3 glasses containing different concentrations of CoO have been prepared. The glasses are characterized by XRD and differential thermal analysis. The results of IR, optical absorption, magnetic susceptibility and refractive index measurements have been analyzed in the light of different oxidation states of cobalt ion. The analysis shows that cobalt ions exist mainly in Co2+ state, occupy tetrahedral positions by majority of Co2+ ions at 0.2 mol% of CoO. However, if CoO is present in higher concentrations beyond 0.2 mol% in the glass matrix, they occupy more octahedral positions than the tetrahedral positions. The value of magnetic moment (evaluated from magnetic susceptibility) has been observed to drop to a value of 3.94 μB from 4.46 μB and refractive index changed from 1.69 to 1.61 at higher concentration beyond 0.2 mol%. From these results it has been concluded that in this concentration range, cobalt ions exist mainly in divalent state.

Keywords: Glasses, Magnetic Susceptibility, Optical absorption and IR spectra.

INTRODUCTION

Transition metal ion doped glasses have attracted a great deal of interest because of their expectant optical and magnetic properties. Addition of PbO and PbF_2 to B_2O_3 gives low rate of crystallization, moisture resistant, stable and transparent glasses due to dual role played by PbO and PbF_2 as glass formers and also as modifiers. Glasses containing transition metal ions have become the subject of interest owing to their potential applications in IR fiber optics, laser windows and multifunctional optical components [1, 2]. These glasses are highly transparent in the mid-infrared range up to 8 m and are more stable against atmospheric moisture. They are also considered as promising candidates for electrochemical applications such as power sources especially in the field of solid state batteries [3]. Further, as any other heavy metal oxide based glasses, these glasses have also got the capacity to accept the transitional metal ions, like cobalt, both in network forming and modifying positions [4]. Rao et al., have carried out extensive studies that include glass transition temperature, ESR spectra, EXAFS and XANES on PbO-PbF_2 glasses containing different transition metal ions [5-8]. These studies have indicated that distorted octahedral structural units like PbO_2F_4 are present in these glasses. Nachimuthu and Jagannathan have also reported wide range of spectroscopic studies on PbO-PbF_2 glasses containing different rare earth ions [9-11]. Co^{2+} ion provides an intense blue colour in host glass matrix and their shade changes with the tetrahedral co-ordination to octahedral with a change in melt composition [12, 13].

Cobalt ions have strong bearing on electrical, optical and magnetic properties of glasses. A large number of interesting studies are available on the environment of Cobalt ion in various inorganic glass systems *viz*., silicate, borate, phosphate, germinate, tellurite glasses [14-25]. Many of the recent studies on the glasses containing CoO indicate, that the Cobalt ions exist in different valence state with different coordinations in glass matrices, for example, Co^{2+} occupy both tetrahedral and octahedral sites[4], whereas Co^{3+}occupy only octahedral positions [26-29]. The content of cobalt in diverse environments with different valence states that exist in the glass, depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc., Hence, the correlation between the state and the position of the cobalt ion in the glass network and its physical properties are expected to be highly interesting. Co^{2+} ion possesses a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital whereas such anisotropic energy of Co^{3+} ions is small as the orbital angular momentum of these ions is zero. Further, it is also quite likely, for cobalt ions to have link with PbO groups that may strengthen the glass structure and raise the chemical resistance of the glass.

Literature survey on PbO-PbF_2 glasses shows that there is virtually, no devoted studies are available on these glasses (with cobalt doped); however, the structural investigations by means of DTA, spectroscopic & magnetic properties, especially optical edge, optical band gap, magnetic susceptibility and magnetic moment of CoO containing PbO-PbF_2-B_2O_3 glasses, are required due to the importance of these glasses in view of their potential applications. Such studies help in assessing these glasses for their applications and may also throw some light on the structural aspects. Therefore, the objective of the present investigation is to have a comprehensive understanding over the influence of cobalt ions on the structure of PbO-PbF_2-B_2O_3 glasses, from a systematic study on optical & magnetic properties and to elucidate the role of cobalt ions and their structural modifying ability with the aid of data on spectroscopic (optical absorption, IR and ESR spectra) and magnetic properties.

MATERIALS AND METHODS

Within the glass forming region of $PbO-PbF_2-B_2O_3$ glass system, the following compositions with successive increase in the concentration of CoO are chosen for the present study:

C_0: 40 PbO-10 PbF_2-50 B_2O_3
C_1: 40 PbO-10 PbF_2-49.9 B_2O_3: 0.1 CoO
C_2: 40 PbO-10 PbF_2-49.8 B_2O_3: 0.2 CoO
C_3: 40 PbO-10 PbF_2-49.7 B_2O_3: 0.3 CoO
C_4: 40 PbO-10 PbF_2-49.6 B_2O_3: 0.4 CoO

Appropriate amounts (all in mol %) of reagent grades of PbF_2, PbO, H_3BO_3 and CoO powders were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range 900 – 950 ^{o}C in a PID temperature controlled furnace for about 1 h to 2 h until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed at 300 ^{o}C. The amorphous state of the glasses was confirmed by X-ray diffraction and scanning electron microscopy studies.

The differential thermal analysis on these samples was carried out using STA 409C, Model DTA-TG with a programmed heating rate of 10 ^{o}C / min in the temperature range of 30-900 ^{o}C.

The samples were then ground and optically polished. The final dimensions of the samples used for optical studies were about 1cm x 1cm x 0.2 cm. The density d of these glasses was determined to an accuracy of 0.001 by standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid.

The IR spectra of the glasses were recorded by KBr pellet method. Glass powders (2 mg) were mixed with anhydrous potassium bromide powder (150 mg) and pressed into pellets at 2000 kg cm^{-2}. The spectra were recorded using a FT- IR Digital Excalibur 3000 Spectrophotometer with resolution of 0.1 cm^{-1} in the range 400-2000 cm^{-1}. The optical absorption spectra of these glasses were recorded at room temperature in the wavelength range 350-2000 nm up to a resolution of 0.1 nm using Shimadzu UV-VIS-NIR Spectrophotometer Model 3101.

The magnetic susceptibility measurements were made at room temperature by Guoy's method using fine powders of these glasses and refractive index of these samples were measured with Abbe's Refractometer.

RESULTS AND DISCUSSION

Our visual examination, the absence of peaks in the X-ray diffraction pattern, the existence of glass transition temperature T_g, crystalline temperature T_c and melting point T_m in the DSC traces, indicate that the samples prepared were of amorphous in nature.

Fig.1 shows typical traces of differential thermal analysis of all the glasses under study. The curves exhibit an endothermic effect due to glass transition temperature T_g; the value of T_g is evaluated from the point of inflection of this change. At still higher temperatures, an exothermic peak T_c due to the crystal growth followed by an endothermic effect due to the melting effect denoted by T_m, are also observed. The values of T_g, T_c and T_m obtained for all the glasses are furnished in Table 2. The appearance of single peak due to the glass transition temperature in DTA pattern of all the glasses indicates the good homogeneity of the glasses prepared. For CoO doped glasses, the quantity (T_c-T_g), which is proportional to glass forming ability, is found to increase up to 0.2 mol% and it is decreased on further increase of CoO mole concentration.

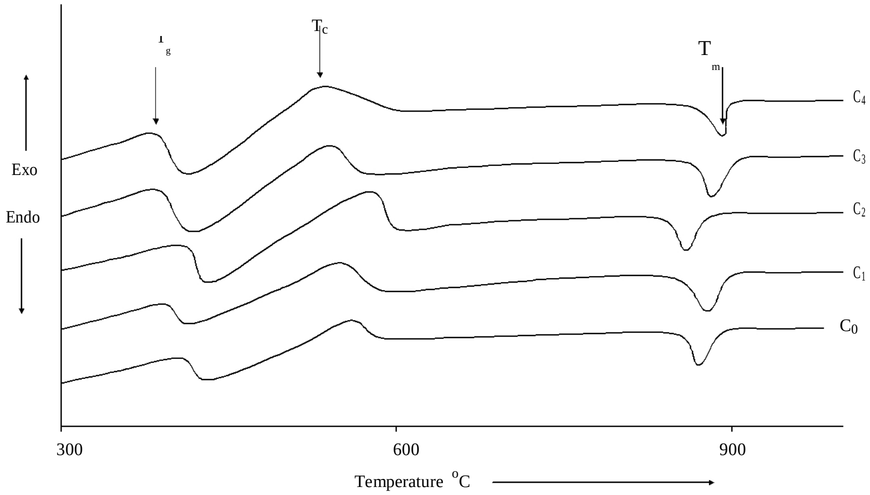

Fig. 1. DTA patterns of PbO-PbF_2-B_2O_3 : CoO glasses

The quantity (T_m-T_c) which is inversely proportional to glass forming ability is found to decrease (Table 2) with increase in the content of CoO up to 0.2 mol% and increased on further increase of CoO. From the measured values of T_g, T_c and T_m, the parameters T_g/T_m, $(T_c-T_g)/T_g$, $(T_c-T_g)/T_m$ and glass forming ability parameter known as Hruby's parameter $(T_c-T_g)/(T_m-T_c)$ are evaluated and presented in Table 2. The variation of the parameter $(T_c-T_g)/(T_m-T_c)$ with the concentration of CoO shows the maximum value for glass C_2 (Table 2) indicating its highest glass forming ability among all the glasses under investigation.

From the measured values of the glass density (d) and calculated average molecular weight ($\overline{M}$), various physical parameters such as cobalt ion concentration (N_i), mean cobalt ion separation (Ri) are evaluated for understanding the physical properties of these glasses using the conventional formulae and the values obtained are presented in Table 1.

Table 1 Summary of data for various physical properties of PbO-PbF_2-B_2O_3: CoO glasses

Property	C_0	C_1	C_2	C_3	C_4
Density, d (g/cm^3)	4.514	4.639	4.722	4.742	4.951
Avg. mol. Wt	148.5	148.6	148.61	148.62	148.63
Co ion concentration Ni (10^{21} ions/cm^3)	-	1.88	3.83	5.77	8.03
Inter ionic distance of Co ions, R_i (Å)	-	8.1	6.39	5.57	4.99
Polaron radius, r_p (Å)	-	3.26	2.57	2.24	2.01
Fi (10^{15} /cm^2)					
avg. dissociation rate (mg/h/cm^2)	-	1.87	3.01	3.96	4.93

Table 2 Summary of data on differential scanning calorimetric analysis of PbO-PbF_2-B_2O_3: CoO glasses

Glass	T_g (K)	T_c (K)	T_m (K)	T_g/T_m	$(T_c-T_g)/T_g$	$(T_c-T_g)/T_m$	$(T_c-T_g)/(T_m-T_c)$
C_0	407	558	870	0.468	0.371	0.174	0.484
C_1	393	550	878	0.448	0.399	0.179	0.479
C_2	410	575	859	0.477	0.402	0.192	0.581
C_3	388	541	881	0.440	0.394	0.174	0.450
C_4	386	537	891	0.433	0.391	0.169	0.427

The infrared transmission spectra of pure PbO-PbF_2-B_2O_3 glasses have exhibited two main groups of bands: (i) in the region 1300-1400 cm^{-1}, (ii) in the region 1100-1200 cm^{-1} and another band at about 711 cm^{-1} (Fig. 2); these bands are identified due to the stretching relaxation of B-O bond of the trigonal BO_3 units, vibrations of BO_4 structural units and due to the bending vibrations of B-O-B linkages respectively [30, 31]. A band due to PbO_4 structural units is also observed in the spectra of all the glasses at about 520 cm^{-1} [32, 33]. Additionally a broad band, presumably due to octahedral distorted PbO_4F_2 vibrational groups [10, 34, 35] is also located around 1050 cm^{-1}. With the introduction of CoO upto 0.2 mol % into the glass network, the intensity of second group of bands (bands due to BO_4 units) is observed to increase with a shifting of meta-center towards slightly lower wave number, whereas, the intensity of the first group of bands (bands due to the BO_3 structural units) is observed to decrease. For further increase of CoO, the intensity of the first group of bands is observed to increase at the expense of second group of bands. The intensity of the band due to PbO_2F_4 is also observed to increase (inset of Fig. 2) clearly with increase in the concentration of CoO from 0.1 to 0.4 - mol % and these observations are reported in Table 3.

The optical absorption spectra of PbO-PbF_2-B_2O_3: CoO glasses recorded in the wavelength region 350-1600 nm are shown in Fig. 3(a). The absorption edge observed at 402.7 nm for the glass C_0 is observed to shift to 382.70 nm with the introduction of CoO up to 0.2 mol%. For further increase in the concentration of CoO, the edge is observed to shift gradually towards higher wavelength and the sample C_4 has an absorption edge at 420 nm. The spectra of the glasses C_1 and C_2 have exhibited absorption bands at 529 nm and a broad band is observed from 1200 - 1450 nm due to Co^{2+} ion transitions. With increase in the concentration of CoO beyond 0.2 mol %, the bands due to Co^{2+} ions have been observed to become paler away slowly.

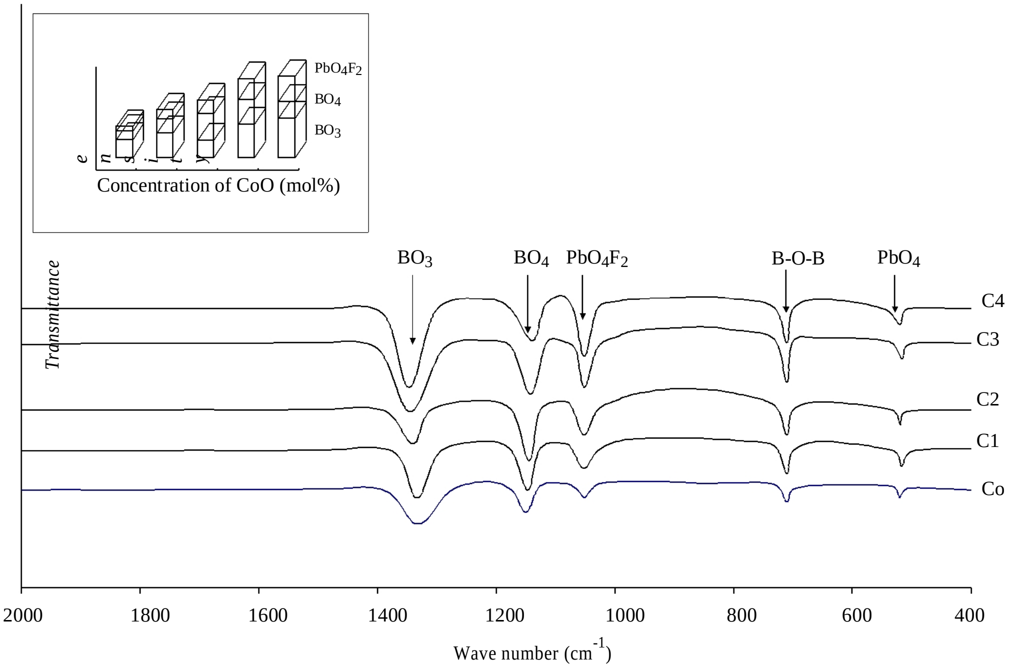

Fig. 2. IR spectra of $PbO\text{-}PbF_2\text{-}B_2O_3$:CoO glasses. Inset shows the variation of intensity of BO_4, BO_3 and PbO_4F_2 units with concentration of CoO

Table 3 Summary of the data on band positions (cm^{-1}) of various absorption bands in the IR spectra of $PbO\text{-}PbF_2\text{-}B_2O_3$: CoO glasses

Glass	Borate groups			Band due to PbO_4F_2 (cm^{-1})	Band due to PbO_4 units (cm^{-1})
	BO_3 (cm^{-1})	BO_4 (cm^{-1})	B-O-B (cm^{-1})		
C_0	1332	1150	711	1052	520
C_1	1334	1147	711	1052	520
C_2	1341	1145	711	1052	520
C_3	1345	1142	711	1052	520
C_4	1347	1139	711	1052	520

From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Urbach plot between $(\alpha\, \hbar\, \omega)^{1/2}$ and $\hbar\, \omega$ as per the eqn.:

$$\alpha(\omega)\, \hbar\, \omega = C\, (\hbar\, \omega - E_o)^2$$

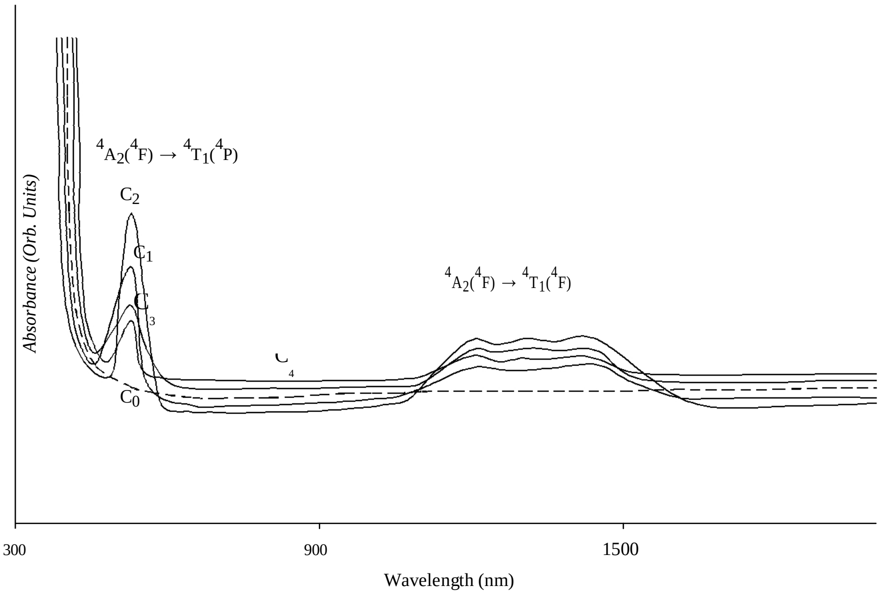

Fig. 3(a). Optical absorption of PbO-PbF$_2$-B$_2$O$_3$: CoO glasses

Fig. 3(b) represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap (E$_o$) obtained from the extrapolation of the linear portions of these plots are presented in Table 4. The value of E$_o$ is found to increase with the increase in concentration of CoO up to 0.2 mol % and it is decreased on further increase of CoO up to 0.4 mol%.

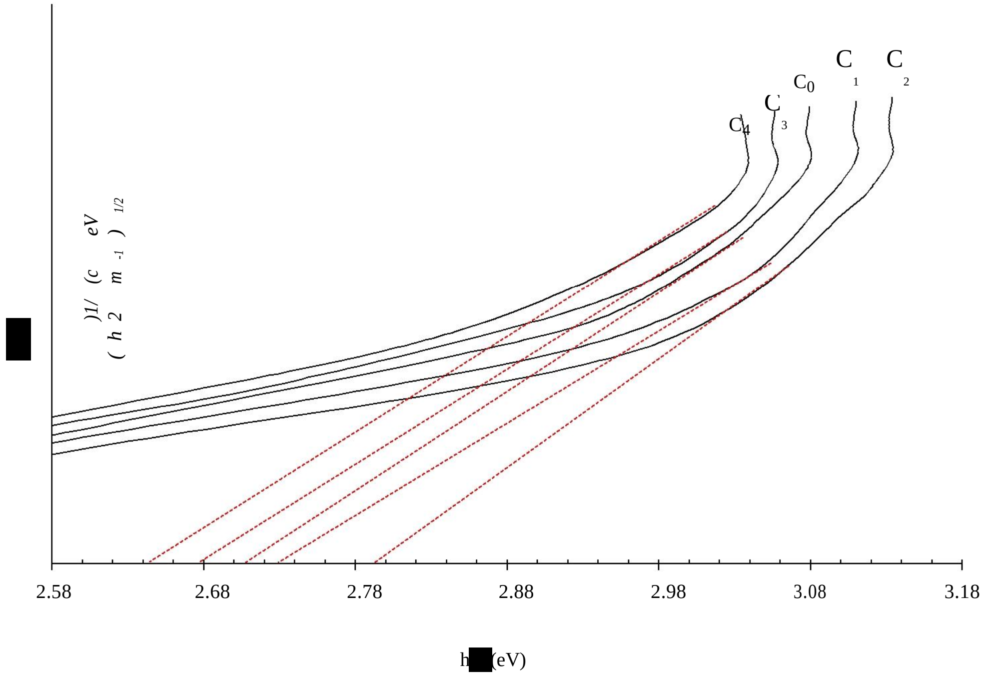

Fig. 3(b). A plot for evaluating the optical band gap of PbO-PbF$_2$-B$_2$O$_3$: CoO glasses

Table 4 Summary of data on optical absorption spectra of $PbO-PbF_2-B_2O_3$: CoO glasses

Glass →	C_0	C_1	C_2	C_3	C_4
Co^{2+} transition (nm)					
$^4A_2(^4F) \rightarrow {}^4T_1(P)$	-	529	529	529	529
$^4A_2(^4F) \rightarrow {}^4T_1(^4F)$	-	1200-1450	1200-1450	1200-1450	1200-1450
Cut-off wavelength (nm)	402.7	391.2	382.7	412	420
Optical band gap (eV)	2.71	2.73	2.79	2.68	2.64

Magnetic susceptibility of $PbO-PbF_2-B_2O_3$ glasses doped with different concentrations of CoO was measured at room temperature by Guoy's method and presented in Table 5. The value of magnetic susceptibility is found to increase gradually with increase in the concentration of CoO in the glass matrix. From the magnetic susceptibility and the concentration of Co^{2+} ions (which are determined in the physical parameters) the magnetic moments were evaluated using the standard relation for the susceptibility and magnetic moment and are presented in Table 5. The refractive index of the glass is also observed to increase with the introduction of CoO in to the glass matrix up to 0.2 mol% and beyond that the refractive index is decreased.

Table 5 Data on magnetic properties & refractive indices of $PbO-PbF_2-B_2O_3$: CoO glasses

Glass	χ (10^{-5} emu)	Magnetic moment μ_{eff}	Refractive index (n)
C_0	-	-	1.63
C_1	25.37	3.97	1.64
C_2	28.54	4.46	1.69
C_3	30.53	4.25	1.65
C_4	31.93	3.94	1.62

Discussion

It is well known fact that the effect of introduction of modifiers like PbO, PbF_2 into B_2O_3 network is to convert the sp^2 planar BO_3 into more stable sp^3 tetrahedral BO_4 units in addition to non-bridging oxygens (NBO's). Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion giving rise to a structure that leads to the formation of long chain tetrahedrons. The presence of such BO_4 units in the present glass system is evident from infrared spectral studies. Earlier NMR investigations by different researchers [36, 37] on fluoro borate glasses indicate that in addition to BO_4 units there exits $B(O, F)_4$ or (BO_3F) and BO_2F_2 units in this type of systems; the probable linkages in the present glass systems is shown in the Fig.4. It is to be noted in the figure that the borate groups are connected by oxygen and lead ion located near the fluorine (in octahedral coordination) serve as charge compensator.

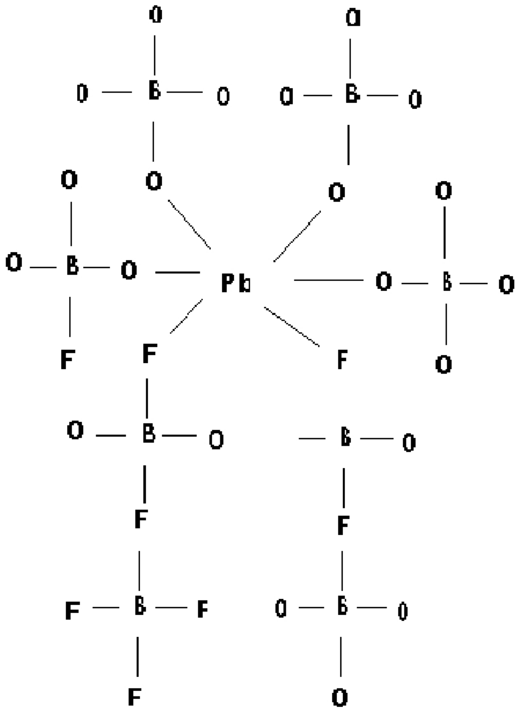

Fig. 4: A schematic illustration of lead oxy fluoro borate glass

PbO in general is a glass modifier and enters the glass network by breaking up the B-O-B bonds (normally the oxygens of PbO break the local symmetry while Pb^{2+} ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. In this case the lead ions are octahedrally positioned with PbO_2F_4 structural units as shown in Fig. 4. To form octahedral units, Pb should be sp^3d^2 hybridized (6s, 6p and 6d orbitals) [5, 6]. The presence of PbO_2F_4 structural units in a number of other glass systems was confirmed by several experimental techniques, like EXAFS and XANES [38]. The band observed in IR spectra at about 1050 cm^{-1} confirms the presence of PbO_2F_4 units in $PbO-PbF_2-B_2O_3$ glass network. However, PbO may also participate in the glass network with PbO_4 structural units when lead ion is linked to four oxygens in a covalency bond configuration. In such a case the network structure is considered to build up from PbO_4 and BO_4 pyramidal units, which are linked together by B-O-Pb bonds. When PbF_2 is added, additional non-bridging Pb-F bonds are expected to be formed at the expense of the bridging B-O-B and B-O-Pb linkages and may also introduce more non-bridging oxygen ions.

Recollecting the data on IR spectra, with the raise in the concentration of CoO upto 0.2 mol%, the intensity of the bands due to BO_4 structural units has been observed to increase at the expense of the bands due to BO_3 units. On further increase of CoO up to 0.4 mol% the intensity of the bands due to BO_3 structural units has been observed to increase at the expense of the bands due to BO_4 units. This observation suggests a gradual increase in the concentration of divalent cobalt ions beyond 0.2 mol% in the glass network that acts as modifiers; as modifiers, these ions create more disorder in the glass network. Normally, the oxygens of CoO break the local symmetry while Co^{2+} ions occupy the interstitial positions. The observed increase in the intensity of the band due to distorted octahedral PbO_2F_4 structural units with the concentration of CoO beyond 0.2 mol% also supports this argument.

In octahedral coordination (Co^{2+}) free ion ground state ^4F splits into the $^4T_1$, $^4T_2$ and $^4A_4$ states with the $^4F_1$ state as the lowest. Co^{2+} in this coordination has three bands which correspond to the spin allowed transitions $^4T_1(F) \rightarrow {}^4T_2(F)$, $^4T_1(F) \rightarrow {}^4A_2(F)$ and $^4T_1(F) \rightarrow {}^4T_1(P)$. The $^4T_1(F) \rightarrow {}^4A_2(F)$ transition occurs only with low intensity due to a forbidden two – electron jump. In a tetrahedral symmetry, the energy levels of Co^{2+} ions are $^4T_2(^4F)$, $^4T_1(^4F)$, $^2E(^2G)$ and $^4T_1(^4P)$, etc., with the ground state of $^4A_2(^4F)$. In a tetrahedral symmetry, co^{2+} ions mainly show two spin forbidden transitions $^4A_2(^4F) \rightarrow {}^4T_1(P)$ and $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$, respectively. The high intensity of the tetrahedrally coordinated band is a consequence of the mixing of the 3d- orbitals with 4p orbitals and ligand orbitals [39, 40]. The visible absorption spectra of Co^{2+} glass are shown in Fig. 3(a) and an absorption band at 529 nm and a broad absorption band centered at about 1325 nm could be noticed, and these are assigned to spin-forbidden transitions $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ and $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ of tetrahedrally coordinated Co^{2+} ions [40, 41]. The spectra of cobalt materials are very typical and unique. For several laser applications of cobalt materials, their optical properties in the near infrared (1.3 – 1.6 μm) [$^4A_2(^4F) \rightarrow {}^4T_1(^4F)$] region of tetrahedrally coordinated Co^{2+} ions are considered more important.

The magnetic properties of these glasses arise from the Co^{2+} ($3d^7$) ions. The value of the effective magnetic moment (4.46 $_B$) obtained for glass C_2 confirms the highest concentration of Co^{2+} ions in this glass. The decrease in the value of $_{eff}$ from 4.46 $_B$ to a value of 3.94 $_B$ (for glass C_4) indicates, a gradual drop in concentration of Co^{2+} ions that take modifying positions in the glass network. Such Co^{2+} ions may increase the degree of disorder in the glass network.

The refractive index of the glass is also observed to increase with the introduction of CoO in to the glass matrix up to 0.2 mol% and beyond that the refractive index is decreased. The refractive index of the pure glass is observed as 1.63. The refractive index of the glass is increased up to 1.69 when CoO concentration is 0.2 mol%. On further increase of CoO concentration to 0.4 mol% the value of refractive index is decreased to 1.62. This result proves that at 0.2 mol% of CoO, majority of cobalt ions occupy the glass forming positions which increases the transparency of the glass. Beyond 0.2 mol%, the Co^{2+} ions enters in to the network modifying positions which increases the degree of disorderness of the system. Also it is evident that the clour of the glass will change when the ion turns from tetrahedral to octahedral sites. In our experimentation we have observed that the glass became dark blue at 0.5 mol% of CoO and lost its transparency.

APPLICATIONS

Leadfluoroborate glasses are moisture resistant, stable and transparent glasses. Doping of cobalt ions in the host glass matrix will improve optical and magnetic properties of glasses. Hence these glasses can be used as laser windows in the proper range mentioned earlier.

CONCLUSION

The summary of conclusions drawn from the study of various properties of $PbO\text{-}PbF_2\text{-}B_2O_3$ glasses doped with CoO is as follows:

(i) The optical absorption spectral studies indicate the presence of part of cobalt ions in Co^{2+} state occupy both tetrahedral and octahedral positions. If CoO is present in lower concentrations up to 0.2 mol% then Co^{2+} occupy more tetrahedral positions. If CoO is increased beyond 0.2 mol% then the octahedral positions are increased with the expense of tetrahedral positions.

(ii) The magnetic moment, evaluated from magnetic susceptibility measurements of the glasses reveals that the magnetic moment is increased from 3.97 to 4.46 $_B$ with increase of CoO from 0.1 mol% to 0.2 mol% latter on further increase of CoO magnetic moment decreased from 4.46 to3.94 $_B$. This result has been attributed to the gradual conversion of cobalt ions from tetrahedral sites to octahedral sites when the concentration increases beyond 0.2 mol%.

(iii) The IR spectral investigations indicate that with the increase in the concentration beyond 0.2 mol% of CoO in the glass matrix, a gradual increase in the concentration of divalent cobalt that occupy octahedral positions and enhances disorderliness in the glass network.

Summarising, the studies with optical absorption, IR magnetic susceptibility and refractive index of PbO-PbF_2-B_2O_3: CoO glasses indicate that when the concentration of CoO in the glass network is low, cobalt ions seems to exist mainly in Co^{2+} state and occupy network forming positions and strengthen the glass structure at 0.2 mol%; if the concentration is increased gradually, these ions seems to exist mainly in Co^{2+} state and occupy modifying positions and increase disorder in the glass network.

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