

## Structural Study of PbO-NaF-B<sub>2</sub>O<sub>3</sub> Glass System Doped with Cr<sub>2</sub>O<sub>3</sub> through Spectroscopic and Magnetic Properties

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### ABSTRACT

PbO-NaF-B<sub>2</sub>O<sub>3</sub> glasses containing different concentrations of Cr<sub>2</sub>O<sub>3</sub> have been prepared. The glasses are characterized by XRD, SEM and differential thermal analysis. These studies have been analyzed in the light of different oxidation states of chromium ion with the aid of the data on IR, ESR, optical absorption and magnetic susceptibility measurements. The analysis shows that chromium ions exist mainly in Cr<sup>3+</sup> state, occupy octahedral positions of the glass if Cr<sub>2</sub>O<sub>3</sub> is present up to 0.3 mol %. However, if Cr<sub>2</sub>O<sub>3</sub> is present in higher concentrations i.e., above 0.3 mol % in the glass matrix, (i) the intensity and the half width of the ESR signal has been observed to increase and (ii) the number of Cr<sup>3+</sup> ion concentration (calculated from the magnetic susceptibility measurements and by taking magnetic moment 3.9 μB) has been observed to decrease and hence increase in the concentration of Cr<sup>6+</sup> ion in the glass and occupy tetrahedral sites in the glass matrix. From these results it has been concluded that up to 0.3 % mole concentration range, chromium ions exist mainly in trivalent state.

**Keyword:** fluoroborate glass, optical absorption, Hurby's Parameter.

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### INTRODUCTION

Borate glasses have been widely investigated due to their technological applications. B<sub>2</sub>O<sub>3</sub> can be considered as having the highest glass formation tendency because molten B<sub>2</sub>O<sub>3</sub> does not crystallize by itself even when cooled at the slowest rate. Boron is the first member of the group III in the periodic table and the size of B<sup>3+</sup> ion is very small. B<sup>3+</sup> can fit in to the trigonal void created by 3 oxide ions in mutual contact and forming a [BO<sub>3/2</sub>] unit. [BO<sub>3/2</sub>] units are the primary building blocks in all borate glasses. Since B in [BO<sub>3/2</sub>] is electron deficient, it can accept two more electrons in the form of a dative bond. This happens when an oxide ion is available in the glass composition for such additional bonding. [BO<sub>4/2</sub>] units are thus readily formed in borate glass structures. [BO<sub>4/2</sub>] units are tetrahedral. Several Structural Studies have been performed on B<sub>2</sub>O<sub>3</sub> and it may be fair to say that there is no consensus as to how the building blocks [BO<sub>3/2</sub>] units are connected in the structure[1]. B<sub>2</sub>O<sub>3</sub> is a glass forming oxide, PbO is a conditional glass former and with these two chemicals in the glass matrix, a low rate of crystallization, moisture resistance, stable and transparent glasses could be achieved due to a dual role played by PbO as a glass former and also as a modifier[2].

Alkali fluoro borate glasses, like PbO-NaF-B<sub>2</sub>O<sub>3</sub> glasses are considered as the best materials for using phosphors, lasers, solar energy converters and in a number of other electronic devices. These are more moisture resistant when compared with alkali oxy borate glasses[3].

Transition metal ions are incorporated into these glasses in order to characterize their optical behaviors. Glasses containing transition metal ions have become the subject of interest owing to their potential applications[4,5]. Among the transition metal ions, Cr<sup>3+</sup> is a typical ion with good potential applications[6-13]. A considerable number of investigations on the role of chromium ions on the physical properties of a variety of glass systems like phosphate, tellurite, arsenate, borate, silicates etc. have also been reported by many researchers in recent years[14-18].

Chromium ion is a paramagnetic transitional metal ion, when dissolved in glass matrix even in very small quantities, makes the glasses coloured and has a strong influence over the physical properties of the glasses. Regardless of the oxidation state of the chromium in the starting glass batch, these ions may exist in different valence states simultaneously in the final glass and occupy a variety of sites with different crystal field strengths due to site variability and compositional disorder. Further, materials containing mixed valence chromium are of recent interest as cathode materials in rechargeable batteries owing to their very high energy density and high capacitance[19,20].

Among various oxidation states of chromium ions, Cr<sup>3+</sup>, Cr<sup>4+</sup>, Cr<sup>5+</sup> and Cr<sup>6+</sup> are the most likely to be active and stable. The chromium (III) ions occupy octahedral sites and the efficiency of the most common lasing transition

${}^4T_2 \rightarrow {}^4A_2$  of this ion is found to be very sensitive to the internal structure of the glass. The chromium (III) ions occupy octahedral sites. A large number of interesting studies are available on the environment and oxidation states of chromium ion in various crystals and inorganic glass systems[21-25].  $Cr^{3+}$  ion has a  $d^3$  electronic configuration. In the ground state these electrons occupy the  $t_{2g}$  orbitals, i.e.  $(t_{2g})^3$ . The two  $e_g$  orbitals are empty, providing two 'holes' into which the electrons can be promoted. The three unpaired electrons give rise to the free ion terms  ${}^4F$ ,  ${}^4P$ ,  ${}^2G$  and several other doublet states of which  ${}^4F$  is the ground state. In the octahedral field the  ${}^4F$  state is split into  ${}^4A_{2g}(F)$ ,  ${}^4T_{2g}(F)$  and  ${}^4T_{1g}(F)$  states, the  ${}^4P$  state is not split but transforms into a  ${}^4T_{1g}(P)$  state and the  ${}^2G$  state splits into  ${}^2A_{1g}(G)$ ,  ${}^2T_{1g}(G)$ ,  ${}^2T_{2g}(G)$  and  ${}^2E_g(G)$ . For convenience the free ion term and the corresponding crystal field terms are given in the parenthesis [24]. The states  ${}^4A_{2g}(F)$ ,  ${}^2E_g(G)$ ,  ${}^2T_{1g}(G)$  and  ${}^2T_{2g}(G)$  correspond to the lowest strong field configuration  $(t_{2g})^3$ . The states  ${}^4T_{1g}(F)$  and  ${}^4T_{2g}(F)$  correspond to  $(t_{2g})^2(e_g)^1$  and  ${}^4T_{1g}(P)$  corresponds to  $(t_{2g})(e_g)^2$ . The ground state for  $Cr^{3+}$  ions is  ${}^4A_{2g}(F)$  at all strengths of the crystal field.  $Cr^{3+}$  ions have the d-electron configuration and have larger octahedral site preference energy<sup>24</sup>. In an octahedral field, its ground level is  ${}^4A_{2g}$ . Under the field action of a low symmetry component and spin orbit coupling, the fourfold degenerate spin states split into two Kramers doublets.

The  $Cr^{5+}(d^1)$  ions either participate in the glass network with  $CrO_4^{3-}$  complexes or go into the modifying positions with octahedral coordination. The  $Cr^{6+}(d^0)$  ions have the closed shell configuration, participate in the glass network with  $CrO_4^{2-}$  structural units and is expected to strengthen the host borate glass network. Hence this paper is aimed at an overall understanding of valence states and the local environment of chromium ions (introduced as  $Cr^{3+}$ ) in PbO-NaF-B<sub>2</sub>O<sub>3</sub> glass network and to probe their role on the structural modifications that take place in the glass network by means of magnetic and spectroscopic viz., optical absorption, ESR, and IR studies.

## MATERIALS AND METHODS

Within the glass forming region of PbO-NaF-B<sub>2</sub>O<sub>3</sub> glass system, the following compositions with successive increase in the concentration of Cr<sub>2</sub>O<sub>3</sub> are chosen for the present study-

- C<sub>0</sub>: 40 PbO-10 NaF-50 B<sub>2</sub>O<sub>3</sub>
- C<sub>1</sub>: 40 PbO-10 NaF -49.9 B<sub>2</sub>O<sub>3</sub>; 0.1 Cr<sub>2</sub>O<sub>3</sub>
- C<sub>2</sub>: 40 PbO-10 NaF -49.8 B<sub>2</sub>O<sub>3</sub>; 0.2 Cr<sub>2</sub>O<sub>3</sub>
- C<sub>3</sub>: 40 PbO-10 NaF -49.7 B<sub>2</sub>O<sub>3</sub>; 0.3 Cr<sub>2</sub>O<sub>3</sub>
- C<sub>4</sub>: 40 PbO-10 NaF -49.6 B<sub>2</sub>O<sub>3</sub>; 0.4 Cr<sub>2</sub>O<sub>3</sub>
- C<sub>5</sub>: 40 PbO-10 NaF -49.5 B<sub>2</sub>O<sub>3</sub>; 0.5 Cr<sub>2</sub>O<sub>3</sub>

Appropriate amounts (all in mol %) of reagent grades of NaF, PbO, H<sub>3</sub>BO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> powders were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range 950-1000 °C in a PID temperature controlled furnace for about 1 hr until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed at 300 °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 °C / min in the temperature range of 30-1000 °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<sup>-2</sup>. The spectra were recorded using a FT-IR Digital Excalibur 3000 Spectrophotometer with a resolution of 0.1 cm<sup>-1</sup> in the range 400-2000 cm<sup>-1</sup>.

The optical absorption spectra of these glasses were recorded at room temperature in the wavelength range 350-650 nm up to a resolution of 0.1 nm using Shimadzu UV-VIS-NIR Spectrophotometer Model 3101.

The ESR spectra of the fine powders of the samples were recorded at room temperature on JES-FA 200 ( $\nu = 9.21$  GHz) ESR spectrometer with 100 KHz field modulation. The magnetic susceptibility measurements were made at room temperature by Guoy's method using fine powders of these glasses.

## RESULTS AND DISCUSSION

Our visual examination, the absence of peaks in the X-ray diffraction pattern shown in Fig.1, the scanning electron microscope pictures of the samples shown in Fig.2, the existence of glass transition temperature  $T_g$ , crystalline

temperature  $T_c$  and melting temperature  $T_m$  in the DTA traces, indicates that the samples prepared were of amorphous in nature.

From the measured values of density  $d$  and calculated average molecular weight  $\overline{M}$ , various physical parameters such as chromium ion concentration  $N_i$  and mean chromium ion separation  $R_i$  of these glasses are evaluated[26] and presented in Table 1.

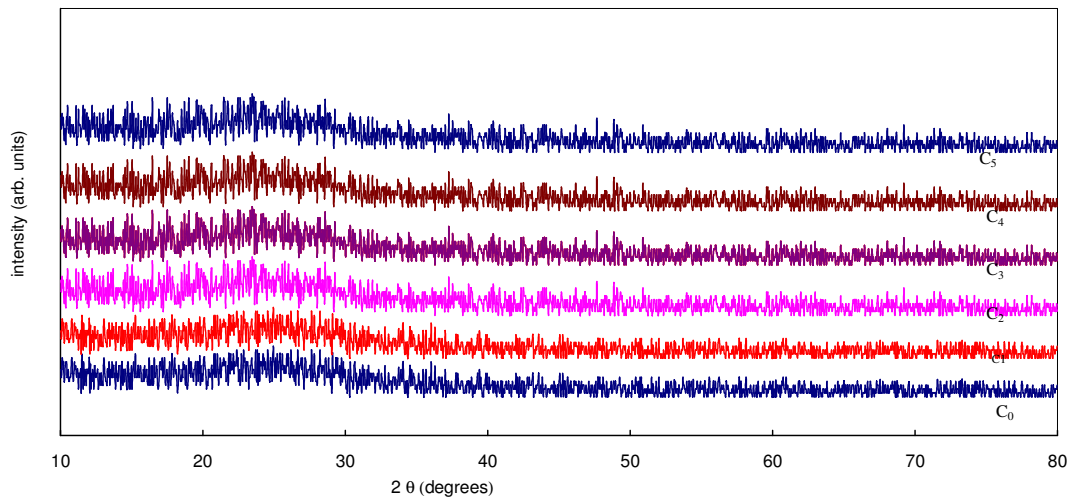


Fig.1. X-Ray diffraction pattern of PbO-NaF -B<sub>2</sub>O<sub>3</sub> glasses doped with different conc. of Cr<sub>2</sub>O<sub>3</sub>

Fig.3 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 Cr<sub>2</sub>O<sub>3</sub> doped glasses, the quantity  $(T_c - T_g)$ , which is proportional to glass forming ability, is found to decrease whereas the quantity  $(T_m - T_c)$  which is inversely proportional to glass forming ability is found to increase (Table 2) with increase in the content of Cr<sub>2</sub>O<sub>3</sub> up to 0.3 % of mole concentration. Later on with increase in concentration of Cr<sub>2</sub>O<sub>3</sub> from 0.3 – 0.5 mol % the quantity  $(T_c - T_g)$ , which is proportional to glass forming ability, is found to increase whereas the quantity  $(T_m - T_c)$  which is inversely proportional to glass forming ability is found to decrease and it is shown in Table 2. From the measured values of  $T_g$ ,  $T_c$  and  $T_m$ , the parameters  $(T_c - T_g)$ ,  $(T_m - T_c)$  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 Cr<sub>2</sub>O<sub>3</sub> shows the maximum value for glass C<sub>5</sub> (Table 2) indicating its highest glass forming ability among all the glasses under investigation.

The variation of glass forming ability parameter called Hruby's Parameter  $K_{gl}$  with the concentration of Cr<sub>2</sub>O<sub>3</sub> in the present glass system is represented in the Fig. 3.A. From the graph it is clear that the glass forming ability is decreased with the increase in the concentration of Cr<sub>2</sub>O<sub>3</sub> up to 0.3 % of mole concentration and later on with the increase in the concentration of Cr<sub>2</sub>O<sub>3</sub> the Hruby's parameter is increased.

The infrared transmission spectra of pure PbO-NaF-B<sub>2</sub>O<sub>3</sub> glasses have exhibited two main groups of bands: (i) in the region 1300-1400 cm<sup>-1</sup>, (ii) in the region 1100-1200 cm<sup>-1</sup> and another band at about 725 cm<sup>-1</sup> (Fig.4), these bands are identified due to the stretching relaxation of B-O bond of the trigonal BO<sub>3</sub> units, vibrations of BO<sub>4</sub> structural units and due to the bending vibrations of B-O-B linkages respectively[27-29]. A band due to PbO<sub>4</sub> structural units is also present in the spectra of all the glasses at about 485 cm<sup>-1</sup> [29]. A band due to vibrations of CrO<sub>4</sub><sup>2-</sup> structural units is also observed at 885 cm<sup>-1</sup> in the FTIR spectrum of C<sub>4</sub> and C<sub>5</sub> samples[30] (the intensity of which is increasing with the increasing concentration of Cr<sub>2</sub>O<sub>3</sub>).

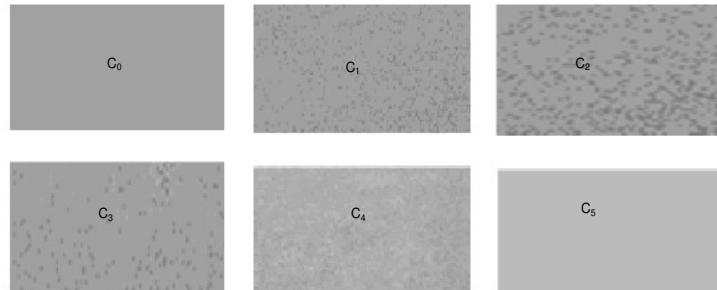


Fig.2: Scanning Electron Micrograms of PbO-NaF-B<sub>2</sub>O<sub>3</sub>: Cr<sub>2</sub>O<sub>3</sub> glasses

With the introduction of Cr<sub>2</sub>O<sub>3</sub> up to 0.3 mol % into the glass network, the intensity of second group of bands (bands due to BO<sub>4</sub> units) is observed to decrease with a shifting of meta-center towards slightly higher wavenumber, where as, the intensity of the first group of bands (bands due to the BO<sub>3</sub> structural units) is observed to increase. For further increase of Cr<sub>2</sub>O<sub>3</sub>, the intensity of the first group of bands is observed to decrease at the expense of second group of bands. The wavenumbers corresponding to these groups are presented in table 3.

The optical absorption spectra of PbO-NaF-B<sub>2</sub>O<sub>3</sub> : Cr<sub>2</sub>O<sub>3</sub> glasses recorded in the wavelength region 350-800 nm are shown in Fig. 5. The absorption edge observed at 393.1 nm for the glass C<sub>0</sub> is observed to shift to 406.7 nm with the introduction of Cr<sub>2</sub>O<sub>3</sub> (0.3 mol %). For further increase in the concentration of Cr<sub>2</sub>O<sub>3</sub>, the edge is observed to shift gradually towards lower wavelength. The spectra of the glasses C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> have exhibited absorption bands at 454 and 666 nm due to Cr<sup>3+</sup> ion transitions and an absorption peak is observed at 380 nm due to Cr<sup>6+</sup> ions is observed in the spectra of C<sub>4</sub> and C<sub>5</sub>. With increase in the concentration of Cr<sub>2</sub>O<sub>3</sub> beyond 0.3 mol %, the bands due to Cr<sup>3+</sup> ions have been observed to fade away slowly where as the intensity of the band due to Cr<sup>6+</sup> ions is observed to increase gradually.

From the observed absorption edges, we have evaluated the optical band gaps (E<sub>0</sub>) of these glasses by drawing Urbach plot between  $(\alpha \hbar \omega)^{1/2}$  and  $\hbar \omega$  as per the eqn.-

$$\alpha(\omega) \hbar \omega = C (\hbar \omega - E_0)^2.$$

Fig. 6 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<sub>0</sub>) obtained from the extrapolation of the linear portions of these plots are presented in Table 4. The value of E<sub>0</sub> is found to increase with the increase in concentration of Cr<sub>2</sub>O<sub>3</sub> from 0.3 mol %.

Table-1: Summary of data on various physical parameters of PbO- NaF -B<sub>2</sub>O<sub>3</sub>: Cr<sub>2</sub>O<sub>3</sub> glasses

Property	Glass Samples					
	C <sub>0</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>
Density d ( g/cm <sup>3</sup> )	4.72	4.79	4.83	4.89	4.95	5.05
Avg. dissociation rate(mg/h/cm <sup>2</sup> )	---	1.0	0.9	0.8	0.6	0.4
Avg. mol. wt. $\bar{M}$	128.29	128.38	128.46	128.54	128.62	124.77
Titanium ion conc. N <sub>i</sub> ( 10 <sup>21</sup> ions/ cm <sup>3</sup> )	----	2.25	4.53	6.87	9.27	1.18
Inter ionic distance of titanium ions R <sub>i</sub> ( Å )	----	7.63	6.04	5.26	4.76	4.39
Field Strength F <sub>i</sub> (10 <sup>15</sup> cm <sup>-2</sup> )	----	2.11	3.37	4.45	5.44	6.39
Polaron Radius r <sub>p</sub> ( Å )	----	3.08	2.44	2.12	1.92	1.77

Table-2: Summary of data on differential thermal analysis of PbO-NaF-B<sub>2</sub>O<sub>3</sub>: Cr<sub>2</sub>O<sub>3</sub> glasses

Sample	T <sub>g</sub>	T <sub>c</sub>	T <sub>m</sub>	T <sub>c</sub> -T <sub>g</sub>	T <sub>m</sub> -T <sub>c</sub>	K <sub>gl</sub> = $\frac{T_c - T_g}{T_m - T_c}$
C <sub>0</sub>	417	568	880	151	312	0.484
C <sub>1</sub>	411	575	874	164	299	0.548
C <sub>2</sub>	405	568	875	163	307	0.531
C <sub>3</sub>	400	562	880	162	318	0.509
C <sub>4</sub>	410	575	874	165	299	0.552
C <sub>5</sub>	417	583	870	166	287	0.578

Table-3: Summary of the data on band positions (cm<sup>-1</sup>) of various absorption bands in the IR spectra of PbO-NaF-B<sub>2</sub>O<sub>3</sub>: Cr<sub>2</sub>O<sub>3</sub> glasses

Glass	Borate groups			Band due to CrO <sub>4</sub> <sup>2-</sup> (cm <sup>-1</sup> )	Band due to PbO <sub>4</sub> units (cm <sup>-1</sup> )
	BO <sub>3</sub> (cm <sup>-1</sup> )	BO <sub>4</sub> (cm <sup>-1</sup> )	B-O-B (cm <sup>-1</sup> )		
C <sub>0</sub>	1360	1175	725	-	485
C <sub>1</sub>	1359	1177	725	-	485
C <sub>2</sub>	1354	1182	725	-	485
C <sub>3</sub>	1348	1188	725	-	485
C <sub>4</sub>	1357	1175	725	885	485
C <sub>5</sub>	1364	1168	725	885	485

Table-4: Summary of data on optical absorption spectra of PbO-NaF-B<sub>2</sub>O<sub>3</sub>: Cr<sub>2</sub>O<sub>3</sub> glasses

Transition	Glass Samples					
	C <sub>0</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>
Cr <sup>3+</sup> transitions (nm)						
<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (F)	---	454	454	454	454	---
<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>2</sub>	---	666	666	666	666	---
Band due to Cr <sup>6+</sup> ions (nm)	---	---	---	---	380	380
Cut off Wavelength(nm)	393.1	397.6	402.4	406.7	374.1	369.4
Optical band gap (eV)	2.05	2.40	2.35	2.30	2.47	2.51

Table-5: Data on Magnetic Susceptibility and Other Related Parameters of PbO-NaF-B<sub>2</sub>O<sub>3</sub>:Cr<sub>2</sub>O<sub>3</sub> Glasses. (Taking m = 3.9 μB)

Glass	Susceptibility, χ (10 <sup>-5</sup> , emu)	Total Conc. of Cr <sub>2</sub> O <sub>3</sub> Ni (10 <sup>20</sup> ions/cm <sup>3</sup> )	Cr <sup>3+</sup> ion concentration N' (10 <sup>20</sup> ions/cm <sup>3</sup> )	N'/Ni
C <sub>1</sub>	7.52	22.5	16.65	0.74
C <sub>2</sub>	9.54	45.3	37.15	0.82
C <sub>3</sub>	12.65	68.7	62.15	0.91
C <sub>4</sub>	13.54	92.7	75.09	0.81
C <sub>5</sub>	19.58	118.0	75.52	0.64

Fig. 7 shows a typical ESR spectrum (recorded at room temperature) of PbO-NaF -B<sub>2</sub>O<sub>3</sub> glasses doped with different concentrations of Cr<sub>2</sub>O<sub>3</sub>; the spectrum of each glass exhibits an intense absorption signal centered at about g = 2.0 and a weak shoulder at g = 4.3. With increase in the concentration of chromium in the glass matrix, the

values of  $g$  almost remain unaltered; however the relative intensity of these lines is observed to increase up to 0.3 mol % and again decreased with increase in the concentration of  $\text{Cr}_2\text{O}_3$ . For chromium free glasses no ESR signal is detected.

Magnetic susceptibility of the present glasses measured at room temperature is observed to increase with  $\text{Cr}_2\text{O}_3$  content in the glass composition. From the values of magnetic susceptibilities, the concentration of  $\text{Cr}^{3+}$  ion is also evaluated (by taking magnetic moment of  $\text{Cr}^{3+}$  ions as  $3.9 \mu_B$ ) and presented in Table 5.

It is well known fact that the effect of introduction of modifiers like  $\text{PbO}$  and  $\text{NaF}$  into  $\text{B}_2\text{O}_3$  network is to convert the  $\text{sp}^2$  planar  $\text{BO}_3$  into more stable  $\text{sp}^3$  tetrahedral  $\text{BO}_4$  units in addition to non-bridging oxygens (NBO's). Each  $\text{BO}_4$  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  $\text{BO}_4$  units in the present glass system is evident from infrared spectral studies[29].  $\text{PbO}$  in general is a glass modifier and enters the glass network by breaking up the B-O-B bonds (normally the oxygens of  $\text{PbO}$  break the local symmetry while  $\text{Pb}^{2+}$  ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. Chromium ions seem to exist in both  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  states in  $\text{PbO-NaF-B}_2\text{O}_3$  glass network;  $\text{Cr}^{3+}$  ion enters the network as modifier whereas  $\text{Cr}^{6+}$  ion enters as network former with  $\text{CrO}_4^{2-}$  structural units [31,32]. As a modifier  $\text{Cr}_2\text{O}_3$  may enter the glass network by breaking up local symmetry and introduces coordinated defects known as dangling bonds in these glasses.

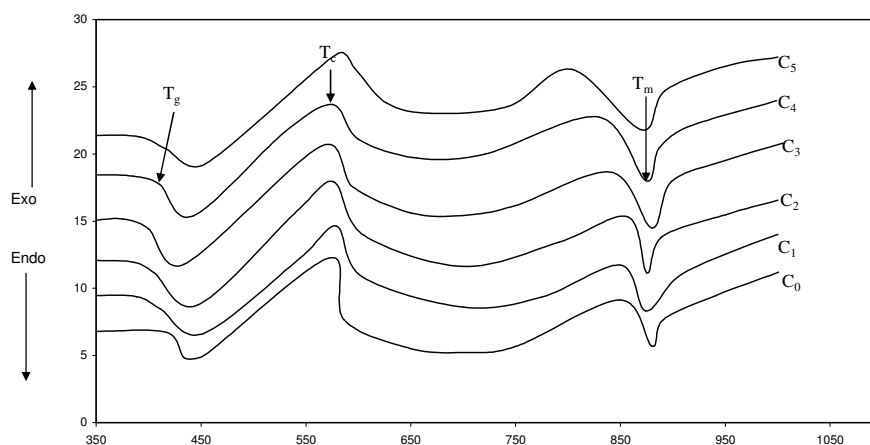


Fig.3. Differential Thermal Analysis patterns of  $\text{PbO-NaF-B}_2\text{O}_3:\text{Cr}_2\text{O}_3$  glasses

With the introduction of chromium ions from 0.1 to 0.3 mol %, the value of the glass transition temperature  $T_g$  has been observed to decrease but found to increase when the concentration of chromium ion is raised from 0.4 to 0.5 mol %, indicating that the glass  $\text{C}_5$  is more stable against devitrification. The augmented cross-link density and closeness of packing are responsible for such high values of  $T_c$  &  $(T_c-T_g)$  for this glass. In other words chromium ions in this glass network take part network forming positions with  $\text{CrO}_4^{2-}$  units. The results of DTA further suggests that in the glass networks of  $\text{C}_1$  to  $\text{C}_3$  chromium ions occupy network modifying positions and may decrease the rigidity of the glass network.

Recollecting the data on IR spectra, with the increase in the concentration of  $\text{Cr}_2\text{O}_3$ , up to 0.3 mol %, the intensity of the bands due to  $\text{BO}_3$  structural units has been observed to increase with a simultaneous decrease in the intensity of band due to  $\text{BO}_4$  units. This observation suggests that in this concentration range of  $\text{Cr}_2\text{O}_3$ , Cr ions in the glass network acts as modifiers and creates more disorder in the glass network. In the IR spectrum of glasses  $\text{C}_4$  and  $\text{C}_5$ , the vibrational band of  $\text{CrO}_4^{2-}$  units appeared at about  $885 \text{ cm}^{-1}$  and the intensity of this band is increasing with the increase of concentration from 0.4 to 0.5 mol %. From the IR spectra of the glasses shown in the Fig. 4 it is clear that the intensity of  $\text{BO}_4$  structural units is more for the glass  $\text{C}_5$  and the intensity due to  $\text{BO}_3$  units is less for the glass  $\text{C}_5$  shows that less number of Chromium ions exists in  $\text{Cr}^{3+}$  state in this glass. This is also very clear from

the data of Table 5. These results suggests that a part of Cr ions also exist in Cr<sup>6+</sup> state, that part occupying network forming positions[33].

Optical absorption spectra of the glasses show two prominent absorption bands at 454 and 666 nm; using Tanabe – Sugano diagrams for d<sup>3</sup> ions, the spectrum has been analyzed and the bands are assigned to <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub>(F), <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>2</sub> transitions respectively. The observed kinks on <sup>4</sup>T<sub>2</sub> band at 684 and 700 nm have been attributed to spin forbidden transitions <sup>4</sup>A<sub>2</sub> → <sup>2</sup>T<sub>1</sub> and <sup>4</sup>A<sub>2</sub> → <sup>2</sup>E respectively. Further, an increase in the widths of <sup>2</sup>E and <sup>2</sup>T<sub>1</sub> bands has clearly been observed with increase in the concentration of chromium ions form 0.1 to 0.3 mol %. Such an increase indicates an increase of disorder in the glass network, may be due to the increasing concentration of induced heterogeneous nucleation centers in the glass network that separate and reduce the long range order of chromium and borate groups[29,30]. In the spectrum of the glasses C<sub>4</sub> and C<sub>5</sub> a kink at 380 nm is observed. This observation indicates the presence of part of chromium ions in Cr<sup>6+</sup> state. This band is attributed to the excitation of Cr<sup>6+</sup> ions, which exist in the form of Cr<sup>6+</sup> and O<sup>2-</sup> centers in the frame of CrO<sub>4</sub><sup>2-</sup> groups [31]. These CrO<sub>4</sub><sup>2-</sup> groups may alternate with BO<sub>4</sub> and PbO<sub>4</sub> structural units. The decrease in the intensity of the absorption bands at 454, 666 nm and the appearance of a new band at 380 nm in the spectrum of glasses C<sub>4</sub> and C<sub>5</sub> indicates the conversion of a part of chromium ions from Cr<sup>3+</sup> state to Cr<sup>6+</sup> state[33]. Since the intensity of the peak at 380 nm is more for C<sub>5</sub> hence Cr<sup>6+</sup> ions are more in the glass C<sub>5</sub> and glass C<sub>5</sub> represents a more stable glass than others in the prepared samples.

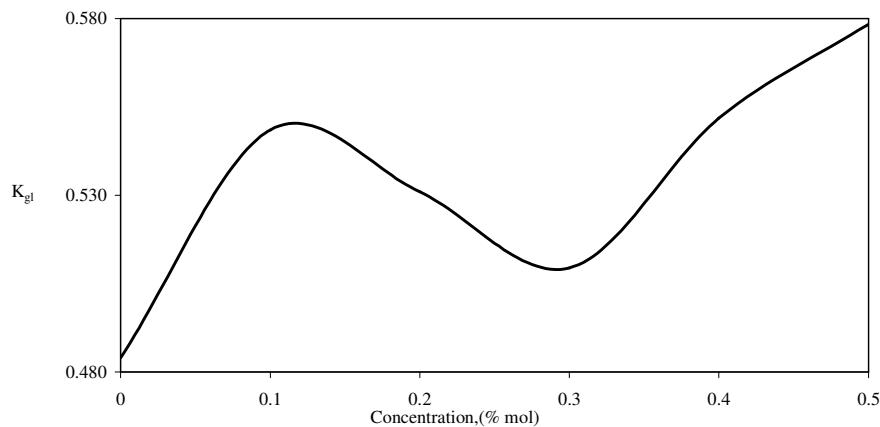


Fig.3A. The Variation of Hurby's parameter K<sub>gl</sub> with concentration of Cr<sub>2</sub>O<sub>3</sub> of PbO-NaF-B<sub>2</sub>O<sub>3</sub> glasses

These Cr<sup>6+</sup> ions act as glass formers and similar to any other conventional glass formers; these former ions in the glass network decrease in the concentration of bonding defects and non-bridging oxygens (NBO's). The higher the concentration of such formers, the lower is the concentration of NBO's in the glass matrix. The increasing presence of these ions increases the optical band gap and shifts the absorption edge towards lower wavelength side as observed for glass C<sub>5</sub> (Fig. 5).

In an octahedral field, the ground level of the Cr<sup>3+</sup> [d<sup>3</sup>] ion is <sup>4</sup>A<sub>2g</sub>; under the field action of low symmetry component and spin orbit coupling, four-fold degenerate spin state splits into two Kramers doublets  $\left| \pm \frac{3}{2} \right\rangle$  and

$\left| \pm \frac{5}{2} \right\rangle$ . The separation between these two doublets leads to the resonance at g = 2 to 5. According to the theory of

Landry the low field portion [at g ~ 5] of the spectrum is attributed to the isolated Cr<sup>3+</sup> ions that have local rhombic sites subjected to strong crystal field effects. The high field signal[34-36] [at g ~ 2] mainly due to the exchange coupled pairs Cr<sup>3+</sup> - Cr<sup>3+</sup>. The fall in the intensity of g ~ 4.3 lines in Fig.7 with increase in the content of chromium beyond 0.3 mol % indicates a decrease in the concentration of isolated Cr<sup>3+</sup> ions[33]. Thus, the measurements on

ESR spectra of the present glasses also predict a decrease in the degree of disorder in the glass network with increase in the content of chromium ions beyond 0.3 mol %.

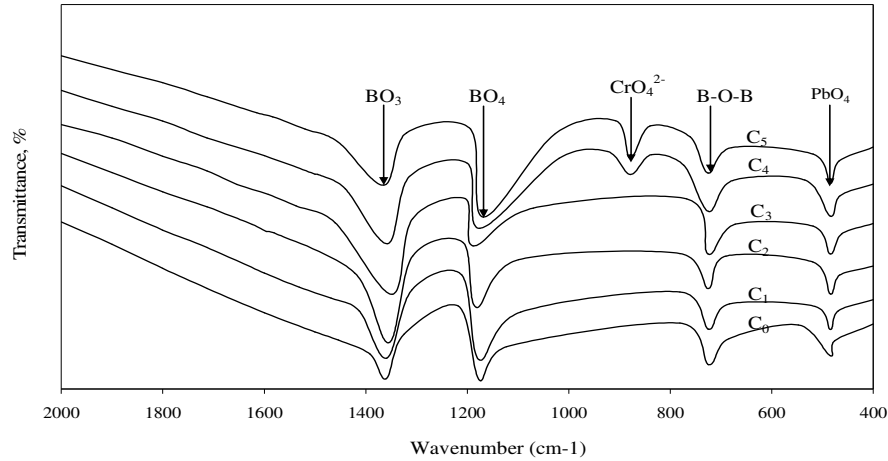


Fig. 4: IR spectra of PbO-NaF-B<sub>2</sub>O<sub>3</sub>:Cr<sub>2</sub>O<sub>3</sub>

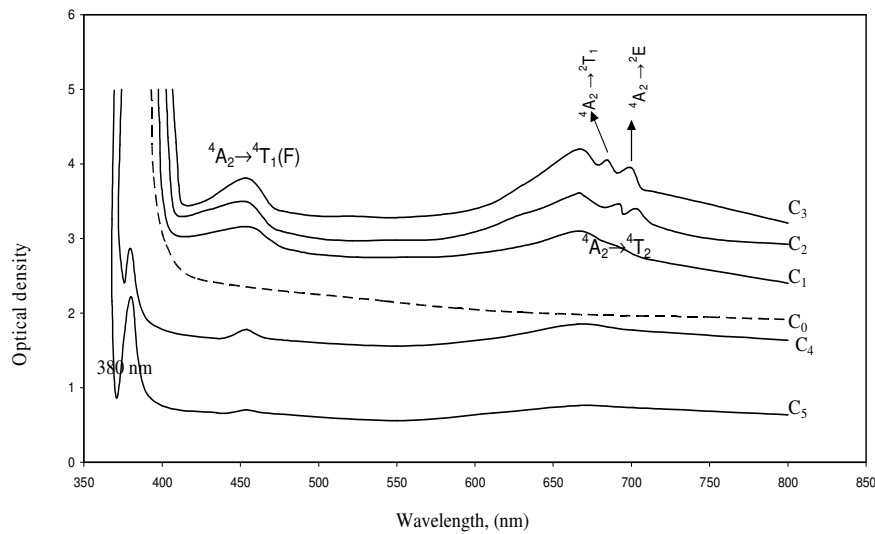


Fig. 5. Optical absorption spectra of PbO-NaF-B<sub>2</sub>O<sub>3</sub>: Cr<sub>2</sub>O<sub>3</sub> glasses.

The magnetic properties of these glasses arise from the paramagnetic Cr<sup>3+</sup> ions with 3d<sup>3</sup> electrons. The concentration of Cr<sup>3+</sup> ions (N') evaluated from magnetic susceptibility is found to increase with increase in the total chromium ion concentration shown in Table 5; however, the fraction (N'/N<sub>i</sub>), i.e., the ratio of Cr<sup>3+</sup> ions (N') to the total concentration of the chromium ions (N<sub>i</sub>) is found to increase up to 0.3 mol % of Cr<sub>2</sub>O<sub>3</sub> and observed to decrease beyond this concentration. From this observation it is also clear that octahedrally coordinated Cr<sup>3+</sup> ions are less in C<sub>5</sub>



glass sample and thus more number of  $\text{Cr}^{3+}$  ions are turned up to  $\text{Cr}^{6+}$  ions which will enter the glass net work as former and leads to much stability.

## CONCLUSIONS

The conclusions drawn from the study of various physical properties of  $\text{PbO-NaF-B}_2\text{O}_3:\text{Cr}_2\text{O}_3$  glasses are summarized as follows:

The optical absorption measurements indicate highest optical band gap for the glass  $\text{C}_5$ . The magnetic susceptibility measurements show the lowest value of the ratio of  $\text{Cr}^{3+}$  ion concentration to the total chromium ion concentration for the glass  $\text{C}_5$  indicating the presence of the highest concentration of  $\text{Cr}^{6+}$  ions which participate in the network forming positions. The glass transition temperature  $T_g$  and the related parameters such as  $T_c-T_g$  and Hurby's parameter ( $K_{g1}$ ) are also found to be the highest for glass  $\text{C}_5$ . These findings indicate the structure of  $\text{PbO-NaF-B}_2\text{O}_3$  glass is more stable when the concentration of  $\text{Cr}_2\text{O}_3$  present in the glass network is around 0.5 mol%.

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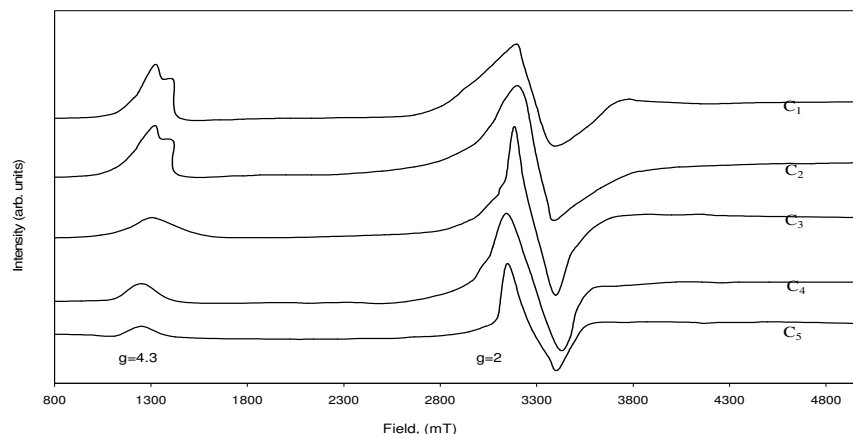


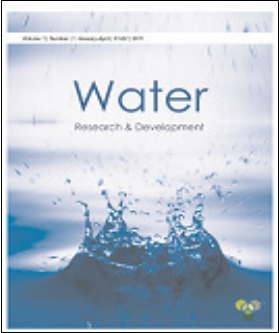
Fig. 7. ESR spectra of  $\text{PbO-NaF-B}_2\text{O}_3:\text{Cr}_2\text{O}_3$  glasses

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