

Physical properties of PbO-Al₂O₃-B₂O₃ glasses doped with Cr₂O₃

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PbO-Al₂O₃-B₂O₃ glasses containing different concentrations of Cr₂O₃ ranging from 0 to 0.4 mol % were prepared. The dielectric properties (constant ϵ , loss $\tan\delta$, ac conductivity σ_{ac} over a range of frequency and temperature and breakdown strength) of these glasses have been studied. The results of these studies were analyzed with the aid of data on optical absorption, IR spectra and thermoluminescence studies on these glasses. The analysis suggests that the chromium ions exist in Cr³⁺ state which act as modifiers. When Cr₂O₃ is present in higher concentrations in the glass matrix, these ions seem to exist in Cr⁶⁺ state and take part in network forming positions with CrO₄²⁻ structural units.

Keywords: PbO-Al₂O₃-B₂O₃, Chromium ions, Optical absorption, Thermoluminescence, Dielectric properties

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1 Introduction

Alkali free alumino borate glasses like PbO-Al₂O₃-B₂O₃ are very stable against devitrification, possess high mechanical strength, toughness, and excellent electrical properties and have very low thermal expansion coefficients. These glasses are well known to resist attack by alkali metals because of the formation of kinetically limiting surface reaction products. In view of these qualities, these glasses find variety of applications in battery sealing and other micro electronic packaging¹⁻³.

Over the past few years, the study on the role of transition metal ions on the physical properties of various inorganic glass systems has been the subject of a great deal of interest⁴⁻¹⁴. These ions are being extensively used in the present days to probe the glass structure since their outer d-electron orbital functions have broad radial distribution and due to their high sensitive response to the changes in the surrounding actions. The transition metal ions such as iron, chromium, manganese etc., dissolved in PbO-Al₂O₃-B₂O₃ glass matrix even in very small quantities, influence the physical properties very strongly and owing to the presence of these ions, the glasses may possess magnetic properties. The presence of transition metal ions in different oxidation states with different coordinations is mainly responsible for bringing significant changes in the physical properties of the glasses. Among various transition metal ions, chromium ions in particular, are well known for their

overwhelming influence on the optical properties; further these ions are expected to raise or lower the chemical durability (depending up on their concentration), mechanical strength and electrical resistance of the glasses. Chromium, exists in Cr²⁺, Cr³⁺, Cr⁵⁺ and Cr⁶⁺ states in glass matrices. Of these, Cr³⁺ and Cr⁵⁺ are paramagnetic ions and in general act as a modifier whereas Cr⁶⁺ ions are expected to take part in the network forming positions¹⁵⁻¹⁷.

Recently, we have reported the results of studies on spectroscopic properties of some rare earth ions (Ho³⁺ and Er³⁺) in PbO-Al₂O₃-B₂O₃ glasses^{18,19}. These studies have yielded valuable information regarding the lasing characteristics of these glasses. The present investigation is aimed at an understanding of the local environment of chromium ions in PbO-Al₂O₃-B₂O₃ glass network and their influence on the stability of the glass network by means of the optical absorption, ESR, IR, thermoluminescence and electrical properties viz., dielectric constant ϵ , dielectric loss $\tan\delta$ and ac conductivity σ_{ac} in the frequency range 10²-10⁵ Hz and in the temperature range 30-300°C and dielectric breakdown strength in air medium.

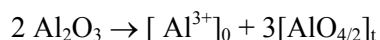
Our earlier studies²⁰ indicated that with in the glass forming region²¹ of PbO-Al₂O₃-B₂O₃ glass system, the glass of the composition: 19 PbO-5Al₂O₃-76B₂O₃, is found to be highly resistant against devitrification and found to possess high mechanical strength. Hence, this composition is chosen for Cr₂O₃ doping in the present study. The details of the composition of

this study are: 19 PbO-5Al₂O₃-(76-x) B₂O₃: x Cr₂O₃ with $0 \leq x \leq 0.4$ in steps of 0.1 (all in mol %) and the glasses are labeled as C₁, C₂, C₃ and C₄ with the concentration of Cr₂O₃ as 0.1, 0.2, 0.3 and 0.4, respectively. Beyond 0.4 mol % of Cr₂O₃, clear transparent glasses could not be formed. The preparation of the glasses and the experimental techniques adopted for measuring dielectric properties and for recording optical absorption, ESR and IR spectra are similar to those reported in earlier papers from our laboratory²²⁻²⁷.

2 Results and Discussion

In general, the properties of a glass depend upon its composition and to a considerable extent upon its structure. Lead alumino borate glasses doped with Cr₂O₃ have complex composition and are an admixture of network formers and modifiers. B₂O₃ is well known network former with BO₃ structural units. It is well known that the effect of introduction of modifier oxide like PbO into B₂O₃ glass matrix is the conversion of sp² planar BO₃ units into more stable sp³ tetrahedral BO₄ units and may also create non-bridging oxygen ions. Each BO₄ unit is linked to two such units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedron.

In addition to the modifier action, PbO may also participate in the glass network with PbO₄ units; the presence of such units can be visualized from the observation of a weak but definite band around 450 cm⁻¹ in the IR spectra of PbO-Al₂O₃-B₂O₃ glasses. Further, aluminium can also occupy both tetrahedral sites (viz., substitutional or network formers) and octahedral sites (viz., interstitial or network modifiers)^{28, 29} i.e.



Chromium may exist in both Cr³⁺ and Cr⁶⁺ states in PbO-Al₂O₃-B₂O₃ glass network; Cr³⁺ ion enters the network as modifier whereas Cr⁶⁺ ion enters as network former with CrO₄²⁻ structural units^{29,30}. As modifier, Cr₂O₃ may enter the glass network by breaking up local symmetry and introduces coordinated defects known as dangling bonds in these glasses. The concentration of such bonding defects in the glass network depends upon the concentration of Cr₂O₃.

From the measured values of density d and calculated average molecular weight $\bar{M}$, various

physical parameters such as chromium ion concentration N_i , mean chromium ion separation R_i which are useful for understanding the physical properties of these glasses are evaluated using standard formulae³¹ and presented in Table 1

Fig. 1 shows the optical absorption spectra of PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses recorded in the wavelength range 275-800 nm at room temperature; absorption spectrum of glass C₁ (glass containing 0.1 mol% of Cr₂O₃), has shown three clearly resolved absorption bands with peaks at 330, 440 and 645 nm and a shoulder at 710 nm. With the increase in the concentration of Cr₂O₃, no considerable changes in the positions of these bands have been observed but the overall intensity of absorption is noticed to decrease; in addition, a kink at about 370 nm, (with increasing intensity with the concentration of Cr₂O₃) has been observed. The absorption edge that observed at 305 nm for glass C₁, is found to shift gradually towards lower wavelength with increase in the concentration of Cr₂O₃. From the observed absorption edges, the optical band gaps (E_o) of these glasses are evaluated by drawing Urbach plot between $(\alpha \hbar \omega)^{1/2}$ and $\hbar \omega$ as per the equation:

$$\alpha(\omega) \hbar \omega = C (\hbar \omega - E_o)^2 \quad \dots (1)$$

Fig. 2 shows the Urbach plots of all these glasses in which a part of each curve is observed to be linear. The values of optical band gap (E_o) obtained from these plots for PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses are presented in Table 2. The value of optical band gap is found to increase with the increase in concentration of Cr₂O₃.

Using Tanabe-Sugano diagrams of d^3 ion, the spectra have been analyzed and the bands at 330, 435 and 645 nm and are assigned to $^4A_2 \rightarrow ^4T_1(P)$, $^4A_2 \rightarrow ^4T_1(F)$, $^4A_2 \rightarrow ^4T_2$ transitions, respectively with the LF parameters D_q (crystal field splitting energy) = 1550 cm⁻¹ and B (Racah parameter) = 670 cm⁻¹. The weak band observed at 710 nm has been identified due to spin forbidden transition $^4A_2 \rightarrow ^2E$ transition³². These observations indicate the presence of chromium ion in Cr³⁺ state in octahedral environment in the glass matrix. The kink observed at 370 nm in the spectra of the glasses containing Cr₂O₃ > 0.1%, has been assigned to CrO₄²⁻ (T_d) ions³³; such an observation indicates the presence of a part of chromium ions in Cr⁶⁺ state in these glasses. With the increase in the concentration of Cr₂O₃, the intensity of this band has been observed to increase at the expense of octahedral

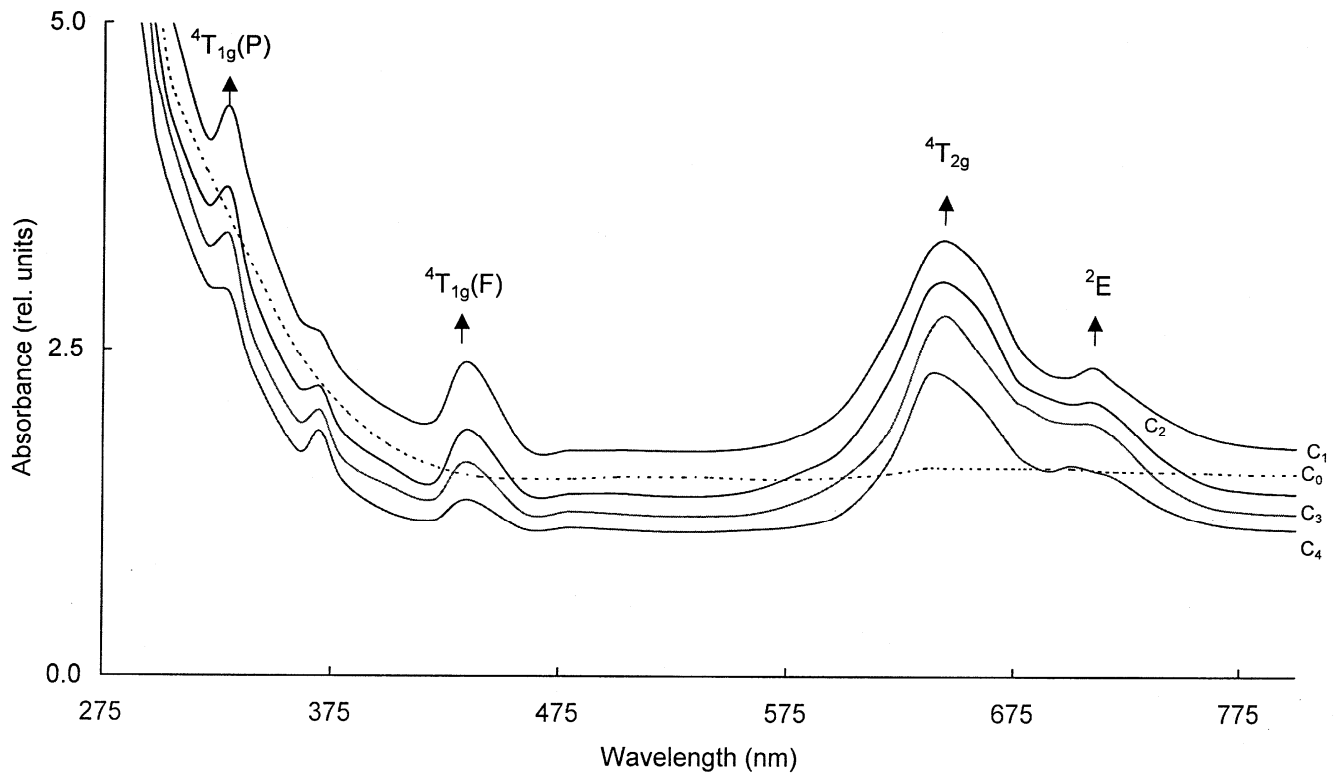


Fig.1—Optical absorption spectra of PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses recorded at room temperature; the transitions shown are from the ground state $4A_2$

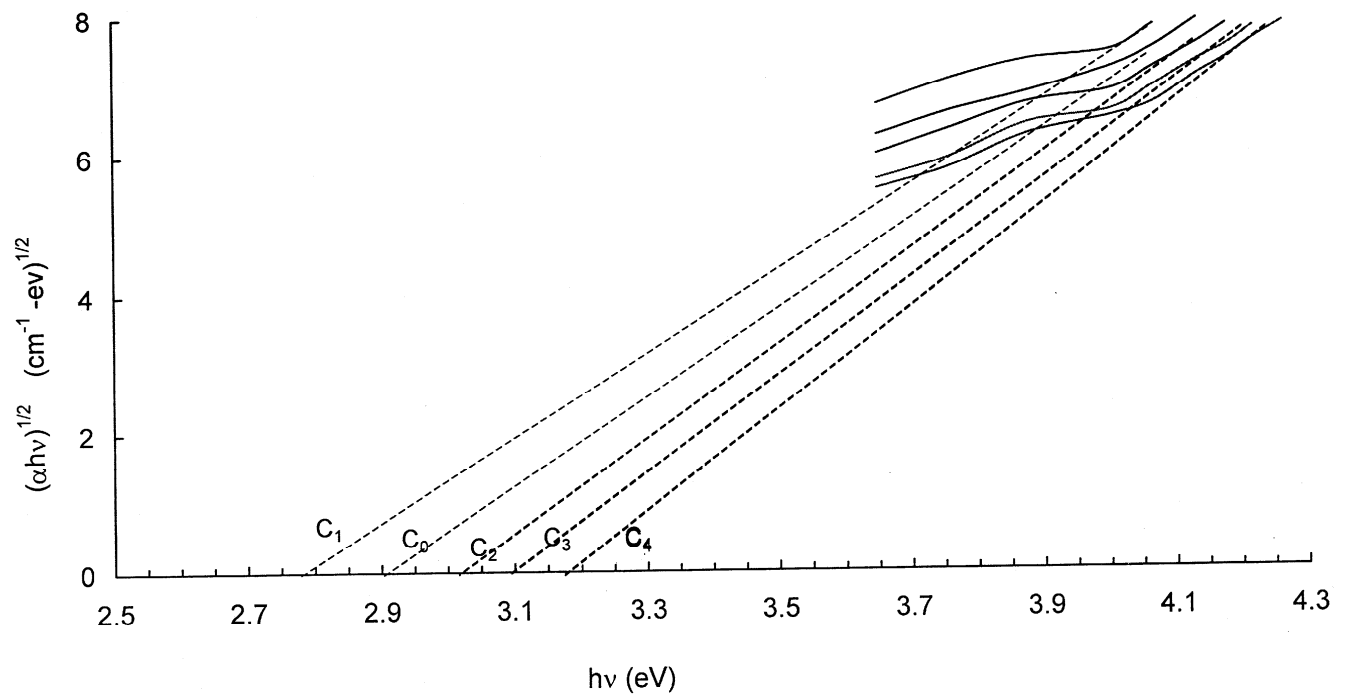


Fig. 2—Urbach plot of PbO-Al₂O₃-B₂O₃ glasses

Table 1—Various physical parameters of PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses

Glass	d (g/cm ³)	$\bar{M}$	N_i (10 ²¹)/cm ³	R_i (Å°)	T_g (°C)
Pure	2.700	100.40	—	—	528
C ₁	2.695	100.49	1.62	8.52	522
C ₂	2.693	100.57	3.23	6.77	540
C ₃	2.692	100.65	4.83	5.91	544
C ₄	2.690	100.73	6.43	5.38	548

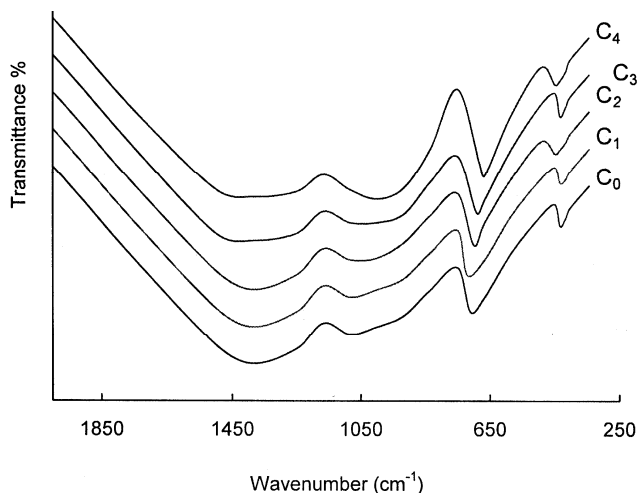
Table 2—Summary of data on optical absorption edge of PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses

Glass	Cut-off wavelength (nm)	Optical band gap E_0 (eV)
Pure	300	2.91
C ₁	305	2.85
C ₂	297	3.05
C ₃	295	3.10
C ₄	291	3.20

bands; these observations reveal that as the concentration of Cr₂O₃ increases, there is a gradual conversion of chromium ions from Cr³⁺ state to Cr⁶⁺ state. The gradual shifting of absorption edge with increase in the concentration of Cr₂O₃ towards lower wavelengths also indicates an increasing concentration of Cr⁶⁺ ions that take part in the network forming positions with CrO₄²⁻ structural units. Lower the concentration of the Cr³⁺ ions that act as modifiers, lower is the concentration of non-bridging oxygen ions (NBO's) in the glass matrix. This leads to a decrease in the degree of localization of the electrons, thereby decreasing the donor centres in the glass matrix. The presence of low concentration of the donor centres raises the optical band gap and shifts the absorption edge towards lower wavelength side (Table 2).

Infrared spectra of PbO-Al₂O₃-B₂O₃ glasses recorded at room temperature in the wavenumber range 200-4000 cm⁻¹ have exhibited three groups of bands: (i) in the region 1200-1600 cm⁻¹ (ii) in the region 800-1200 cm⁻¹ and (iii) a band around 710 cm⁻¹. In addition, in the spectra of all the glasses, a weak but a definite band around 450 cm⁻¹ is also observed; the introduction of Cr₂O₃ into the glass matrix does not show any additional bands. In the spectrum of C₁, the intensity of the second group of bands decreased considerably and the meta-center is shifted towards slightly higher wave number; with the successive increase in the concentration of Cr₂O₃ the intensity of this group bands is observed to increase (Fig. 3).

The first group of bands observed in the region 1200-1600 cm⁻¹ represent the conventional stretching

Fig. 3—Infrared spectra of PbO-Al₂O₃-B₂O₃ glasses recorded at room temperature

vibrations of boron-oxygen bond of trigonal BO₃ units whereas the second group of bands in the region 800-1200 cm⁻¹ is identified due to B-O bond stretching vibrations of the tetrahedral BO₄ units. The distinct band observed at 710 cm⁻¹ can be attributed to the bending of B-O-B linkages in borate network^{34,35}. Incidentally a band due to AlO₄ structural units also lie in this region³⁶. In view of this, we may expect the linkages of the type B-O-Al. The weak band observed around 450 cm⁻¹ is an indicative of the presence of PbO₄ units in the glass network^{37,38}. The successive increase in the intensity of the second group of bands with increase in the concentration of Cr₂O₃ beyond 0.1 mol % indicates an increase in the presence of structurally more ordered BO₄ units that strengthen the glass network. Thus, the results of IR spectra also supports the viewpoint that as the concentration of Cr₂O₃ increases gradually, the concentration of chromium ions that take part modifying positions with Cr³⁺ state will be gradually converted to Cr⁶⁺ state that participate in the network forming with structural units.

Fig. 4 presents the thermoluminescence glow curves of PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses irradiated with X-rays. The pure glass exhibits a TL peak at 400 K. The introduction of Cr₂O₃ (0.1 mol %) into the glass does not produce any additional glow peaks; however, the intensity of the existing glow peak is observed to decrease. Further, increase in the concentration of Cr₂O₃ caused shifting of peak temperature towards lower side with increase in the intensity of the glow curve. The variation of TL light output with the concentration of Cr₂O₃ is shown in the

inset of Fig. 3. The trap depth parameters corresponding to these glow curves are evaluated using Chen's formulae³⁹ and presented in Table 3.

The action of X-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse in the glass network depending upon their energy and the composition of the glass and are finally be trapped, thus forming colour centres (or alternatively they may form excitons with energy states in the forbidden gap). The trapping sites may be the metal cations which constitute the glass structure, ions of admixtures to the main composition and the structural defects due to impurities in the glass. Thus, this process leads to the formation of (1) boron electron centres, (2) non-bridging oxygen hole centres and (3) boron oxygen hole centres. Thermoluminescence is a consequence of radiative recombination between the electrons (released by heating from electron centre) and an anti-bonding molecular orbital of the nearest of the oxygen hole centres.

The optical absorption spectra of X-ray irradiated glasses were also recorded prior to the TL measurements; the spectra do not reveal any new bands and no noticeable change in the positions of the existing bands, has been observed. Thus, the X-ray

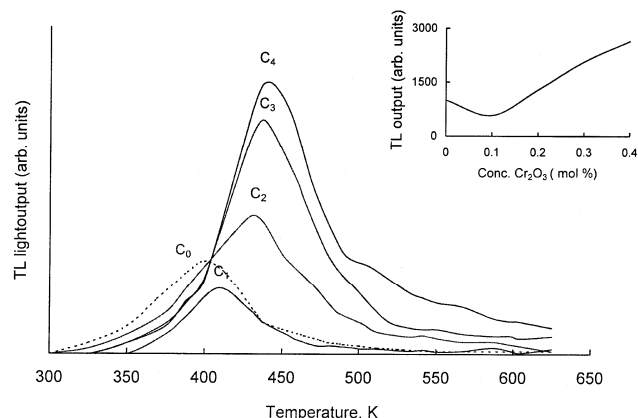


Fig.4—Thermoluminescence light output of X-ray irradiated PbO-Al₂O₃-B₂O₃ glasses doped with different concentrations of Cr₂O₃. Inset gives the variation of TL light output with the concentration of Cr₂O₃

irradiation of the glasses does not cause any change in the existing oxidation states of the transition metal ions in the glass network.

The most probable local structure likely to occur for Cr³⁺ is as a CrO₆ octahedron entwined with a BO₄ tetrahedrons, CrBO₉. Let us assume that the Cr³⁺ ions are uniformly distributed throughout the glass, and each Cr³⁺ ion acts as a TL killer. In the absence of Cr³⁺ ion from the centre of sphere of killing action, each electron released by heating from electron centre would be caught by an anti-bonding molecular orbital of the nearest of the oxygen hole centre present in this volume. In the presence of Cr³⁺ ions, the electrons released by heating from electron centres would be trapped at Cr³⁺ ions and inhibits the radiative recombination of electron and hole centres leading to a reduction in the TL light output. When Cr₂O₃ is present in higher concentrations (> 0.1%), the concentration of Cr³⁺ ions seems to be decreasing, resulting in a gradual increase of TL light output. Thus, the study on thermoluminescence of PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses indicates, when the concentration Cr₂O₃ is >0.1% in the glass network, there is a decrease in the concentration of Cr³⁺ ions that act as TL killers.

The dielectric constant ϵ and loss $\tan \delta$ at room temperature (30°C) of PbO-Al₂O₃-B₂O₃ glass (pure) at 100 kHz are measured to be 8.8 and 0.0009, respectively; these values are found to increase with the decrease in frequency. With the introduction of Cr₂O₃ (0.1%), the values of dielectric constant ϵ and loss $\tan \delta$ are found to increase slightly and thereafter these parameters are found to decrease gradually with the concentration of Cr₂O₃; further, for any particular concentration of Cr₂O₃, the values of ϵ and $\tan \delta$ are found to decrease considerably with increase in frequency. Fig. 5 shows the variation of dielectric constant and loss with the concentration of Cr₂O₃ at a frequency of 1 kHz measured at room temperature.

The temperature dependence of dielectric constant ϵ at different frequencies for glass C₁ is shown in Fig. 6(a); ϵ increases slowly up to about 100°C and

Table 3—Data on various trap depth parameters of PbO-Al₂O₃-B₂O₃:Cr₂O₃ glasses

Glass	T_m (K)	τ (K)	δ (K)	μ_g	$E\tau$ (eV)	E_δ (eV)	area(au)
Pure	400	30	46	1.53	0.58	0.29	1003
C ₁	409	25	37	1.48	0.75	0.38	577
C ₂	428	32	33	1.02	0.61	0.48	1290
C ₃	437	27	34	1.25	0.78	0.46	2071
C ₄	444	35	34	0.97	0.60	0.48	2650

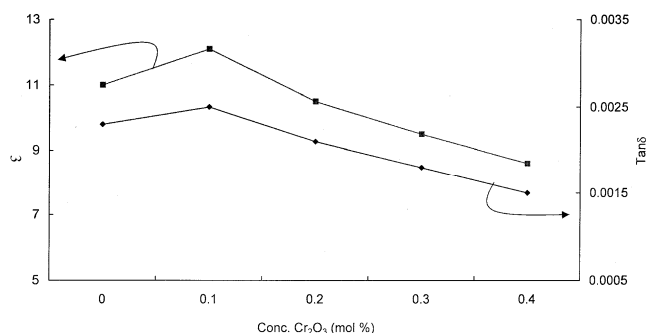


Fig. 5—Variation of dielectric constant and loss with the concentration of Cr₂O₃ at room temperature measured at 1 kHz

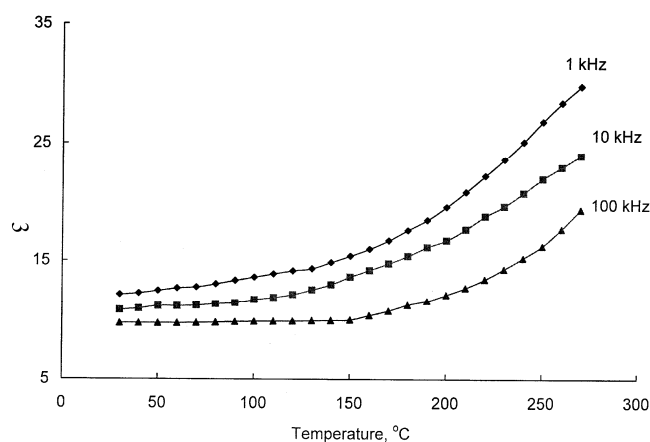


Fig. 6(a)—Variation of dielectric constant with temperature at different frequencies for glass C₁

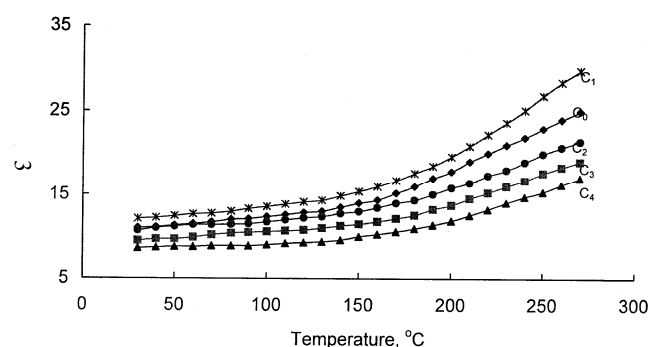


Fig. 6 (b)—Comparison plot of variation of dielectric constant with temperature (measured at 1 kHz) for PbO-Al₂O₃-B₂O₃ glasses doped with different concentrations of Cr₂O₃

beyond this temperature, ϵ increases rapidly and is highly frequency dependent with larger values at lower frequencies. Similar behaviour is shown by ϵ with temperature for all the other glasses. Fig. 6(b) shows the variation of ϵ with temperature measured at 1 kHz for PbO-Al₂O₃-B₂O₃ glasses doped with

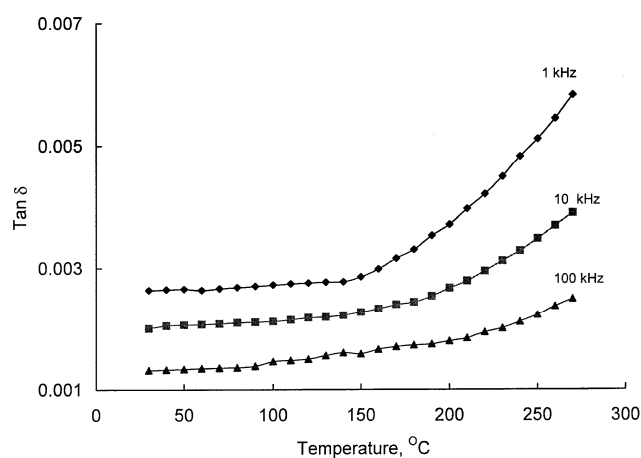


Fig. 7(a)—Variation of dielectric loss with temperature at different frequencies for glass C₂

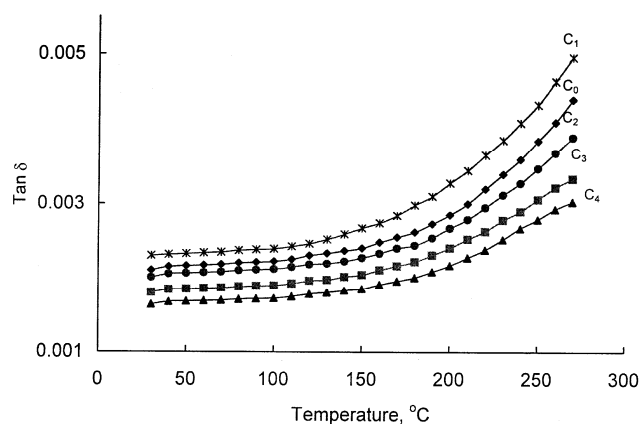


Fig. 7(b)—Comparison plot of variation of dielectric loss with temperature (measured at 10 kHz) for PbO-Al₂O₃-B₂O₃ glasses doped with different concentrations of Cr₂O₃

different concentrations of Cr₂O₃. It is observed that the rate of increase of ϵ with temperature is decreased gradually from glass C₁ to glass C₄. The variation of dielectric loss $\tan \delta$ with temperature also exhibited a similar behaviour. A plot of variation of dielectric loss $\tan \delta$ with temperature at different frequencies for glass C₂ is shown in Fig.7(a) and for different concentrations at 10 kHz is shown in Fig.7(b).

The *ac* conductivity σ_{ac} is calculated at different temperatures using,

$$\sigma_{ac} = \omega \epsilon \epsilon_0 \tan \delta \quad \dots (2)$$

where ϵ_0 is the vacuum dielectric constant for different frequencies and the plots of $\log \sigma_{ac}$ against

$1/T$ are shown in Fig. 8 for all the glasses at 100 kHz. From these plots, the activation energy for conduction in the high temperature region over which a near linear dependence of $\log \sigma_{ac}$ with $1/T$ could be observed, is evaluated and presented in Table 4; the activation energy is found to be the lowest for the glass containing 0.1% Cr_2O_3 and observed to decrease with further increase in the concentration of Cr_2O_3 .

The dielectric breakdown strength for pure glass is determined to be 18.80 kV/cm. With the introduction of Cr_2O_3 (0.1%), the value of this breakdown strength is lowered to 18.50 kV/cm and for further increase of Cr_2O_3 , the breakdown strength is observed to increase (Table 4). Among various electrical polarizations (viz., electronic, ionic, orientation and space charge), the space charge polarization depends on the purity and perfection of the glasses. The considerably higher values of dielectric constant and loss of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{:Cr}_2\text{O}_3$ glasses at room temperature observed at low frequencies, may be ascribed to the bonding defects produced in the glass network which contributes to the space charge polarization.

With the introduction of Cr_2O_3 up to 0.1%, the values ϵ , $\tan \delta$ and σ_{ac} are found to increase at any frequency and temperature and activation energy for *ac* conduction is observed to decrease with respect to those of pure sample; such variations of these parameters are obviously due to the presence of

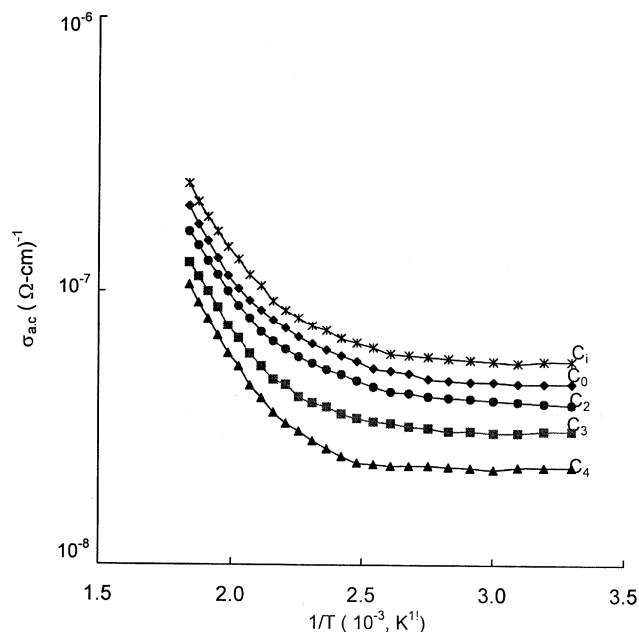


Fig. 8—Comparison plot of variation of *a.c.* conductivity with $1/T$ (at 100 kHz) for $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses doped with different concentrations of Cr_2O_3

Table 4—Summary of data on *ac* conductivity and dielectric breakdown strength of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{:Cr}_2\text{O}_3$ glasses

Glass	$N(E_F)$ (10^{20} , $\text{eV}^{-1}/\text{cm}^3$)	AE (eV)	Breakdown strength (kV/cm)
Glass C_1	1.06	0.27	18.50
Glass C_2	0.90	0.30	19.25
Glass C_3	0.78	0.31	21.55
Glass C_4	0.65	0.33	22.36

octahedral Cr^{3+} ions in the glass network which acts as modifiers. As modifiers, these ions, weaken the glass network and create pathways suitable for migration of free ions that build-up space charge. The weaker the glass network more is the space charge polarization, resulting an increase in the dielectric parameters.

However, when Cr_2O_3 is present in higher concentrations (greater than 0.1%), we observe that the values of the dielectric parameters to decrease with increase in Cr_2O_3 concentration. Such a decrease of these parameters suggests the presence of chromium ions in Cr^{6+} state with CrO_4^{2-} -structural units that take part in network forming positions in this concentration range. This causes a decrease in the degree of depolymerisation of the glass network leading to a decrease in the space charge polarization. Further, in these glasses there is a possibility for the cross-linking of a part of AlO_3 units with CrO_4^{2-} -units to form Al-O-Cr bonds in the glass network which is reasonable because of close ionic radii of Al^{3+} (0.51 Å) and Cr^{6+} (0.52 Å). Such cross-links also decrease the space charge polarization leading to reduction in the values of dielectric parameters in the glasses.

A near linear relationship seems to exist between $\sigma(\omega)$ versus activation energy for conduction (in the high temperature region) (Table 4). This observation suggests a random cite model for conduction in these glasses and the conductivity enhancement is directly related to the increasing mobility of the charge carriers in the high temperature⁴⁰.

The low temperature part of the conductivity (a near temperature independent part, as in the case of present glasses up to nearly 100°C) can be explained on the basis of quantum mechanical model⁴¹ similar to many other glass systems reported recently from our laboratory⁴²⁻⁴⁴. The value of $N(E_F)$ i.e. the density of the energy states near the Fermi level, evaluated using the equation⁴¹.

$$\sigma\omega = (\pi/3) e^2 kT [N(E_F)]^2 \alpha^{-5} \omega [\ln(v_{ph}/\omega)]^4 \quad \dots (3)$$

with the usual meaning of the symbols reported in earlier papers⁴²⁻⁴⁴ and furnished in Table 4. The value

of $N(E_F)$ is found to decrease from glass C₁ to glass C₄ indicating a decrease in the concentration of Cr³⁺ ions that take modifier positions.

The insulating strengths of a dielectric, may be regarded as the breakdown intensity of an electric field i.e. magnitude of the intensity of field in a dielectric upon attainment of which a breakdown occurs. Electric breakdown develops as a results of inelastic displacement of bound charges such as electrons, ions in a dielectric under the action of external electric field.

Additionally, in the electric field, the heat of dielectric loss is liberated. If the applied field is an alternating field, the specific dielectric loss i.e., the loss per unit volume of the dielectric is given by⁴⁵:

$$\rho_i = E^2 \omega \epsilon \epsilon_0 \tan \delta \text{ W/m}^3 \quad \dots (4)$$

Eq.(4) indicates that the higher the values of $\epsilon \tan \delta$ of the glass at a given frequency, higher are the values of ρ_i . In a dielectric across which the voltage is applied, heat is liberated, the temperature of the dielectric then raises and the loss increases still more. The dielectric breakdown strength is in fact inversely proportional to the specific dielectric loss represented by Eq. (4).

Our observations on breakdown strengths of PbO-Al₂O₃-B₂O₃ glasses doped with either Cr₂O₃ indicate the rate of increase of $\epsilon \tan \delta$ with temperature which is the highest for C₁ glass and the lowest for glasses C₄. Though, the breakdown strengths are actually determined at room temperature, the heat liberated during the breakdown, raises the temperature of the glass and hence raises the $\epsilon \tan \delta$ value. Since the rate of increase of $\epsilon \tan \delta$ with temperature is the highest for glass C₁, the breakdown strength (which is inversely proportional to ρ_i) is the lowest when compared with the other glasses. Thus, the experiments on the dielectric breakdown strength of PbO-Al₂O₃-B₂O₃ glasses doped with Cr₂O₃ reveal that there is a decrease in the disorderliness in the glass network with increase in concentration of Cr₂O₃ beyond 0.1 mol %.

3 Conclusions

Hence, the optical absorption spectral studies indicate that chromium ions are predominantly in the Cr³⁺ state and adopt octahedral (or modifier) positions if Cr₂O₃ is present in low concentrations (~ 0.1 mol %) in the glass matrix. The concentration of such ions is found to be decrease as the concentration of Cr₂O₃

increases in the glass matrix. These studies also indicate the presence of chromium ions in the Cr⁶⁺ state in CrO₄²⁻ structural groups that adopt network-forming positions if Cr₂O₃ is present in higher concentrations. The results of IR spectral studies show, an increasing concentration of more orderly structured borate groups (BO₄ structural units), if the concentration of Cr₂O₃ is increased beyond 0.1 mol % in the glass network. This result indicates a decreasing concentration of Cr³⁺ ions that act as modifiers or an increasing concentration of Cr⁶⁺ ions that adopt network-forming positions with CrO₄²⁻ structural units which strengthen the glass network. Quenching of thermoluminescence light output has been observed in the glasses containing 0.1 mol % of Cr₂O₃. This is attributed to the presence of a larger concentration of Cr³⁺ ions (that act as luminescence killers) in this glass. The high TL light output observed for the glasses containing high concentration of Cr₂O₃ > 0.1 mol %, vividly indicates the presence of low concentration of chromium ions in Cr³⁺ state. The dielectric parameters viz., ϵ , $\tan \delta$ and σ_{ac} are found to increase whereas the dielectric breakdown strength and the activation energy for ac conduction are found to decrease (when compared with those of pure glass). if Cr₂O₃ is present in low concentrations (~ 0.1 mol %) in the glasses, this is an indicative of an increasing depolymerization (or increasing disorder) of the glass network due to the presence of large concentration of Cr³⁺ ions that act as modifiers in this glass. The decreasing values of dielectric parameters (viz., ϵ' , $\tan \delta$ and σ_{ac}) and the increasing value of the activation energy for ac conduction, observed with increase in the concentration of Cr₂O₃ beyond 0.1 mol %, obviously suggests an increasing presence of chromium ions in Cr⁶⁺ state that take part in network forming positions with CrO₄²⁻ structural units in the glass network that ultimately cause to decrease the space charge polarization.

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