

Influence of manganese ions on electrical, spectroscopic and magnetic properties of PbO-Al₂O₃-B₂O₃ glasses

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PbO-Al₂O₃-B₂O₃ glasses containing small concentrations of MnO (ranging from 0 to 1.0 mol%) have been prepared. A number of studies, viz., dielectric properties (constant ϵ' , loss $\tan\delta$, a.c. conductivity σ_{ac} over a range of frequency and temperature), infrared, optical absorption and ESR spectra and magnetic susceptibility of these glasses have been carried out. The analysis of the results indicates that manganese ions exist mostly in Mn³⁺ state in these glasses when the concentration of MnO is greater than 0.5 mol% in the glass matrix.

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PbO-Al₂O₃-B₂O₃ glasses are well known to resist the attack by alkali metals because of the formation of kinetically limiting surface reaction products. These glasses are stable against devitrification, possess high mechanical strength, toughness, and excellent electrical properties and have very low thermal expansion coefficients. In view of these qualities, these glasses find variety of applications in battery sealing and other micro electronic packaging^{1,2}.

Manganese ions have strong bearing on optical, magnetic and electrical properties of glasses. A large number of interesting studies are available on the environment of manganese ion in various inorganic glass systems³⁻⁶. The lasing action from Mn²⁺ ions has also been observed in some inorganic glasses⁷. A considerable number of investigations on the role of manganese ions on the physical properties of a variety of glass systems like tellurite, arsenate, phosphate, has also been reported earlier^{8,9}. Manganese ions exist in different valence states with different co-ordinations in glass matrices, for example as Mn³⁺ in borate glasses with octahedral coordination whereas in silicate and germinate glasses as Mn²⁺ with both tetrahedral and octahedral environment¹⁰. Both Mn³⁺ and Mn²⁺ ions are well known paramagnetic ions. Mn³⁺ ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital whereas such anisotropy energy of Mn²⁺ ion is small because its orbital angular momentum is zero. Further, it is also quite likely for manganese ions to have link with

alumino/borate groups, strengthen the glass structure and may raise the chemical resistance of the glass.

Thus, the aim of the present investigation is to understand the local environment of manganese ions in PbO-Al₂O₃-B₂O₃ glass network and their influence on the stability of the glass network by means of dielectric, magnetic and spectroscopic studies.

With in the glass forming region of PbO-Al₂O₃-B₂O₃ glass system¹¹, a particular composition 19 PbO-5 Al₂O₃-76 B₂O₃ is chosen for MnO doping. Our earlier studies^{12,13} indicated that with in the glass-forming region, of PbO-Al₂O₃-B₂O₃ glass system, this particular composition is found to be highly resistant against devitrification and is observed to possess high mechanical strength. Hence, this composition is chosen for MnO doping for the present study, The details of the compositions selected for this study are: 19 PbO-5Al₂O₃-(76-x) B₂O₃: xMnO with 0 ≤ x ≤ 1 in steps of 0.25 (all in mol%) and the glasses are labeled as M₀ (pure), M₁ (0.25 mol% of MnO), M₂ (0.50 mol% of MnO), M₃ (0.75 mol% of MnO), M₄ (1.0 mol% of MnO).

The preparation of the glasses^{12,13} and the experimental techniques adopted for measuring dielectric properties and for recording optical absorption, ESR and IR spectra are similar to those reported earlier¹²⁻¹⁵.

Results and Discussion

Figure 1a shows the optical absorption spectra of PbO-Al₂O₃-B₂O₃:MnO glasses recorded at room temperature in the wavelength region 275-800 nm.

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The absorption edge observed at 300 nm for glass M₀ (pure glass) is found to shift slightly to higher wavelength with increase in the concentration of MnO up to 0.5 mol%, beyond this concentration the edge is shifted towards lower wavelength. The glasses with $x \leq 0.5$ mol%, exhibited two absorption bands at 510 and 415 nm due to ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ and ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$ transitions of Mn²⁺ ions respectively¹⁵. These Mn²⁺ ion bands are observed to obscure with the presence of a broad absorption band in between 490 and 495 nm when the concentration of MnO is increased beyond 0.5%. This band is identified due to ${}^5E_g \rightarrow {}^5T_{2g}$ transition of Mn³⁺ ions¹⁶.

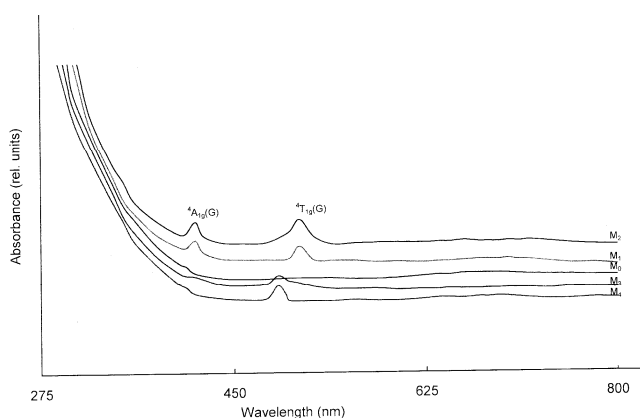


Fig. 1a — Optical absorption spectra of PbO-Al₂O₃-B₂O₃:MnO glasses recorded at room temperature; the transitions shown are from the ground state ${}^6A_{1g}(S)$

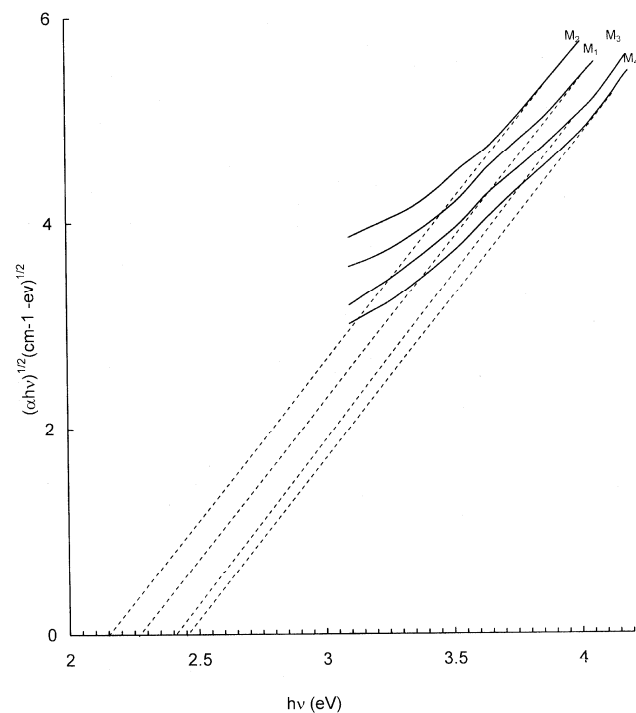


Fig. 1b — Urbach plot of PbO-Al₂O₃-B₂O₃:MnO glasses

The values of optical band gap (E_0) obtained from the Urbach plots (Fig. 1b) for PbO-Al₂O₃-B₂O₃: MnO glasses are presented in Table 1. These values are found to increase with the increase in concentration of MnO beyond 0.5 mol%.

The infrared spectra of MnO doped PbO-Al₂O₃-B₂O₃ glasses have exhibited three groups of bands in the regions 1200-1600 cm⁻¹, 800-1200 cm⁻¹ and an another band around 710 cm⁻¹ (Fig. 2). The spectra of these glasses have also exhibited a weak band around 450 cm⁻¹. With increase in the concentration of MnO up to 0.5 mol% in the glass matrix, the intensity of the second group of bands is observed to decrease and

Table 1 — Summary of data on optical absorption of PbO-Al₂O₃-B₂O₃: MnO glasses

Glass	Pure	M ₁	M ₂	M ₃	M ₄
Mn ²⁺ transitions (nm)					
${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$	—	—	510	510	—
${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$	—	—	415	415	—
Mn ³⁺ transition (nm)					
${}^5E_g \rightarrow {}^5T_{2g}$	—	—	—	495	490
Cut off wavelength (nm)	300	305	309	296	291
Optical band gap E_0 (eV)	2.91	2.60	2.40	2.95	3.00

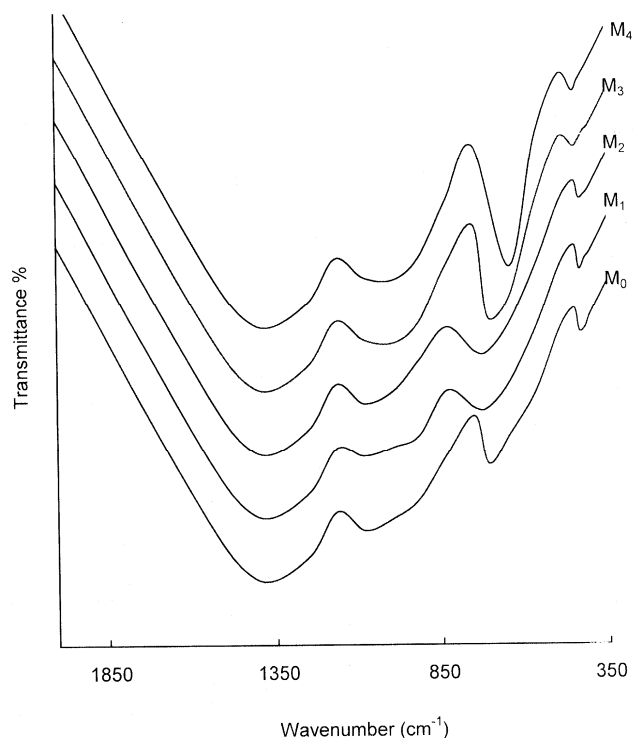


Fig. 2 — Infrared transmission spectra of PbO-Al₂O₃-B₂O₃:MnO glasses recorded at room temperature

shifted towards slightly higher wavenumber; beyond this concentration the intensity of this group of bands is found to increase.

Magnetic susceptibility (χ) of the $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{:MnO}$ glasses measured (by Guoy's method) at room temperature are observed to increase with MnO content in the glass composition (Table 2). From the values of magnetic susceptibilities, the effective magnetic moments (μ_{eff}) are evaluated. The value of μ_{eff} is found to be the highest ($5.7 \mu_{\text{B}}$) for glass M_2 and observed to decrease to a value of $4.5 \mu_{\text{B}}$ for the glass containing 1.0 mol% of MnO (glass M_4).

No ESR signal is detected in the spectra of MnO free glasses. Figure 3 represents a typical ESR spectrum of one of the glasses under study (Glass 1, glass containing 0.25 mol% of MnO). The spectra are characterized by six-line hyperfine structure centered at about $g \sim 2.006$ and another signal at $g \sim 4.3$; a considerable increase in the effective value of g is

Table 2 — Data on magnetic properties of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{:MnO}$ glasses

Glass	Conc. MnO (mol%)	Magnetic susceptibility $\chi(10^{-5} \text{ emu})$	$\mu_{\text{eff}} (\mu_{\text{B}})$	g value
M_1	0.25	8.66	5.6	2.006
M_2	0.50	18.00	5.7	2.010
M_3	0.75	19.10	4.8	2.014
M_4	1.00	22.21	4.5	2.014

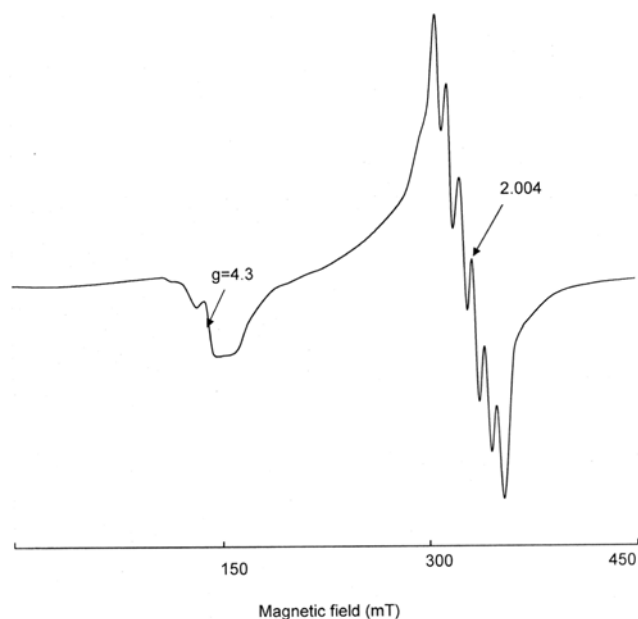


Fig. 3 — ESR spectra of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{:MnO}$ glasses for glass M_2

observed with increase in the concentration of MnO in the glass matrix up to 0.5 mol% (Table 2). With the increase in concentration of MnO beyond 0.5 mol%, the intensity (peak-to-peak height \times width²) and resolution of the sextet pattern is observed to decrease.

Figure 4a presents the TL glow curves of X-ray irradiated $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{:MnO}$ glasses doped with different concentrations of MnO. A gradual increase

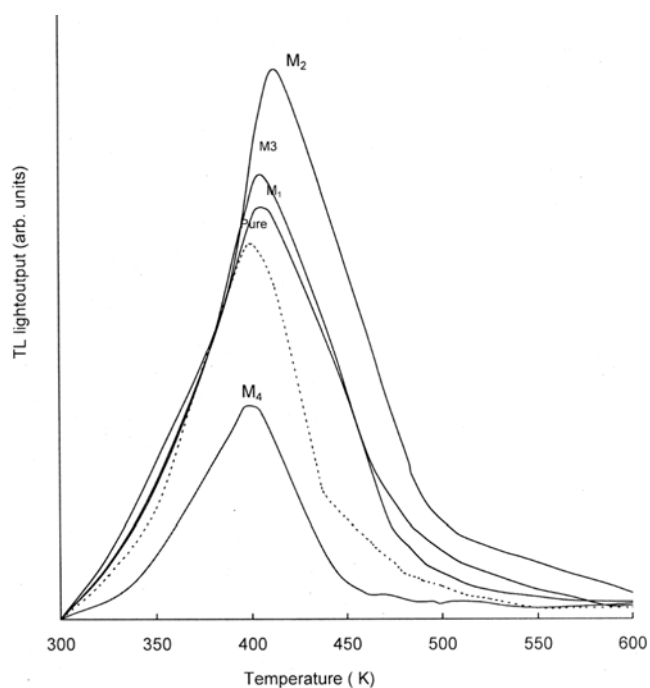


Fig. 4a — Thermoluminescence light output of X-ray irradiated $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses doped with different concentrations of MnO

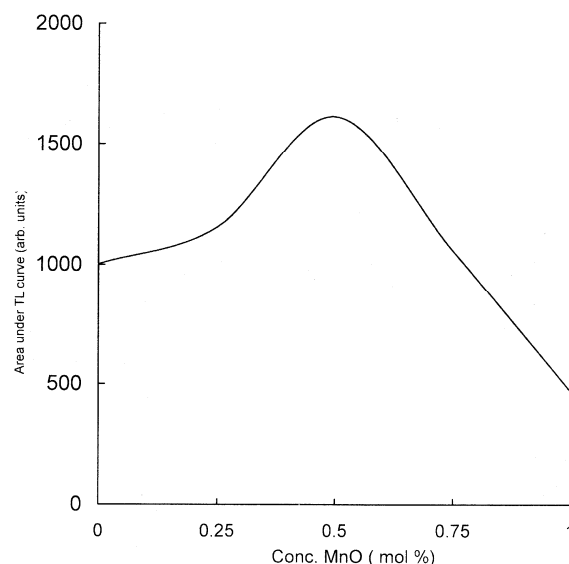


Fig. 4b — Variation of TL light output of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses with the concentration of MnO

of thermoluminescence light output with shifting of glow peak temperatures towards slightly higher value is observed for the glasses containing MnO up to 0.5 mol% with respect to that of pure glass. When $x > 0.5$ mol%, the TL light output is observed to decrease considerably (Fig. 4b). The activation energies corresponding to these glow peaks are computed and given in Table 3.

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 MnO up to 0.5 mol%, the value of ϵ' at room temperature at any frequency is found to increase;

beyond this concentration, the value of ϵ' is found to decrease. The dielectric loss ($\tan \delta$) with the concentration of MnO exhibited similar behaviour at room temperature.

The temperature dependence of ϵ' at different frequencies for glass M₂ (containing 0.5 mol% of MnO) is shown in Fig. 5a and for different concentrations of MnO at 10 kHz in Fig. 5b; dielectric constant ϵ' is found to exhibit a considerable increase at higher temperatures especially at lower frequencies. The variation of dielectric loss $\tan \delta$ of PbO-Al₂O₃-B₂O₃ glasses containing 0.25 mol% MnO (M₁) with temperature at different frequencies is shown in Fig. 6a. The curves exhibit distinct maxima; indicating the relaxation character of dielectric losses

Table 3 — Data on various trap depth parameters associated with TL glow peak of PbO-Al₂O₃-B₂O₃: MnO glasses

Glass	T_m (K)	τ (K)	δ (K)	μ_g	E_t (eV)	E_δ (eV)	Area under glow Peak (arb.units)
M ₁	405	30	43	1.43	0.597	0.316	1156
M ₂	415	31	53	1.71	0.606	0.269	1613
M ₃	404	29	45	1.55	0.618	0.300	1057
M ₄	397	30	33	1.10	0.572	0.390	469

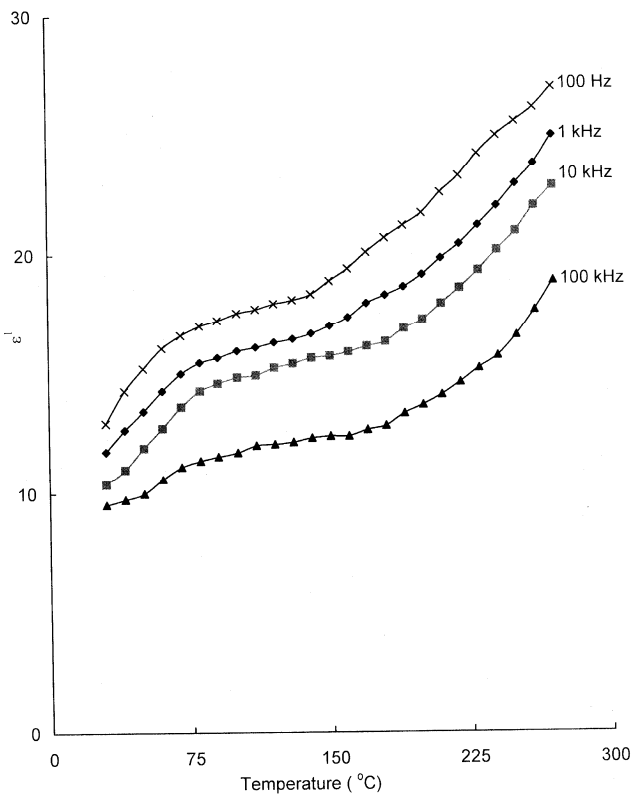


Fig. 5a — Variation of dielectric constant with temperature at different frequencies for glass M₂

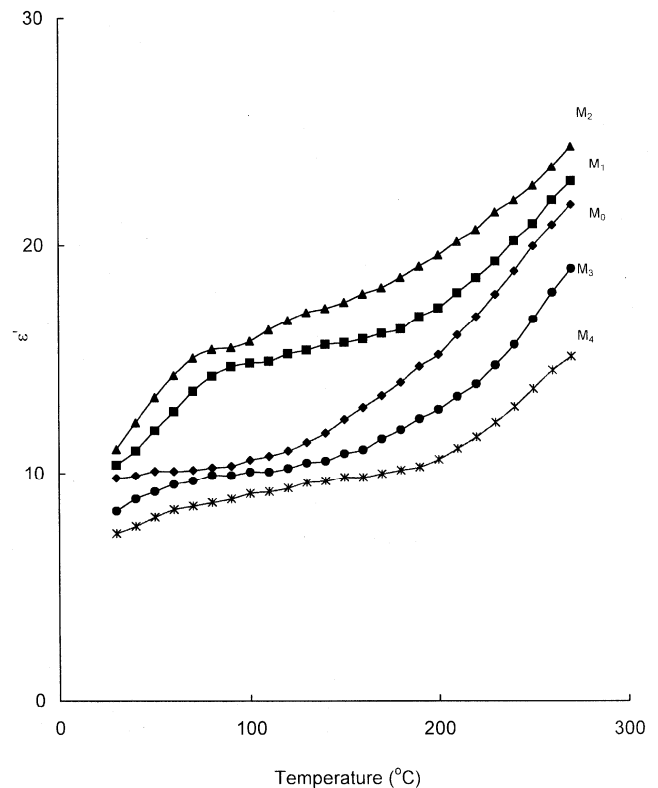


Fig. 5b — A comparison plot of variation of dielectric constant with temperature (measured at 10 kHz) for PbO-Al₂O₃-B₂O₃ glasses doped with different concentrations of MnO

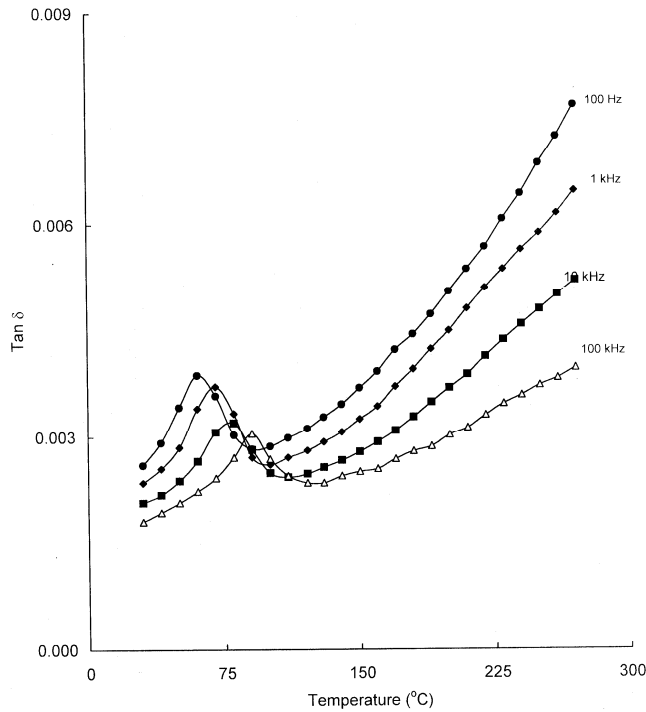


Fig. 6a — Variation of dielectric loss with temperature at different frequencies for glass M_1

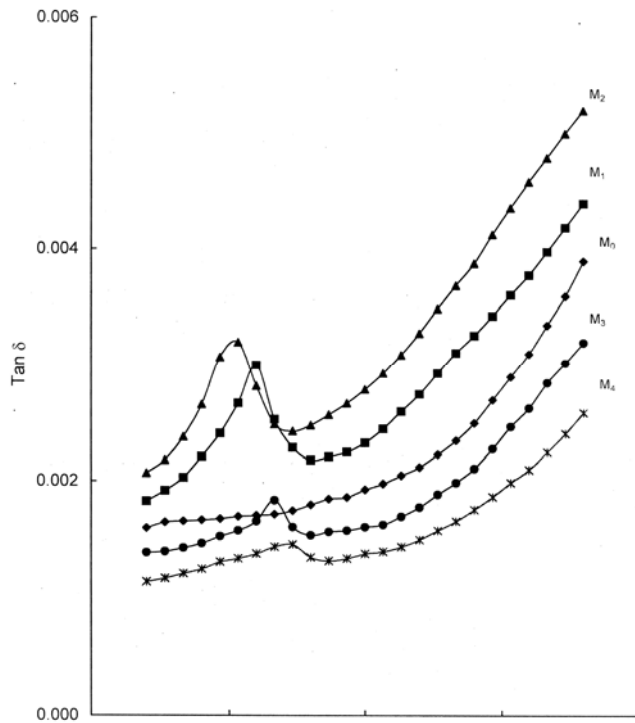


Fig. 6b — A comparison plot of variation of dielectric loss with temperature (measured at 10 kHz) for $PbO-Al_2O_3-B_2O_3$ glasses doped with different concentrations of MnO

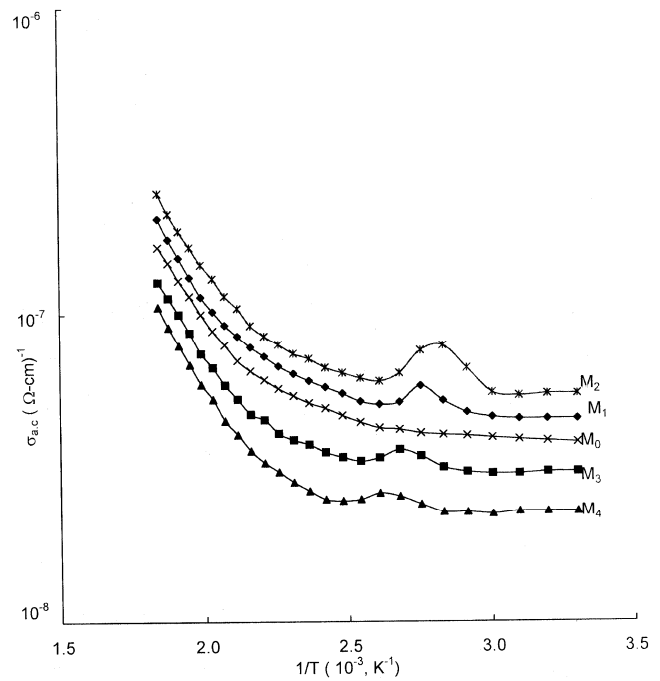


Fig. 7 — A comparison plot of variation of a.c. conductivity with $1/T$ (at 10 kHz) for $PbO-Al_2O_3-B_2O_3$ glasses doped with different concentrations of MnO

in these glasses; such relaxation effects are not observed in manganese free glasses. The effect of MnO dopant on the relaxation strength of these glasses can be clearly understood from Fig. 6b, where $\tan\delta$ is plotted at 10 kHz against temperature for different concentrations of MnO; the relaxation behaviour $\tan\delta$ in the glasses can be visualized clearly only for the glasses with $x \leq 0.5$ mol% MnO and in the glasses containing MnO > 0.5 mol%, such behaviour seems to be feeble. Using the relationship $f = f_0 \exp(-W_d/KT)$, the effective activation energy W_d for dipoles is evaluated as 0.47 eV and 0.36 eV for the glasses M_1 and M_2 respectively.

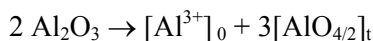
The a.c. conductivity σ_{ac} , is calculated at different temperatures using the equation $\sigma_{ac} = \epsilon_0 \omega \epsilon' \tan\delta$ and the plots of $\log\sigma_{ac}$ against $1/T$ for all the glasses at 10 kHz are shown in Fig. 7. The activation energy for conduction in the high temperature region over which a nearly linear dependence of $\log\sigma_{ac}$ with $1/T$ could be observed, is evaluated and presented in Table 4; this activation energy is found to be the lowest for the glass M_2 (containing 0.5 mol% MnO) and observed to increase with further increase in the concentration of MnO.

With the introduction of MnO (0.5 mol%), the value of the breakdown strength is lowered to 16.85 kV/cm from 18.80 kV/cm. (value of pure glass) and

for further increase in MnO content, the breakdown strength is observed to increase (Table 4).

It is well known that the borate network consists of sp² planar BO₃ units and more stable sp³ tetrahedral BO₄ units. 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. The presence of such BO₄ units in the present glasses is evident from the IR spectral studies. PbO in general is a glass modifier and enters the glass network by breaking up the B-O-B, B-O-Al bonds (normally the oxygens of PbO break the local symmetry while Pb²⁺ ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. In this case Pb²⁺ is octahedrally coordinated. However, PbO may also participate in the glass network with PbO₄ structural units when lead ion is linked to four oxygens in a covalency bond configuration¹⁷.

Further, aluminum can also occupy both tetrahedral sites (*viz.*, substitutional or network formers) and octahedral sites (*viz.*, interstitial or network modifiers)¹⁸ with AlO₄ units, *i.e.*



Manganese ions seem to exist in Mn²⁺ and Mn³⁺ states in PbO-Al₂O₃-B₂O₃ glass network. The electronic configuration of Mn²⁺ ion is 3d⁵, which corresponds to a half filled d shell. Most of the Mn²⁺ complexes are octahedral, and have a high spin arrangement with five unpaired electrons¹⁹.

The observed optical absorption bands are from the ground state ⁶A_{1g} to some quartet states and these are both spin and parity forbidden. In general, ⁶A_{1g}(S) → ⁴E_g(G), ⁶A_{1g}(S) → ⁴A_{1g}(G) and ⁶A_{1g}(S) → ⁴E_g(D) bands are expected to be sharp as they arise from intra configurational transitions, where as the transitions ⁶A_{1g}(S) → ⁴T_{1g}(G) and ⁶A_{1g}(S) → ⁴T_{2g}(G) involve a change of configuration from (t_{2g})³(e_g)² to (t_{2g})⁴(e_g)¹ and are therefore anticipated to be broad²⁰. Since all the excited states are spin quartet states, no spin allowed transitions would occur for Mn²⁺ ions. Hence, Mn²⁺ ions are characterized by weak bands, which arise due to the spin forbidden transitions. Out of the five predicted bands, only ⁶A_{1g}(S) → ⁴A_{1g}(G) and ⁶A_{1g}(S) → ⁴T_{1g}(G) have been observed in the spectra of the present glasses. By diagonalising the energy matrices for d⁵ configuration, the clearly resolved bands observed at 510, and 415 nm in the optical

Table 4 — Summary of data on a.c.conductivity and dielectric breakdown strength of PbO- Al₂O₃- B₂O₃:MnO glasses

Glass	N(E _F) (10 ²⁰ , eV ⁻¹ /cm ³)	A.E (eV)	Breakdown strength (kV/cm)
M ₁	0.9	0.27	17.20
M ₂	0.10	0.26	16.85
M ₃	0.78	0.32	18.36
M ₄	0.64	0.35	19.14

absorption spectra of PbO-Al₂O₃-B₂O₃ glasses (containing MnO up to 0.5 mol%) are assigned to ⁶A_{1g}(S) → ⁴T_{1g}(G) and ⁶A_{1g}(S) → ⁴A_{1g}(G), transitions and the crystal field parameter Dq and Racah inter electronic repulsion parameter B have been determined as 690 cm⁻¹ and 770 cm⁻¹ respectively. The existence of these bands indicates the presence of manganese ion in Mn²⁺ (d⁵) state in the glasses M₁ and M₂. The non-resolution of 510, and 415 nm absorption peaks and the presence of a broad band at about 490 nm due to ⁵E_g → ⁵T_{2g} transition²¹ in the optical absorption spectra of the glasses containing MnO beyond 0.5%, indicate the presence of manganese ions in Mn³⁺ (d⁴) state in these glass. Thus the data on optical absorption spectra point out that when MnO is present in lower concentrations (≤ 0.5 mol%), majority of manganese ions exist in Mn²⁺ state and when MnO is present in higher concentrations (> 0.5%) these ions seem to exist mainly in Mn³⁺ state in these glasses. Further, in the networks of the glasses M₃ and M₄, there is a possibility for the cross-linking of a part of AlO₄ units with Mn³⁺ ions units to form Al-O-Mn bonds in the glass network which is reasonable because of close ionic radii of Al³⁺ (0.51 Å) and Mn³⁺ (0.66 Å) and due to the same valence state. Mn²⁺ ions are expected to be in both octahedral and tetrahedral co-ordinations in glass matrices¹⁰. In the present glasses these ions (Mn²⁺ ions) seem to act as modifiers. Higher the concentration of such Mn²⁺ ions, higher is the concentration of non-bridging oxygens (NBO's) in the glass matrix. This leads to increase in the degree of localization of electrons thereby increasing the donor centers. The presence of large concentration of these donor centers lowers the optical band gap and shifts the absorption edge towards higher wavelength side (Fig. 1b). This may be the reason why the values of optical band gaps are smaller for glasses M₁ and M₂.

The increase in the intensity of the band due to BO₃ units and a simultaneous decrease in the intensity of

band due to BO_4 structural units in the IR spectra of glasses (containing $\text{MnO} < 0.5$ mol%) also suggests an enhanced degree of depolymerisation of the glass network due to the presence of large concentration of Mn^{2+} ions that act as modifiers.

The $g \sim 2.01$ line in the ESR spectrum is a characteristic of Mn^{2+} ions with a nuclear spin of $I = 5/2$ (ref. 22). The $g = 4.3$ line is an indicative of a distorted crystalline field in the vicinity of some Mn^{2+} ions and presumably due to a very limited number of Mn^{2+} ions experiencing rhombic symmetry. The effective value of g obtained from ESR spectra is observed to increase from 2.006 to 2.01 with increase in the concentration of MnO in the glass matrix up to 0.5 mol%. This is partly ascribable to the contribution of orbital angular momentum to the magnetic moment of Mn^{2+} ions¹⁵. The decrease in the intensity (peak-to-peak height \times width²) of the sextet with the increase in the concentration of MnO beyond 0.5 mol% indicates a decrease in the concentration of Mn^{2+} ions in the glass matrix.

The magnetic properties of these glasses arise from the paramagnetic Mn^{2+} ($3d^5$) and Mn^{3+} ($3d^4$) ions. The value of the effective magnetic moment, $5.60 \mu_B$, obtained for glass M_1 confirms the highest concentration of Mn^{2+} ions in this glass. The decrease in the value of μ_{eff} from $5.60 \mu_B$ to $4.50 \mu_B$ (M_4) indicates that the glass M_4 consists of manganese ions mostly in Mn^{3+} state¹⁹ that take part network forming positions in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass network.

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). Thus this process leads to the formation of (i) boron electron centres, (ii) non-bridging oxygen hole centres and (iii) 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 oxygen hole centres²³.

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 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 Mn^{3+} is as a MnO_6 octahedron entwined with BO_4 tetrahedrons, MnBO_9 . In the absence of Mn^{3+} 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. Let us assume that Mn^{3+} ions are uniformly distributed throughout the glass; the electrons are released by heating from electron centres would be trapped at Mn^{3+} ions (there by converting these ions into Mn^{2+} ions); this process inhibits the radiative recombination of electron and hole centres leading to a reduction in the TL light output²⁴ as observed. When MnO is present in higher concentrations (> 0.5 mol%), the concentration of Mn^{3+} ions seems to be high, resulting in a gradual decrease of TL light output. Thus, the study on thermoluminescence of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{: MnO}$ glasses indicate when the concentration MnO is > 0.5 mol% in the glass network, there is an increase in the concentration of Mn^{3+} ions that act as TL killers.

In general, the electronic, ionic, dipolar and space charge polarization contribute to the dielectric constant. Normally, increasing the temperature of the glasses decreases the electronic part of the dielectric constant. Similarly, it appears that the changes in the ionic polarization are not large. Even assuming the presence of a small number of dipoles and their contribution to the dielectric constant, we know from Debye's theory, ϵ^l is inversely proportional to temperature. However, in the present measurements of ϵ^l and $\tan \delta$ versus temperature on these glasses, we notice a considerable increase of ϵ^l and $\tan \delta$ with temperature beyond relaxation region; such behaviour can only be attributed to space charge polarization^{8,9} due to the bonding defects of the type mentioned earlier in these glasses.

With the introduction of MnO up to 0.5%, the values ϵ^l , $\tan \delta$ and σ_{ac} are found to increase at any frequency and temperature and the values of dielectric breakdown strength and activation energy for a.c. conduction are observed to decrease with respect to the values of pure glasses. Obviously within this concentration range, MnO acts as modifier similar to PbO and enters the glass network by breaking up B-O-B bonds and introduce coordinated defects known as dangling bonds. The decrease in the intensity of second group of bands in the IR spectra of these

glasses (up to 0.5% of MnO) indicates a decrease in the concentration of BO₄ units, thus supporting the conclusion of presence of manganese ions mostly in the Mn²⁺ state, which act as modifiers in this concentration range. The bonding defects thus produced create easy path ways for the migration of charges that would build up space charge polarization leading to the increase in the dielectric parameters as observed.

However, when MnO is present in higher concentrations (greater than 0.5 mol%), we observe that the values of the dielectric parameters to decrease with increase in MnO concentration. Such a decrease of these parameters in this concentration range suggests that manganese ions present mainly in Mn³⁺ state in these glasses (as evidenced from optical absorption measurements), establish cross-linkages with a part of AlO₃ units to form Al-O-Mn bonds, such cross-links decrease the space charge polarization leading to reduction in the values of dielectric parameters in these glasses.

Tangent δ versus temperature curves for the MnO doped (≤ 0.5 mol%) PbO-Al₂O₃-B₂O₃ glasses exhibit dipolar relaxation effects; these effects may be attributed to divalent manganese ions²⁵. A near linear relationship between $\log\sigma(\omega)$ versus activation energy for conduction (in the high temperature region) seems to exist (Table 4) for these glasses; 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 temperature²⁶.

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 model²⁷, similar to many other glass systems reported recently from our laboratory^{28,29}. The value of $N(E_F)$, i.e., the density of the energy states near the Fermi level, evaluated using the equation.

$$\sigma(\omega) = (\pi/3e^2KT N(E_F)]^2 \alpha^{-5} \omega \ln(v_{ph}/\omega)]^4 \quad \dots(1)$$

(with the usual meaning of the symbols as reported earlier²⁷⁻²⁹) and furnished in Table 4. The value of $N(E_F)$ is found to be the highest for glass M₁ and the lowest for glass M₄ indicating the presence of a low concentration of Mn²⁺ ions that take modifier positions in glass M₄.

Our observations on breakdown strengths of PbO-Al₂O₃-B₂O₃ glasses doped with MnO, as mentioned

earlier, indicate the rate of increase of $\epsilon' \tan\delta$ with temperature is the highest for glass M₁ and the lowest for glasses M₄. 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 M₁, the breakdown strength (which is inversely proportional to $\epsilon' \tan\delta$) is the lowest when compared with the other glasses. Thus the experiments on the dielectric breakdown strength of PbO-Al₂O₃-B₂O₃ glasses doped with MnO reveal that there is a decrease in the disorderliness in the glass network with increase in concentration of MnO beyond 0.5 mol%.

Conclusions

In conclusion the analysis of the results of various physical properties of PbO-Al₂O₃-B₂O₃ glasses doped with different concentrations of MnO indicates that when the concentration of MnO > 0.5 mol% in the glass matrix, manganese ions mostly exist in Mn³⁺ states and occupy network forming positions.

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