

Influence of titanium ions on dielectric and other physical properties of AF-PbO-B₂O₃ glasses

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Dielectric properties, viz., dielectric constant, ϵ , loss, $\tan \delta$, a.c. conductivity, σ , in the frequency range 10^2 - 10^6 Hz and in the temperature range 30-300°C and the dielectric breakdown strength in air of AF-PbO-B₂O₃ (A = Li, Na, K) glasses containing different concentrations of TiO₂ (in the range 0-0.6 mol %) have been investigated. Results have been analyzed in the light of different oxidation states of titanium ions in the glass matrix with the aid of data on optical absorption, ESR and IR spectral studies.

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The study of dielectric properties, such as dielectric constant ϵ , loss $\tan \delta$ and a.c. conductivity $\sigma_{a.c}$ over a wide range of frequency and temperature and also the dielectric breakdown strength of the glasses helps in assessing their insulating character; such study may also help as a tool for understanding the structural aspects of the glass to some extent. Work along these lines was carried out in recent years on a variety of inorganic glasses by a number of researchers yielding valuable information¹⁻⁴. Alkali fluoro borate glasses are well known due to their variety of applications in radiation dosimetry, phosphors, solar energy converters and in a number of electronic devices⁵. The physical properties of these glasses can however be improved by the addition of PbO to these glasses, since PbO has the ability to form stable glasses due to its dual role—one as modifier and the other—as glass former⁶.

Among various transition metal oxide doped glasses, the titanium oxide doped glasses have gained much importance in recent years due to their possible applications in non-linear optical devices such as ultra fast switch and power limiter⁷. In general, titanium oxide is considered as a nucleating agent of crystallization in silicate glasses. However, the presence of small quantities of TiO₂ in the other glass matrices is observed to enhance the glass forming ability and chemical durability of the glasses⁸. Further, the investigation on the co-ordinate chemistry of titanium ions in alkali fluoro borate glass networks is highly interesting, because, the presence of these

ions can have a dramatic effect on mechanical and insulating strengths⁹. Thus, the objective of the present study is to investigate the role of titanium ions on the structural aspects of PbO-B₂O₃ glasses mixed with three alkali fluorides (viz. LiF, NaF and KF) by studying their dielectric properties with the aid of the data on optical absorption, ESR and IR spectral studies.

Experimental Procedure

Within the glass-forming region of AF-PbO-B₂O₃:TiO₂ glass system, the following particular compositions are chosen for the present study:

20 AF-10 PbO-(70-x) B₂O₃: xTiO₂ all in mol % with $0 \leq x \leq 0.6$ in steps of 0.2 and the samples are labeled as AT₀ (x = 0), AT₂ (x = 0.2), AT₄ (x = 0.4) and AT₆ (x = 0.6) where A = Li, Na and K.

The method of preparation of these glasses and the details of the apparatus used in the present study for measuring dielectric properties and for recording ESR, optical absorption and IR spectra are similar to those reported earlier¹⁰⁻¹².

Results

The dielectric constant ϵ , at room temperature ($\approx 30^\circ\text{C}$) and at 100 kHz for pure AF-PbO-B₂O₃ glasses is measured to be 5.91 (LiT₀), 8.56 (NaT₀) and 6.52 (KT₀) and the values of $\tan \delta$ for the same glasses are determined as 0.003, 0.012 and 0.01 respectively. With the addition of TiO₂ (0.2 mol %),

the values of ϵ and $\tan\delta$ are observed to decrease for all the three series of glasses; for further increase of TiO_2 in the glass matrix, both the parameters were observed to increase at a given frequency (Fig. 1).

Fig. 2 shows the temperature dependence of ϵ , for all the three series of glasses doped with different concentrations of TiO_2 measured at 1 kHz. Inset of Fig. 2 represents a comparison plot of dielectric constant variation with the concentration of TiO_2 measured at 200°C and at a frequency of 1 kHz; among the three doped series, the rate of increase of ϵ with temperature is found to be the largest for NaT series of glasses for any concentration of TiO_2 indicating the highest influence of titanium ions on

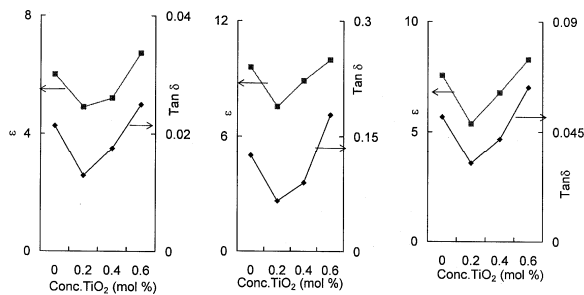


Fig. 1—Variation of ϵ and $\tan\delta$ with the concentration of TiO_2 of AF-PbO- B_2O_3 glass at room temperature measured at 1 kHz

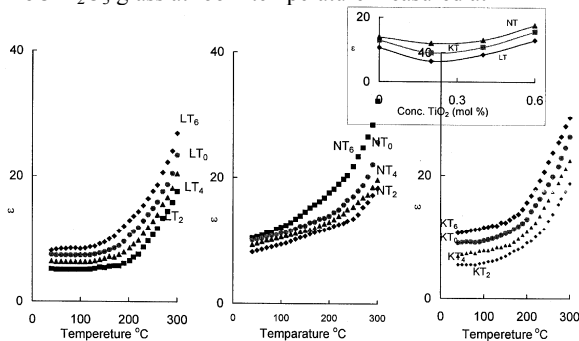


Fig. 2—Variation of dielectric constant with temperature of AF-PbO- B_2O_3 glass containing different concentrations of TiO_2 measured at 1 kHz. Inset shows the variation of dielectric constant with the concentration of TiO_2 for all the three series of glasses at 200°C

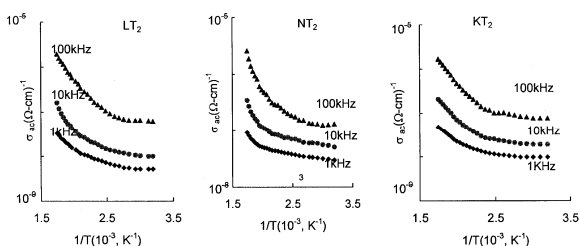


Fig. 3—Variation of ϵ_{ac} with $1/T$ for AF-PbO- B_2O_3 glasses containing 0.2 mol % of TiO_2

dielectric constant for these glasses. The variation of $\tan\delta$ with temperature for all the three series is observed to be similar.

The a.c. conductivity σ_{ac} is calculated at different temperatures using the equation:

$$\sigma_{ac} = \omega \epsilon \epsilon_0 \tan \delta \quad \dots (1)$$

(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. 3 for glasses LiT_2 , NaT_2 and KT_2 at different frequencies; Fig. 4 represents a comparison of a.c. conductivity isotherms drawn at 250°C with the concentration of TiO_2 measured at a frequency of 10 kHz for the three series of glasses. From the conductivity 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 its variation with the concentration of TiO_2 is shown in the inset of Fig. 4; the activation energy is found to decrease for all the three series of glasses with increase in the concentration of TiO_2 beyond 0.2 mol %.

The dielectric breakdown strength of pure glasses, viz., LiT_0 , NaT_0 and KT_0 are determined to be 10.60, 9.85 and 10.22 kV/cm, respectively; the variation of breakdown strength with the concentration of TiO_2 exhibited minimum value at 0.2 mol % of TiO_2 for all the three series of glasses (Table 1). For any particular concentration of TiO_2 , the value of breakdown strength is found to be the highest for Li-series and the lowest for Na-series.

The infrared transmission spectra of pure AF-PbO- B_2O_3 glasses are expected to exhibit two groups of

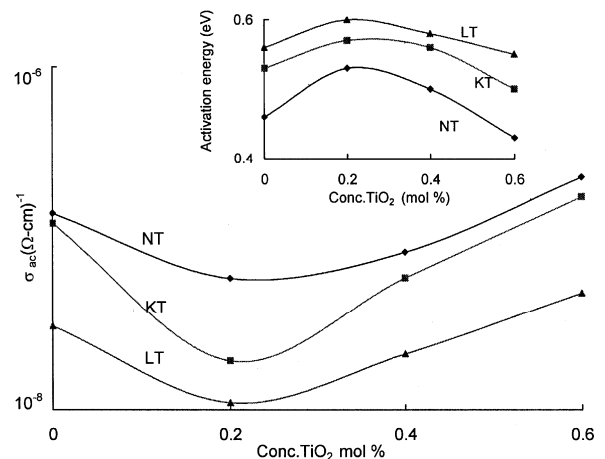


Fig. 4—Variation of ϵ_{ac} for AF-PbO- B_2O_3 glasses containing different concentrations of TiO_2 at 250°C

Table 1—Summary of the data on a.c. conductivity and dielectric breakdown strength of AF-PbO-B₂O₃-TiO₂ glasses

Glass	N(E _F) in (10 ²⁰ , eV ⁻¹ /cm ³)			A.E (eV) for conduction	Breakdown strength (kV/cm)
	Austin and Mott ²¹	Butcher and Hyden ²⁴	Pollak ²⁵		
LiT ₀	-	-	-	0.56	14.81
LiT ₂	2.57	1.07	2.61	0.60	19.12
LiT ₄	2.94	1.22	2.99	0.58	16.78
LiT ₆	4.5	1.87	4.58	0.55	10.60
NaT ₀	-	-	-	0.46	12.50
NaT ₂	4.82	2.00	4.90	0.53	15.67
NaT ₄	5.84	2.42	5.94	0.50	13.28
NaT ₆	9.21	3.82	9.36	0.43	8.72
KT ₀	-	-	-	0.53	13.67
KT ₂	2.81	1.17	2.85	0.57	16.13
KT ₄	4.97	2.06	5.05	0.56	14.78
KT ₆	8.6	3.57	8.74	0.50	9.81

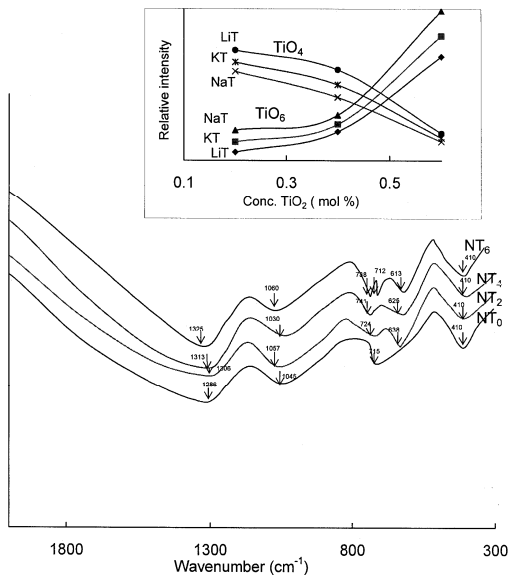


Fig. 5—IR spectra of NaF-PbO-B₂O₃ glasses doped different concentrations of TiO₂

bands: (i) in the region 1200-1600 cm⁻¹ (due to the stretching relaxation of the B-O bond of the trigonal BO₃ units), (ii) in the region 900-1050 cm⁻¹ (due to BO₄ units) and an another band at about 715 cm⁻¹ (bending of B-O linkages in the borate network)^{13,14}. It may be worth mentioning here that the earlier studies on the IR spectra of various other glasses containing TiO₂ indicate that the presence of a vibrational band at about 715 cm⁻¹ due to vibrations of TiO₄ groups¹⁵. Hence, there is a possibility for the formation of single boron-oxygen – titanium framework in the glass network. Fig. 5 represents the infrared transmission spectra of NaF-PbO-B₂O₃ glasses containing different concentrations of TiO₂ recorded

at room temperature. With the introduction of TiO₂ (0.2 mol %) into the NaF-PbO-B₂O₃ glass network, the intensity of the band due to BO₄ vibrational groups is observed to increase whereas the intensity of the band due to BO₃ groups, is observed to decrease. When the concentration of TiO₂ is increased beyond 0.2 mol %, the intensity variation of these two bands exhibited a reversal trend. Additionally, the spectrum of NaT₂ glass has exhibited a broad band at 724 cm⁻¹ (identified as due to vibrations of TiO₄ groups, in this case it may be assumed due to the vibrations of B-O-Ti linkages) and another band at 650 cm⁻¹ (identified as due to Ti-O-Ti symmetric stretching vibrations of TiO₆ structural units¹⁶). With increase in the concentration of TiO₂ from 0.2 to 0.4 mol %, the intensity of band due to B-O-Ti linkages is observed to decrease with shifting of meta-center towards higher wavenumber. The common meta-center is observed to split at about 0.6 mol % of TiO₂. The intensity of band due to TiO₆ structural units is observed to increase gradually with the increase in the concentration of TiO₂ from 0.2 to 0.6 mol %. The IR spectra of other two series of the glasses have exhibited a similar behaviour. However, the comparison of spectra of the three series of glasses shows that the intensity of the band due to TiO₆ structural units is maximum for NaF modifier glass containing any concentration of TiO₂. (inset of Fig. 5). Further, the spectra of all the glasses exhibited a band at 410 cm⁻¹ (which is assigned to PbO₄ structural vibrations)^{6,14}.

The ESR spectra, recorded at room temperature for AF-PbO-B₂O₃: TiO₂ glasses under investigation

exhibit a weak asymmetric signal with $g = 1.93$. A considerable intensity of the signal is observed, only when the concentration of TiO_2 is more than 0.4 mol % for all the three series of glasses. With further increase in the content of TiO_2 (0.6 mol %), an increase in the half-width of the signal is observed for all the three series of glasses. However, among the three series of glasses (for a given concentration of TiO_2) the weak intensity of the signal is observed for LiT glasses. Fig. 6a represents ESR spectra of the three glasses containing 0.4 mol % TiO_2 .

Fig. 6b shows the comparison plot of optical absorption spectra of AF-PbO- B_2O_3 glasses containing 0.4 mol % of TiO_2 recorded at room temperature in the wavelength region 400-850 nm; the spectra have exhibited two absorption bands at about 512 nm and 680 nm. The spectra show the highest intensity for both the bands for NaT_4 glass. The comparison of the spectra of the glasses containing other concentrations of TiO_2 has also exhibited similar behaviour.

Discussion

It is well known that the effect of introduction of modifiers like AF, PbO into B_2O_3 network is the conversion of sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units and may also create non-bridging oxygens. Titanium ions seem to exist mainly in Ti^{4+} state in the present AF-PbO- B_2O_3 glass network. However, the reduction of Ti^{4+} to Ti^{3+} appears to be viable (since the reduction, $\text{Ti}^{4+} + e = \text{Ti}^{3+}$ takes place, with $E^0 = 0.2$ V only) during melting and annealing process of the present glasses. The Ti^{4+} ions are largely in six-fold coordination as corner-sharing $[\text{TiO}_6]^{2-}$ units in the glass network. The formula $[\text{TiO}_6]^{2-}$ suggests that additional oxygen atoms are required for the co-ordination of titanium

(since TiO_2 can generate $[\text{TiO}_{4/2}]$ in the network) and it has to be provided by host network¹⁷. The band observed in the IR spectra between 640 cm^{-1} and 650 cm^{-1} is due to Ti-O-Ti symmetric stretching vibrations of that TiO_6 units¹⁶.

Nevertheless, these ions are also present in the glass network with TiO_4 structural units; the band observed in the IR spectra between 710 cm^{-1} and 745 cm^{-1} , in fact represents vibrations due to such tetragonal units¹⁵. Tetragonally positioned Ti^{4+} ions do not induce the formation of any non-bridging oxygen ions but octahedrally positioned ions may act as modifiers¹⁵. The TiO_4 tetrahedrons enter the glass network and also alternate with borate structural units and form linkages of the type B-O-Ti. The modifier ions are expected to break such linkages; as a result there is a possibility for increase in the degree of deformation in the glass network with increase in the size of the modifier ion and we expect more disorder in KT series of glasses. However, the closer values of ionic radii of K^+ (0.133 nm) and Pb^{2+} (0.132 nm) may cause the linkages between these two ions and make the network of KT series glasses more rigid when compared with that of NaT series of glasses since the ionic radius of Na^+ (0.098 nm) is far from that of Pb^{2+} ion. The highest values of dielectric constant, loss and conductivity observed for NaT series of glasses may be understood due to such reason.

The presence of clearly resolved bands in the optical absorption spectra at 520 nm and 680 nm corresponding to ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g}$ transitions of $3d^1$ electron of the Ti^{3+} ions¹⁸. These results further suggest the presence of Ti^{3+} ions in tetragonal distorted octahedral sites in these glasses¹⁹. The highest intensity of these bands observed in the spectrum of glass T_6 indicates the highest concentration of such Ti^{3+} ions. The ESR measurements also support the presence of Ti^{3+} ions in these glasses, since the weak asymmetric signal in ESR spectra with $g = 1.93$ arises only due to $3d^1$ -unpaired electron of Ti^{3+} ions in a tetragonally distorted octahedral field¹⁹. Further, the comparison of the optical absorption and ESR spectra of the three series of glasses shows the highest concentration of such Ti^{3+} ions in NaT series of glasses.

With the introduction of TiO_2 more than 0.2 mol %, the values ϵ , $\tan \delta$ 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 increase with respect to

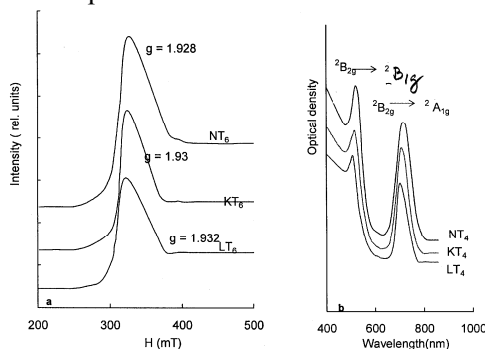


Fig. 6—(a) ESR spectra (recorded at room temperature) of AF-PbO- B_2O_3 glasses containing 0.6% concentration of TiO_2 , (b) Optical absorption spectra (recorded at room temperature) of AF-PbO- B_2O_3 glasses containing 0.4% of TiO_2

the values of pure glasses for all the three series of glasses. Obviously, above this concentration range, Ti⁴⁺ ions mostly present in octahedral positions and large concentration of titanium ions exist in Ti³⁺ state, act as modifiers and create bonding defects. The defects thus produced create easy pathways for the migration of charges that would build up space charge polarization leading to the increase in the dielectric parameters as observed^{4,11,12}. The low values of dielectric parameters observed for all the series of the glasses containing 0.2 mol % of TiO₂ indicate the presence of large concentration of titanium ions in Ti⁴⁺ state that take part network forming positions with TiO₄ structural units in these glasses.

The conductivity variation with the concentration of TiO₂ at higher temperature (Fig. 4) shows a decreasing trend (zone I) up to 0.2 mol.% of TiO₂ and beyond this concentration, the conductivity is found to increase (zone II). The conduction in the zone I (where σ_{ac} decreases with TiO₂) is identified as electronic conductive zone whereas the zone II is identified due to mobility of ions²⁰. It may be stated here that the highest conductivity and the lowest activation energy observed for the glass T₆ of all the series is obviously due to the highest concentration of charge carriers, which may find easy paths for migration in the high disordered network. The low temperature part of the conductivity (a near temperature independent part, as in the case of present glasses up to nearly 380 K) can be explained on the basis of quantum mechanical model²¹ similar to many other glass systems reported recently from our laboratory^{4,22,23}. The value of N(E_F), i.e., the density of the energy states near the Fermi level, evaluated using the equation²¹,

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

(with $\eta = \pi/3$ (Austin & Mott²¹), $= 3.66 \pi^2/6$ (Butcher & Hyden²⁴), $= \pi^4/96$ (Pollak²⁵) with the other symbols carry the usual meaning as reported earlier^{11,22,23} and furnished in Table 1. The value of N(E_F) is found to increase from glass T₂ to glass T₆ maintaining the highest values for NaT series.

Our observations on dielectric properties of AF-PbO-B₂O₃:TiO₂ glasses, as mentioned earlier, indicate the rate of increase of the product of ϵ and $\tan\delta$ with temperature is the highest for glasses AT₂. 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 lowest for AT₂ glasses, the breakdown strength (which is inversely proportional to ρ_1) is the highest when compared with that of other glasses. Thus, the experiments on the dielectric breakdown strength of AF-PbO-B₂O₃:TiO₂ glasses reveal that the glass T₂ of all the three series possesses maximum insulating strength that possesses the highest concentration of Ti⁴⁺ ions in tetragonal positions. The comparison of the three series of glasses however shows the highest breakdown strength for LiT glasses containing any concentration of TiO₂.

Conclusions

Conclusions drawn from the study of dielectric properties along with the spectroscopic studies of AF-PbO-B₂O₃ glasses doped with different concentrations of TiO₂ is as follows. The optical absorption and ESR spectral studies indicate that titanium ion exists in Ti³⁺ (tetragonally distorted octahedral sites) state with maximum concentration when TiO₂ is present in higher quantities (0.6 mol %) in the glass matrices; the IR spectral studies indicate that the titanium ions exist in Ti⁴⁺ (situated in both tetrahedral and octahedral positions). The dielectric parameters, viz., ϵ , $\tan\delta$ and σ_{ac} are found to increase while the dielectric breakdown strength and the activation energy for a.c. conduction are found to decrease with the increase in TiO₂ concentration from 0.2 to 0.6 mol % in all the three series of glasses; this has been attributed to the increasing concentration of Ti³⁺ and also Ti⁴⁺ ions with TiO₆ structural units that act as modifiers and induce bonding defects. Further, when TiO₂ is present in lower concentrations (0.2 mol %), we observe that the values of the dielectric parameters to decrease when compared with those of pure glasses; such changes have been understood due to presence of the highest concentration of Ti⁴⁺ ions that take part in network forming positions with TiO₆ structural units. The temperature independent part of the conductivity could successively be explained on the basis of QMT model.

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