Influence of titanium ions on dielectric and other physical properties of
AF-PbO-B_2O_3 glasses

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Received 6 July 2004; accepted 17 November 2005

Dielectric properties, viz., dielectric constant, \( \varepsilon \), loss, \( \tan \delta \), a.c. conductivity, \( \sigma \), 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-B_2O_3 (A = Li, Na, K) glasses
containing different concentrations of TiO_2 (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.

IPC Code: C03C3/21

The study of dielectric properties, such as dielectric constant \( \varepsilon \), 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 information^{1-4}. 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 devices’^5. 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
former^6.

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 limiter^7. In general, titanium
oxide is considered as a nucleating agent of
crystallization in silicate glasses. However, the
presence of small quantities of TiO_2 in the other glass
matrices is observed to enhance the glass forming
ability and chemical durability of the glasses^8. 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 strengths^9. Thus, the objective of the
present study is to investigate the role of titanium ions
on the structural aspects of PbO-B_2O_3 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-B_2O_3:
TiO_2 glass system, the following particular compositions are chosen for the present study:

20 AF-10 PbO-(70-x) B_2O_3: xTiO_2 all in mol %

with 0 \( \leq x \leq 0.6 \) in steps of 0.2 and the samples are
labeled as AT_0 (x = 0), AT_2 (x = 0.2), AT_4 (x = 0.4)
and AT_6 (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 earlier^{10-12}.

Results

The dielectric constant \( \varepsilon \), at room temperature
(\( \approx 30^\circ \text{C} \)) and at 100 kHz for pure AF-PbO-B_2O_3
glasses is measured to be 5.91 (LiT_0), 8.56 (NaT_0) and
6.52 (K\text{T}_0) 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 TiO_2 (0.2 mol %),
the values of \( \varepsilon \) 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 \( \varepsilon \), 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\(^\circ\)C and at a frequency of 1 kHz; among the three doped series, the rate of increase of \( \varepsilon \) 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 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 \( \sigma_{ac} \) is calculated at different temperatures using the equation:

\[
\sigma_{ac} = \omega \varepsilon \varepsilon_0 \tan \delta \quad (1)
\]

(where \( \varepsilon_0 \) 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\(^\circ\)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\(_2\)O\(_3\) glasses are expected to exhibit two groups of
bands: (i) in the region 1200-1600 cm\(^{-1}\) (due to the stretching relaxation of the B-O bond of the trigonal BO\(_3\) units), (ii) in the region 900-1050 cm\(^{-1}\) (due to BO\(_4\) units) and 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 TiO\(_2\) indicate that the presence of a vibrational band at about 715 cm\(^{-1}\) due to vibrations of TiO\(_4\) groups\(^{15}\). 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-B\(_2\)O\(_3\) glasses containing different concentrations of TiO\(_2\) recorded at room temperature. With the introduction of TiO\(_2\) (0.2 mol %) into the NaF-PbO-B\(_2\)O\(_3\) glass network, the intensity of the band due to BO\(_4\) vibrational groups is observed to increase whereas the intensity of the band due to BO\(_3\) groups, is observed to decrease. When the concentration of TiO\(_2\) is increased beyond 0.2 mol %, the intensity variation of these two bands exhibited a reversal trend. Additionally, the spectrum of NaT\(_2\) glass has exhibited a broad band at 724 cm\(^{-1}\) (identified as due to vibrations of TiO\(_4\) 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 TiO\(_6\) structural units\(^{16}\)). With increase in the concentration of TiO\(_2\) 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-centre is observed to split at about 0.6 mol % of TiO\(_2\). The intensity of band due to TiO\(_6\) structural units is observed to increase gradually with the increase in the concentration of TiO\(_2\) 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 TiO\(_6\) structural units is maximum for NaF modifier glass containing any concentration of TiO\(_2\). (inset of Fig. 5). Further, the spectra of all the glasses exhibited a band at 410 cm\(^{-1}\) (which is assigned to PbO\(_4\) structural vibrations)\(^{6,14}\).

The ESR spectra, recorded at room temperature for AF-PbO-B\(_2\)O\(_3\): TiO\(_2\) 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ glass network. However, the reduction of Ti$^{4+}$ to Ti$^{3+}$ appears to be viable (since the reduction, Ti$^{4+} + e = Ti^{3+}$ takes place, with $E^0 = 0.2$ V only) during melting and annealing process of the present glasses. The Ti$^{3+}$ ions are largely in six-fold coordination as corner-sharing [TiO$_6$]$^{2-}$ units in the glass network. The formula [TiO$_6$]$^{2-}$ suggests that additional oxygen atoms are required for the co-ordination of titanium (since TiO$_2$ can generate [TiO$_4$]$^{2-}$ in the network) and it has to be provided by host network$^{17}$. 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$_6$ units$^{16}$.

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 units$^{15}$. Tetragonally positioned Ti$^{4+}$ ions do not induce the formation of any non-bridging oxygen ions but octahedrally positioned ions may act as modifiers$^{15}$. 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 $^2$B$_{2g} ightarrow ^2$B$_{1g}$ and $^2$B$_{2g} ightarrow ^2$A$_{1g}$ transitions of 3d$^1$ electron of the Ti$^{3+}$ ions$^{18}$. These results further suggest the presence of Ti$^{3+}$ ions in tetragonal distorted octahedral sites in these glasses$^{19}$. 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 field$^{19}$. 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 $\varepsilon$, $\tan \delta$ and $\sigma_{ac}$ 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
the values of pure glasses for all the three series of glasses. Obviously, above this concentration range, Ti^{4+} ions mostly present in octahedral positions and large concentration of titanium ions exist in Ti^{3+} 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 TiO_{2} indicate the presence of large concentration of titanium ions in Ti^{4+} state that take part network forming positions with TiO_{4} structural units in these glasses.

The conductivity variation with the concentration of TiO_{2} at higher temperature (Fig. 4) shows a decreasing trend (zone I) up to 0.2 mol.% of TiO_{2} and beyond this concentration, the conductivity is found to increase (zone II). The conduction in the zone I (where \( \sigma_{ac} \) decreases with TiO_{2}) is identified as electronic conductive zone whereas the zone II is identified due to mobility of ions^{20}. It may be stated here that the highest conductivity and the lowest activation energy observed for the glass T_{6} 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 model\(^{21}\) 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 equation\(^{21}\),

\[
\sigma(\omega) = (\pi/3)e^{2}kT [N(E_{F})]^{2} \alpha^{-5} \omega [\ln(\nu_{ph}/\omega)]^{4} \quad \ldots (2)
\]

(with \( \eta = \pi/3 \) (Austin & Mott \(^{21}\)), \( = 3.66 \pi^{2}/6 \) (Butcher & Hyden \(^{24}\)), \( = \pi^{4}/96 \) (Pollak\(^{25}\)) 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 T_{2} to glass T_{6} maintaining the highest values for NaT series.

Our observations on dielectric properties of AF-PbO-B_{2}O_{3}:TiO_{2} glasses, as mentioned earlier, indicate the rate of increase of the product of \( \varepsilon \) and tan\( \delta \) with temperature is the highest for glasses AT_{2}. 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 \( \varepsilon \) tan\( \delta \) value. Since the rate of increase of \( \varepsilon \) tan\( \delta \) with temperature is the lowest for AT_{2} glasses, the breakdown strength (which is inversely proportional to \( \rho_{0} \)) is the highest when compared with that of other glasses. Thus, the experiments on the dielectric breakdown strength of AF-PbO-B_{2}O_{3}:TiO_{2} glasses reveal that the glass T_{2} of all the three series possesses maximum insulating strength that possesses the highest concentration of Ti^{4+} 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 TiO_{2}.

**Conclusions**

Conclusions drawn from the study of dielectric properties along with the spectroscopic studies of AF-PbO-B_{2}O_{3} glasses doped with different concentrations of TiO_{2} is as follows. The optical absorption and ESR spectral studies indicate that titanium ion exists in Ti^{3+} (tetragonally distorted octahedral sides) state with maximum concentration when TiO_{2} is present in higher quantities (0.6 mol %) in the glass matrices; the IR spectral studies indicate that the titanium ions exist in Ti^{4+} (situated in both tetrahedral and octahedral positions). The dielectric parameters, viz., \( \varepsilon \), \( \tan \delta \) and \( \sigma_{ac} \) 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 TiO_{2} concentration from 0.2 to 0.6 mol % in all the three series of glasses; this has been attributed to the increasing concentration of Ti^{5+} and also Ti^{4+} ions with TiO_{6} structural units that act as modifiers and induce bonding defects. Further, when TiO_{2} 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 Ti^{4+} ions that take part in network forming positions with TiO_{6} structural units. The temperature independent part of the conductivity could successively be explained on the basis of QMT model.

**References**