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Composition dependence of electrical properties of ZnF_2–MO–TeO_2 glasses

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Abstract. Dielectric constant (*e*′), loss (tan *d*), a.c. conductivity (*s*) of ZnF_2–MO–TeO_2 glasses with varying concentrations of MO (P_2O_5, As_2O_3 and Bi_2O_3) were measured as a function of frequency and temperature over moderately wide ranges. From the analysis of these studies along with IR spectra and DTA results of these glasses, the structural changes in the systems with the concentration of metal oxides are discussed.

Keywords. Tellurite glasses; dielectric properties; IR spectra.

1. Introduction

Tellurium oxide glasses, especially ZnF_2–MO–TeO_2 systems (where MO stands for modifier oxide), are well known due to their high transparency in the far infrared region and for their high density and refractive index. These glasses are nontoxic, very stable against devitrification and are resistant to moisture. In view of the above qualities, these glasses were considered as the best materials for optical components such as IR domes, optical filters, modulators, memories and laser windows. Further, these glasses are considered as very good materials for hosting rare-earth ions, since these provide a low phonon energy environment to minimize non-radiative losses (Oishi *et al* 1999). There have been numerous studies on mechanical, electrical and optical properties of tellurite glasses containing different rare earth ions with PbO as modifier (Ravikumar *et al* 1995, 1997a,b; Ravikumar and Veeraiah 1997; Komatsu and Mohri 1999). These studies have yielded valuable information regarding the mechanical and insulating strengths and have thrown some light on the possible use of these glasses as host materials for laser emission. However, in recent years, it has been observed that, these TeO_2 based glasses exhibit semiconducting behaviour when the conventional modifiers like PbO are replaced with other metal oxides like Sb_2O_3, MoO_3, Fe_2O_3, Bi_2O_3, P_2O_5, As_2O_3 etc (Tanaka *et al* 1990; Chowdari and Pramod Kumari 1997; Qiu *et al* 1996, 1997) in these systems. Further, it is expected that these metal oxides may influence the physical properties of these glasses to a greater extent. Out of these, for example, P_2O_5 participates in the glass network with different structural groups like PO_4, PO_4^{3-}, P–O^-, P=O, etc. Similarly, As_2O_3 is a strong network former and is found to affect the far infrared transmission of tellurite glasses to a less extent, since the frequencies of some of the fundamental modes of vibration of As_2O_3 structural groups lie in the region of vibration of TeO_2 structural groups and also make the glasses suitable for long distance optical transmission with low losses. Further, the heavy metal ions such as bismuth dissolved in tellurite glass matrix, influence the insulating character of these glasses very strongly, because of its dual role, one as modifier with BiO_6 (octahedral) and the other as glass former with BiO_3 (pyramidal) structural units. Though considerable studies on electrical properties along with optical properties (Sabadel *et al* 1997; Reddy *et al* 1998; El-Damrawi and Abd-el-Maksoud 2000) of some TeO_2 based glasses are available in literature, majority of these studies are devoted to binary tellurite glasses and further, they are mainly concentrated on d.c. conductivity studies (Hampton *et al* 1987; El-Samanoudy 1995; Jayasinghe *et al* 1995; Inque *et al* 1998), and not much information is available on dielectric relaxation, a.c. conductivity and dielectric breakdown strength on particularly interesting ZnF_2–MO–TeO_2 (where MO stands for P_2O_5, As_2O_3 and Bi_2O_3) systems; knowledge on these properties is highly helpful for estimating the influence of these oxides on the insulating strength of these glasses. These studies may also pave way for the analysis of the structure of this glass system to some extent if these studies are coupled with differential thermal analysis (DTA) and infrared spectra (IR).

The objective of present investigation is to have a comprehensive understanding over the influence of three different interesting metal oxides, viz. P_2O_5, As_2O_3 and Bi_2O_3, on the insulating character of ZnF_2–TeO_2 glasses, from a systematic study on dielectric constant (*e*′), loss (tan *d*), a.c. conductivity (*s*) in the frequency range

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10^2–10^5 Hz and in the temperature range 30–250°C. Dielectric breakdown strength in air medium along with infrared spectra and DTA have also been studied.

2. Experimental

The following five particular compositions of the ZnF_2–MO–TeO_2 glass system with successive increase in the concentrations of MO (P_2O_5–series P, As_2O_3–series A and Bi_2O_3–series B) are chosen for the present study: (i) $40ZnF_2$–05 MO–$55TeO_2$, (ii) $40ZnF_2$–10MO–$50TeO_2$, (iii) $40ZnF_2$–12MO–$48TeO_2$, (iv) $40ZnF_2$–15MO–$45TeO_2$ and (v) $40ZnF_2$–20MO–$40TeO_2$.

However, we wish to point out here that clear glasses were not formed for all the three series when concentration of MO was increased beyond 20%.

Appropriate amounts (all by wt%) of reagent grade TeO_2 (99·99% pure, Aldrich), MO [P_2O_5, As_2O_3 and Bi_2O_3 (99·9% pure)] and ZnF_2 (99·99% pure, Loba) were thoroughly mixed in an agate mortar and melted in a platinum crucible between 700 and 750°C in a PID temperature controlled furnace for about 30 min until a bubble free liquid was formed. The resultant melt was then cast in a brass mould and subsequently annealed at 200°C. The amorphous nature of the glasses was checked by X-ray diffraction. The samples were then ground and finely polished. The final dimensions of the samples used for the present measurements were about $1 \times 1 \times 0{\cdot}2$ cm. The density (*d*) of the glasses was determined to an accuracy of 0·001 by standard principle of Archimedes' using xylene (99·99% pure) as the buoyant liquid. A thin coating of silver paint was applied (to the larger area faces) on either side of the glasses to serve as electrodes for dielectric measurements. The dielectric measurements were made on LCR Meter (Hewlett-Packard Model-4263B) in the frequency range 10^2–10^5 Hz. The accuracy in the measurement of dielectric constant ε' is ~ ± 0·001 and that in dielectric loss tan *d* is ~ 10^{-4}. Dielectric breakdown strength for all the glasses was determined at room temperature in air medium using a high a.c. voltage breakdown tester (ITL Model AAH-55, Hyderabad) operated with an input voltage of 250 V of frequency 50 Hz; it was ensured that all the glasses used for this study were of exactly identical thickness. Infrared transmission spectra for these glasses was recorded using a BRUKER IFS 66v, FT-IR spectrometer in the frequency range 400–4000 cm^{-1} by KBr pellet method. The differential thermal analysis of these samples is carried out in air with a SEIKO TG/DTA 32 balance with a programmed heating rate of 20°C per minute in the temperature range 30–1000°C.

3. Results and discussion

The density, *d*, glass transition temperature, T_g and Hruby's parameter, K_{gl} which are useful for understanding dielectric properties of the glasses of all the three series (series P, series A and series B) are presented in table 1.

Figure 1 presents isotherms of dielectric constant (e') with concentration of MO measured at 1 kHz. It is observed that for series P and A the dielectric constant (e') decreases with increase in concentration of MO up to about 12%; beyond that the value of e' increases. However, for the series B, the value of e' is found to increase with increase in the concentration of Bi_2O_3 up to 12% and beyond that it is found to decrease.

The temperature dependence of tan *d* for a representative glass no. 2 (containing 10% of MO) for all the three series is shown in figure 2. The variation of dielectric loss tan *d* of ZnF_2–MO–TeO_2 glasses with temperature at different frequencies is found to exhibit distinct maxima; with increasing frequency, the temperature maximum shifts towards higher temperatures and with increasing temperature the frequency maximum shifts towards higher frequencies, indicating dipolar relaxation character of dielectric loss in these glasses. The effect of the content of MO on the relaxation strength of these glasses can be clearly understood from figure 3 in which tan *d* is plotted against temperature at 10 kHz for all these glasses; it is observed that the region of relaxation shifts towards higher temperatures (with narrowing relaxation peaks) with increase in the concentration up to 12% for the series P and A and beyond this concentration, the relaxation peaks are found to be relatively broad and shift towards lower temperatures (table 2).

Table 1. Certain physical properties of ZnF_2–MO–TeO_2 glasses; here P, A, B denote the glasses with P_2O_5, As_2O_3 and Bi_2O_3, respectively.

	Density, *d* (g/cm^3)			Transition temperature, T_g (K)			Hruby's parameter, (K_{gl})		
Glass no.	P	A	B	P	A	B	P	A	B
1. (05% MO)	4·95	5·56	6·01	620	605	610	0·224	0·222	0·227
2. (10% MO)	4·75	5·39	6·38	635	622	607	0·282	0·302	0·203
3. (12% MO)	4·62	5·30	6·55	640	630	598	0·322	0·344	0·172
4. (15% MO)	4·52	5·21	6·71	630	605	603	0·264	0·238	0·197
5. (20% MO)	4·36	5·03	7·06	616	599	608	0·143	0·186	0·221

We have analyzed the relaxation effects exhibited by these glasses by a pseudo Cole–Cole plot method (instead of conventional Cole–Cole plot between $e'(w)$ and $e''(w)$ at a fixed temperature) suggested by Sixou *et al* (1967) in which $e'(T)$ vs $e''(T)$ are plotted at a fixed frequency. The nature of variation of $e'(T)$ and tan d with temperature for these glasses indicates that the Cole–Davidson equation

$$e^*(w) = e_\infty + \frac{e_s - e_\infty}{(1+iwt)^b}, \tag{1}$$

can safely be applied to these glasses. The pseudo Cole–Cole plot cuts e' axis at e_s (high temperature dielectric constant) and e_∞ (low temperature dielectric constant). The plot cuts e' axis (as per Sixou) at low temperature

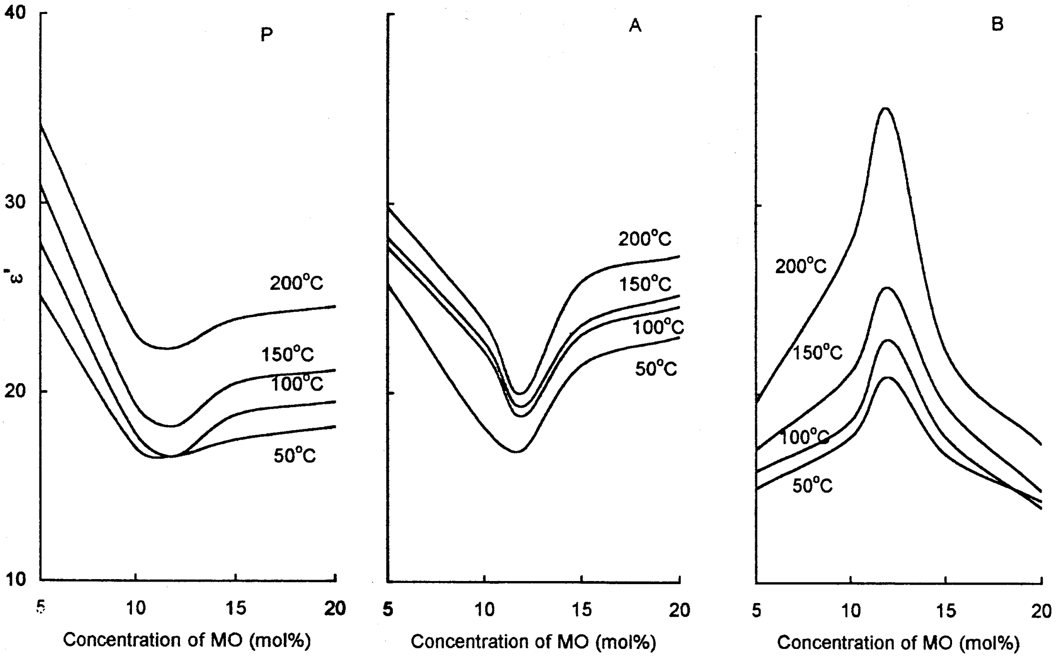

Figure 1. Variation of dielectric constant at different temperatures for ZnF_2–TeO_2 glass (containing P_2O_5, As_2O_3 and Bi_2O_3) with concentration.

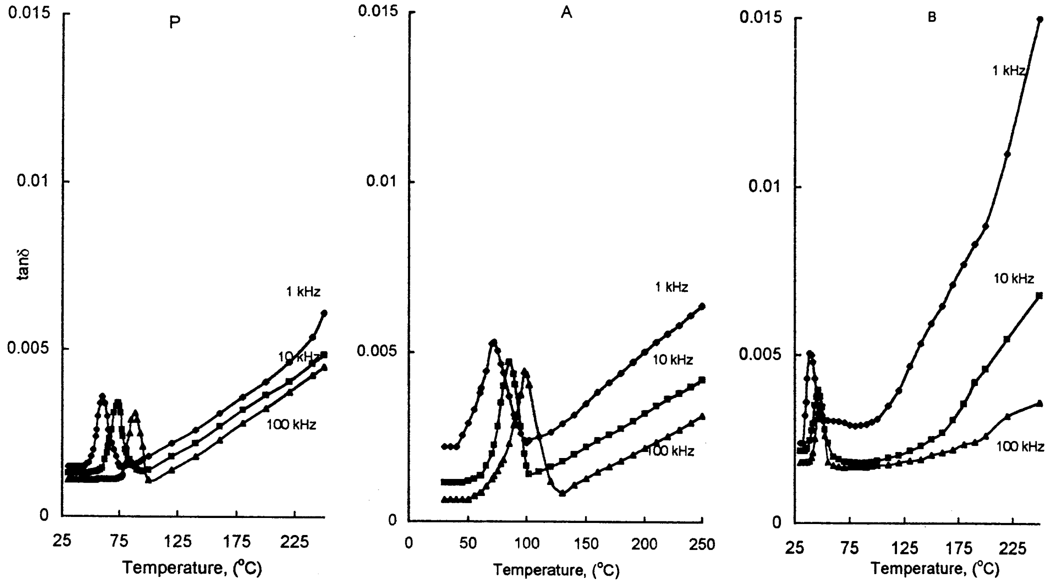

Figure 2. Variation of dielectric loss with temperature at different frequencies for ZnF_2–TeO_2 glass containing 10% of P_2O_5, As_2O_3 and Bi_2O_3.

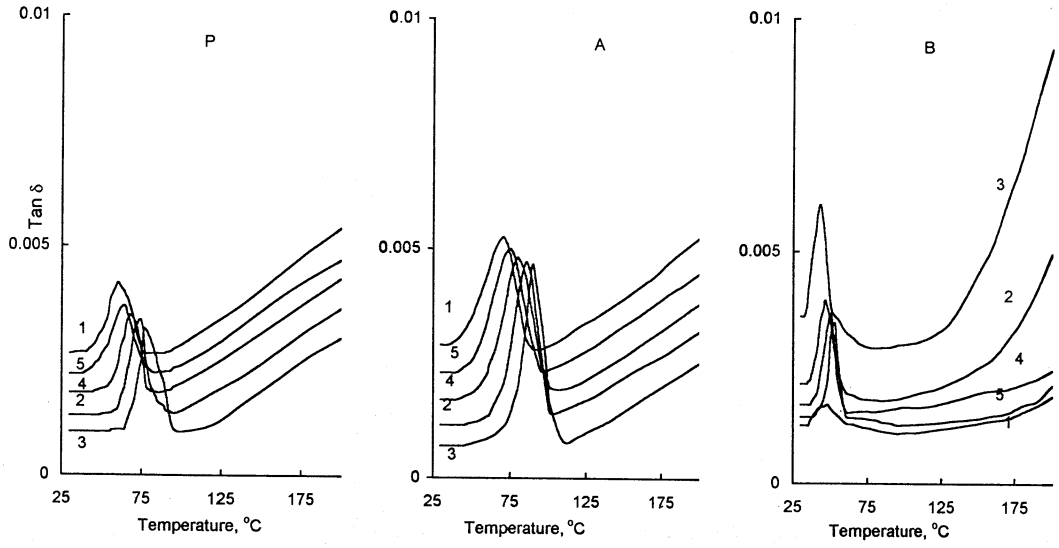

Figure 3. Comparison of tan *d* with temperature at 10 kHz for ZnF_2–TeO_2 glass containing P_2O_5, As_2O_3 and Bi_2O_3.

Table 2. Temperature region of relaxation and spreading factor of ZnF_2–MO–TeO_2 glasses.

	Temperature region of relaxation (°C)			Spreading factor, *b*		
Glass	P	A	B	P	A	B
No. 1	45–77	55–89	43–50	0·60	0·61	0·50
No. 2	60–89	72–103	40–48	0·56	0·56	0·55
No. 3	65–93	78–108	36–46	0·54	0·50	0·60
No. 4	55–85	65–97	45–52	0·57	0·54	0·54
No. 5	50–81	61–94	46–53	0·59	0·58	0·52

side at an angle of $(p/2)b$, where *b* is the spreading factor for relaxation times. For ZnF_2–As_2O_3–TeO_2 glass containing 5% of As_2O_3 (glass no. 1), the pseudo Cole–Cole plot at 1 kHz is shown in figure 4. The spreading factor *b* estimated from this plot is 0·61; such plots have also been drawn for glasses of all the three series and the value of *b* is estimated in a similar way; for the series P and A the values of *b* are found to decrease slightly when concentration of MO is low (12%), for higher concentration the value is found to increase. For series B a reverse trend is observed (table 2).

Further, for series P and A, the value of $(\tan d)_{\max}$ is found to decrease with increase in concentration of MO up to 12% and beyond this concentration the value of $(\tan d)_{\max}$ is observed to increase (figure 5a). For series B, it is noticed that the region of relaxation shifts towards lower temperatures (with broadening relaxation peaks) with ascending values of $(\tan d)_{\max}$ with increase in concentration of Bi_2O_3 up to 12%, beyond this concentration the relaxation peaks are found to become narrow with decreasing values of $(\tan d)_{\max}$ (figure 5a) and shift towards higher temperatures (table 2).

Among the three constituents viz. ZnF_2, MO (P_2O_5, As_2O_3 or Bi_2O_3) and TeO_2 of these glasses, the bonds of tellurium with oxygen are known to be polar in nature (Sanderson 1971) and hence, it is reasonable to attribute the observed dipolar effects in these glasses to the TeO_2 molecules (Ravikumar *et al* 1997b; Singh and Dhawan 1983). The spreading of relaxation times in these glasses may be understood as due to the experience of an approximately random potential energy by the dipoles on diffusing through the distorted structure of the glass (Elliot 1987).

Using the relationship:

$$f = f_0 e^{-W_d/kT}, \qquad (2)$$

the effective activation energy for the dipoles is calculated for these glasses and its variation with concentration of MO is shown in figure 5b for all the series.

It is well known that electronic, ionic, dipolar, and space charge polarizations contribute to the dielectric constant. Among these, the space charge polarization depends on the perfection of the glasses. In the present measurements of e' and tan *d* on these glasses, we notice, a large increase of these parameters with temperature beyond the relaxation region; such a behaviour can only be attributed to space charge polarization due to the bonding defects of the type mentioned earlier in these glasses (Ravikumar *et al* 1995, 1997b).

The a.c. conductivity *s* is calculated at different temperatures for these glasses using the equation

$$s = w e_0 e' \tan d, \qquad (3)$$

(where e_0 is the vacuum dielectric constant) for different frequencies and the plot of log *s* against $1/T$ is shown in

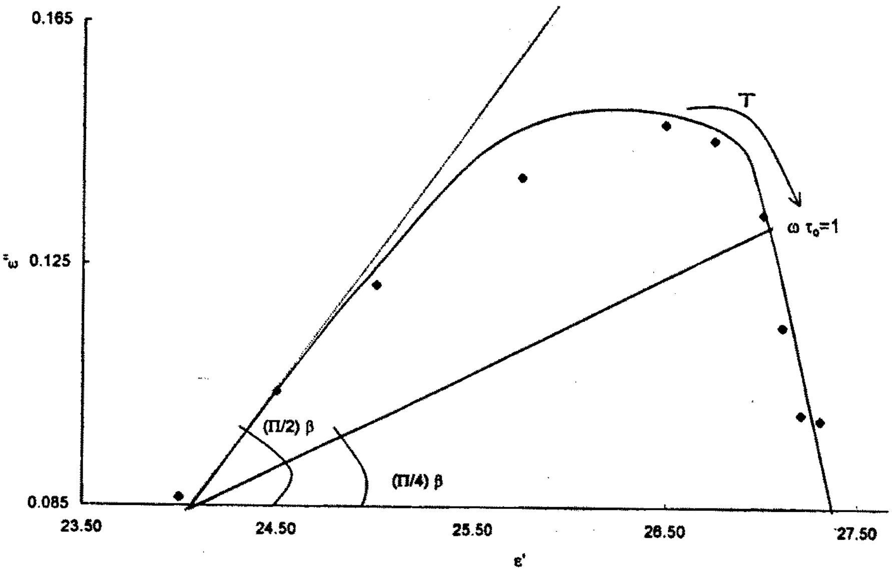

Figure 4. A pseudo Cole–Cole plot for glass no. 1 of series A at 1 kHz.

figure 6 for all 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 σ with $1/T$ could be observed, is calculated and presented in table 3; the activation energy is found to be maximum for glass no. 3 of the series P and series A and is found to be minimum for glass no. 3 of series B.

In general, the a.c. conductivity of the amorphous material, where the charge carriers experience an approximately random potential energy on diffusing, is found to obey the equation (Austin and Mott 1969):

$$\sigma(\omega) = A\omega^s, \tag{4}$$

with the exponent $s < 1$ (up to the frequency 1 MHz), is considered to signify the coupling of an ion's movement with its environment (Austin and Mott 1969; Nagai 1979, 1980) and the values of s obtained for all the three series are given in table 3.

The equation for a.c. conductivity due to quantum mechanical tunneling is given by (Austin and Mott 1969):

$$\sigma(\omega) = \eta e^2 KT[NE_F]^2\alpha^{-5}\omega[\ln \nu_{ph}/\omega]^4, \tag{5}$$

where $N[E_F]$ is the density of energy states near the Fermi level, α the electronic wave function decay constant and its average value is determined from $\sigma = e^{-2\alpha R_i}$, ν_{ph} the phonon frequency ($\sim 5 \times 10^{12}$ Hz) and η a constant and its value is given by: $\eta = \pi/3$ (Austin and Mott 1969), $\eta = 3{\cdot}66\pi^2$ (Butcher and Hyden 1977), $= \pi^4/96$ (Pollak 1971).

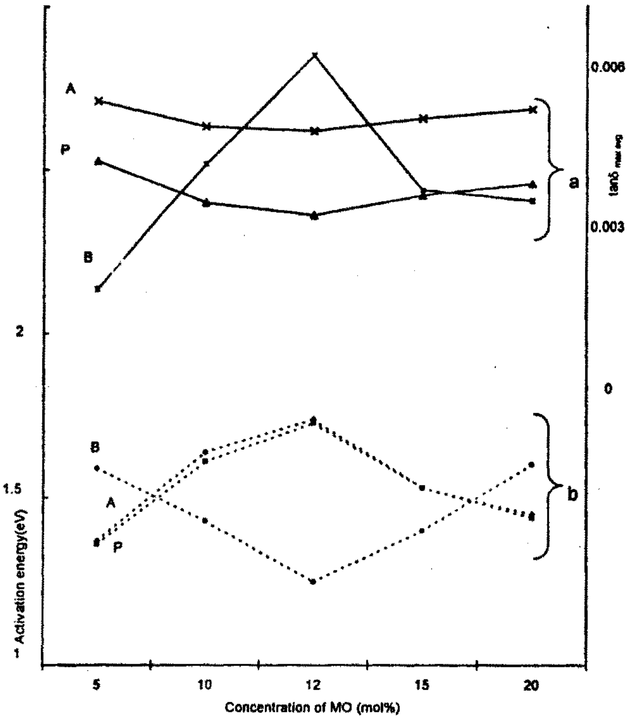

Figure 5. Variation of a. (tan $\delta)_{\text{max. avg}}$ and b. activation energy for dipoles with the concentration of metal oxides for all the series.

Among various mechanisms for conduction in the amorphous materials, the conduction in the localized states near the Fermi level corresponds to the case in which a.c. conductivity is nearly temperature independent and varies linearly with frequency. The conduction in the ZnF$_2$–MO–TeO$_2$ glasses in the low temperature region (up to 315 K) can be attributed to this mechanism. The value of $N[E_F]$, i.e. the density of energy states near the Fermi level is calculated using (5), with value of numerical constant η suggested by Austin and Mott (1969) and presented in table 3. In series P and series A, the value of

N[E_F] is found to decrease from glass no. 1 to 3 (12% MO) and its value is found to increase beyond 12% concentration of MO. Further, the range of *N*[E_F] values obtained was ~ 10^{20} eV^{-1}/cm^3. Such values of *N*[E_F] suggest the localized states near the Fermi level (Elliot 1987). The decrease in the conductivity from glass no. 1 to 3 can be understood due to the decrease in the density of these energy states. Further, the increase in conductivity beyond 12% MO concentration is due to the increase in the density of such energy states. In series B the trend in the values of *N*[E_F] seem to be reversed.

When the dielectric is placed 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 by (Tareev 1979):

$$r_1 = E^2 wee_0 \tan d \ \text{W/m}^3. \qquad (6)$$

This equation indicates that the higher the values of *e¢* tan *d* of the glass at a given frequency, the higher are the losses. In a dielectric across which the voltage is

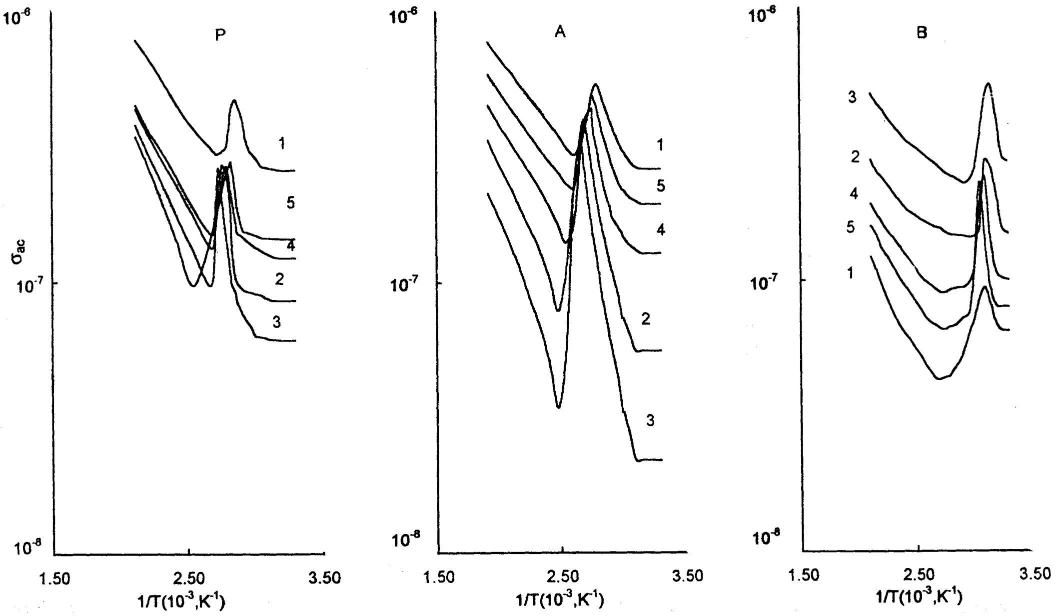

Figure 6. A comparison plot of conductivity with 1/*T* for ZnF_2–MO–TeO_2 glasses at 100 kHz (MO–P_2O_5, As_2O_3 and Bi_2O_3).

Table 3. Data on density of energy states, activation energy and breakdown strength for series P, A and B.

	Density of energy states *N*(E_F) in (10^{20} eV^{-1}/cm^3) (according to Austin and Mott)			Activation energy (eV)			s_{exp}		
Glass	P	A	B	P	A	B	P	A	B
No. 1	0·40	0·53	0·20	0·31	0·30	0·39	0·85	0·84	0·91
No. 2	0·23	0·24	0·36	0·36	0·36	0·26	0·86	0·86	0·88
No. 3	0·19	0·15	0·51	0·38	0·38	0·23	0·88	0·90	0·86
No. 4	0·28	0·37	0·26	0·35	0·34	0·28	0·87	0·88	0·87
No. 5	0·30	0·46	0·22	0·30	0·32	0·33	0·84	0·85	0·90

Breakdown strengths of the three series (kV/cm)

Series	Glass no. 1	Glass no. 2	Glass no. 3	Glass no. 4	Glass no. 5
P	13·3	19·2	20·4	16·8	15·5
A	12·5	18·5	19·1	16·1	15·1
B	18·8	16·9	12·6	17·1	17·3

applied, heat is liberated, the temperature of the dielectric then rises and the loss increases still more. The dielectric breakdown strength is in fact inversely proportional to the specific dielectric loss represented by (6).

The measured values of breakdown strengths of ZnF$_2$–MO–TeO$_2$ glasses are presented in table 3. It is observed that for series P and A the value of breakdown strength is maximum for glass no. 3, whereas, for series B it is minimum. This indicates the decrease of e¢ and tan d with temperature for series P and A up to about 12% of MO and increase in these parameters for series B at about the same concentration. Thus, the experiments on the dielectric breakdown strength of ZnF$_2$–MO–TeO$_2$ glasses reveal that there is a decrease in the disorder with increase in concentration of MO ($\leq$ 12%) for series P and A; there is an increase in the disorder in the glasses with increase in the concentration of Bi^{3+} ions up to 12%.

Figure 7a shows the DTA traces for glass no. 1 for all the series of glasses under investigation. The curves show glass transition temperature T_g; an exothermic peak (T_c) due to crystallization followed by an endothermic effect due to the re-melting of the glass (symbolized by T_m). A similar analysis was carried out for all the other glasses and the values of T_g and K_{gl} are furnished in table 1. It is observed that the glass transition temperature (T_g) and the Hruby's (1972) parameter $K_{gl} = [(T_c - T_g)/(T_m - T_c)]$ increases up to 12% concentration of P$_2$O$_5$ and As$_2$O$_3$ and further increase in the concentration of these oxides causes a decrease in the values of T_g and K_{gl}. However, for series B, a reverse trend is observed (figures 7b and c). These results indicate that the glasses of series P and A have good glass forming ability, when the metal oxides P$_2$O$_5$ and As$_2$O$_3$ are present at about 12% in the glass composition; whereas, for series B, a good glass forming ability is observed, when Bi$_2$O$_3$ is present beyond 12%.

Figure 8a shows infrared transmission spectra of glass no. 1 of all the three series of ZnF$_2$–MO–TeO$_2$ glasses along with that of crystalline TeO$_2$. IR spectrum of crystalline TeO$_2$ exhibited two absorption bands at 650 cm^{-1} and 772 cm^{-1} which are assigned to the stretching vibrations of axial (n_{ax}) and equatorial (n_{eq}) bonds respectively. In the IR spectra of the glasses of all the series the (n_{eq}) band is found to be missing. However, the axial band is observed to shift towards lower wave numbers in the series P and A with increase in the concentration of MO up to 12% whereas in bismuth series it shifts towards higher wave numbers at about the same concentration. But beyond 12% concentration of MO the trend seems to be reversed in all the three series (figure 8b).

In addition to the TeO$_2$ axial band, bands due to P$_2$O$_5$, As$_2$O$_3$ and Bi$_2$O$_3$ are also observed in these glasses. The phosphate series exhibit two prominent absorption bands, one in the wave number range (915–935 cm^{-1}) and another in the range (1040–1060 cm^{-1}) which are identified due to P–O–P bending and asymmetric stretching of PO$_3$ groups respectively (Ouchetto *et al* 1991); with increase in the concentration of P$_2$O$_5$, the P–O–P bending band shifts towards slightly higher wave numbers up to about 12%

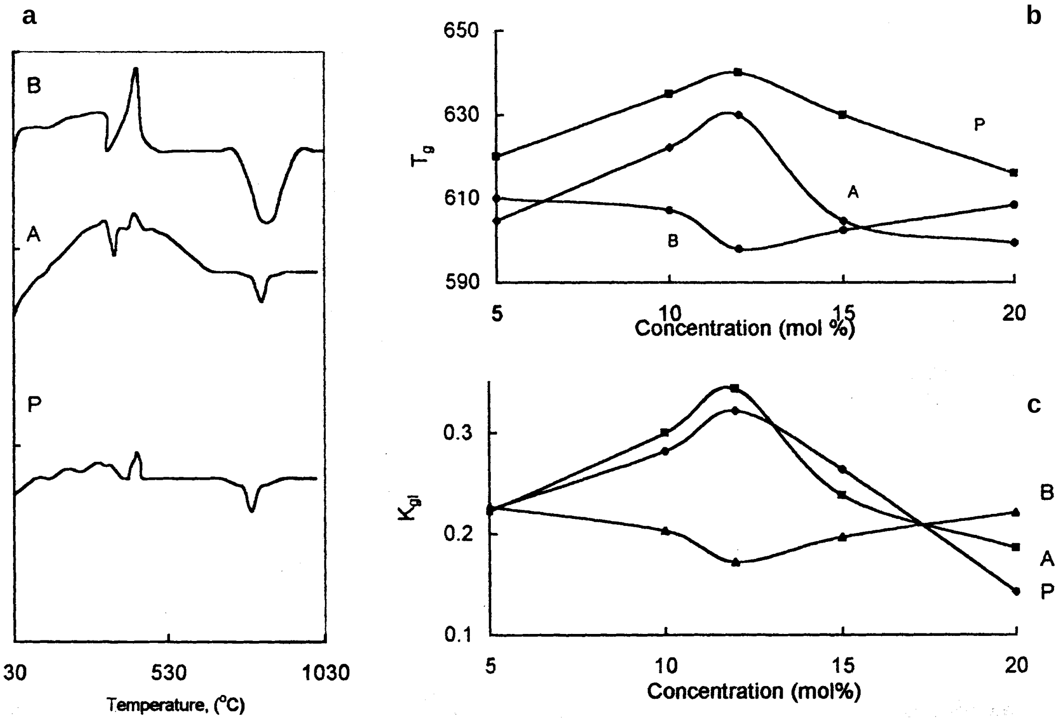

Figure 7. **a.** DTA traces for 5% of MO and variation of **b.** T_g and **c.** K_{gl} of the three series with concentration of metal oxide.

concentration. This indicates a more number of linkages of phosphate groups with each other rather than cross linking with other metal cations causing the observed gradual decrease of dielectric parameters up to this concentration. When concentration of P_2O_5 is more than 12%, the P–O–P bending band shifts towards lower wave number (figure 8b, P) which indicates a larger number of cross linkages between the neighbouring phosphate chains and the metal cations with two non-bridging oxygens of PO_4 tetrahedra. This results in the increase in the dielectric parameters beyond 12% concentration of P_2O_5. The band due to PO_3 groups also exhibits similar behaviour.

The arsenic series shows two prominent bands in the wave number ranges (620–625 cm^{-1}) and (1036–1052 cm^{-1}) which are attributed to the totally symmetric bending (n_2) vibration and totally symmetric stretching (n_1) vibration, respectively. With increase in the concentration of As_2O_3 the n_2 band shifts to lower wave numbers up to 12% and beyond this concentration it is found to shift to higher values (figure 8b, A). The n_1 band exhibits similar behaviour. Further, the n_{ax} band and n_2 band of AsO_3 groups are noticed to be unresolved. The non resolution of n_2 bands of TeO_2 and AsO_3 groups may indicate the cross linking of a part of TeO_4 units with AsO_3 units to form As–O–Te bonds in the glass network; this is reasonable because of close ionic radii of As^{3+} (0·58 Å) and Te^{4+} (0·70 Å). A similar linkage As–O–Zn is also possible as the ionic radius of Zn^{2+} (0·74 Å) is nearer to that of As^{3+} ions. As more number of arsenic units enter into the glass network, the number of such type of linkages will also increase making the glass network more stronger. The decrease in the dielectric constant, loss tan *d*, a.c. conductivity, *s* and increase in transition temperature, T_g, with increase in the concentration of As_2O_3 up to 12% may be ascribed due to such linkages. When As_2O_3 is present in larger quantities (beyond 12%), it is quite likely

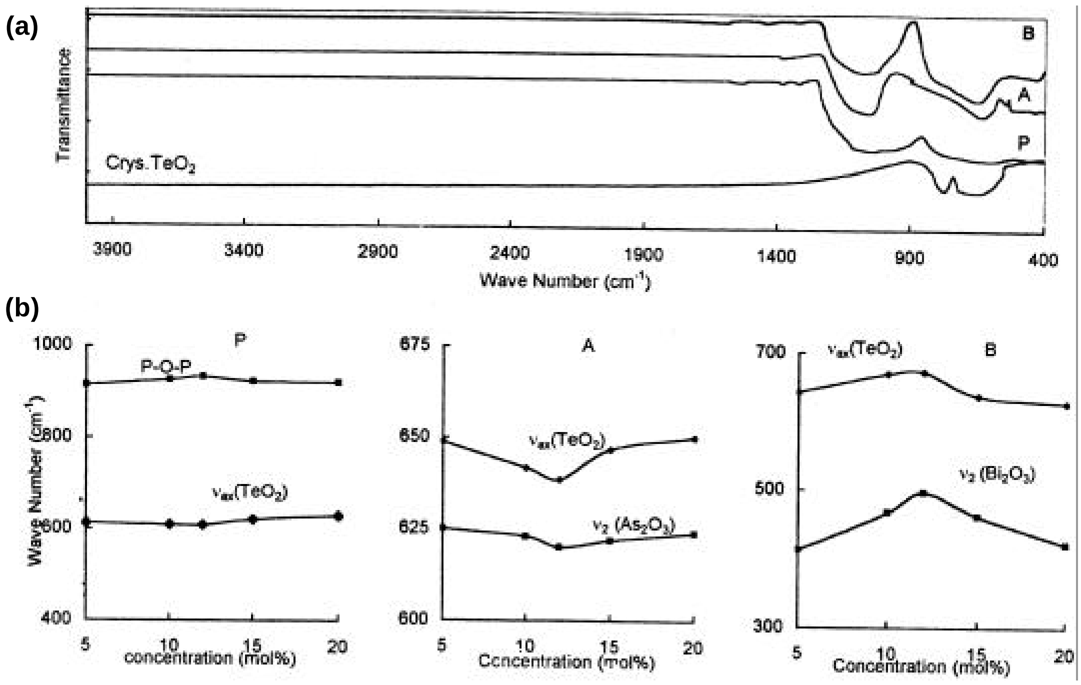

Figure 8. (**a**) IR spectra of glass no. 1 (5%) of three series and (**b**) variation of position of n_{ax} band and band 2 of all the three series with concentration of MO.

Table 4. Positions of the absorption bands in the infrared spectra of ZnF_2–MO–TeO_2 glasses.

Glass no.	IR bands of TeO_2 (cm^{-1})			Band 2 (cm^{-1})			Band 3 (cm^{-1})		
	P	A	B	P	A	B	P	A	B
No. 1	612·6	648·8	642·6	915·0	625	423·5	1040	1051	1094
No. 2	610·2	641·6	669·9	926·6	623	467·6	1050	1051	1089
No. 3	609·0	638·4	672·1	933·6	620	497·0	1057	1038	1093
No. 4	620·9	646·7	637·4	922·8	622	462·4	1041	1044	1093
No. 5	629·6	650·1	627·4	920·8	624	422·4	1039	1050	1092

that the bond angle of O–As–O at the pyramidal face of AsO_3 units may increase. Such increase in the bending leads to asymmetrical bending vibrations; the shifting of symmetrical bending vibration of n_2 band towards higher wave numbers with decreasing intensity in fact supports this. The larger the bending, higher is the degree of deformation leading to larger space charge polarization causing an increase in the dielectric parameters.

In the IR spectra of bismuth series, two intense bands are observed in the ranges (400–500 cm^{-1}) and (1089–1094 cm^{-1}) which are due to (n_2) totally symmetric bending vibration (Hazra and Ghosh 1995) and the presence of BiO_nF_m polyhedra, respectively. The band due to totally symmetric bending shifts to higher wave number with increase in the concentration of Bi_2O_3 up to 12% and beyond this concentration it shifts to lower wave numbers (figure 8b, B). The other band also shows a similar behaviour. The data of IR spectra for various bands of ZnF_2–MO–TeO_2 glasses is given in table 4. The values of *e*¢ and tan *d* (at a fixed temperature and frequency) of series B are found to increase with increase in Bi_2O_3 concentration up to 12%; obviously this indicates when Bi_2O_3 is present in smaller concentrations, these molecules mainly occupy the octahedral positions and act as modifiers. This is also borne out by the fact that the symmetrical vibrational wave numbers of n_{ax}^{s}-bonds of TeO_4 groups are shifted towards higher wave numbers with decreasing intensity for such concentrations. The decrease in the values of *e*¢ and tan *d* beyond 12% concentration of Bi_2O_3 indicates a decrease in the distortion of glass network which suggest that these molecules take the network forming positions with BiO_3 pyramidal units at such concentrations. This is also evidenced from IR spectra (of glasses no. 3 to 5 of series B) in which the n_{ax}^{s}-bonds of TeO_4 groups are shifted towards lower wave numbers with increasing intensities indicating higher symmetry of the network (figure 8 b, B).

4. Conclusions

Finally our analysis on detailed studies of the dielectric properties coupled with IR spectra and DTA on ZnF_2–P_2O_5–TeO_2, ZnF_2–As_2O_3–TeO_2 and ZnF_2–Bi_2O_3–TeO_2 glass systems indicate that the structure of glass in the first two systems is more stable when P_2O_5 and As_2O_3 are present in smaller quantities (< 12%), whereas the third system seems to be more stable when $Bi_2O_3 \geq 12\%$.

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