

Spectroscopic and Dielectric Relaxation Studies in Chromium Doped Lead-Tellurite Glasses

^{1,2}C. Laxmikanth, ²Mengesha Ayene ²Eyob Daniel

¹Department of Physics, The University of Dodoma, Dodoma, Tanzania.

²Department of Physics, College of Natural Science, Wollo University, Dessie, Ethiopia.

Abstract- Different concentrations of Cr₂O₃ doped ZnF₂-PbO-TeO₂ glasses were prepared by melt quench method. The characterization of these glasses was done by means of x-ray diffractometry, differential scanning calorimetric and IR spectroscopic techniques. The studies on some of these techniques confirmed glassy nature and exposed the variation of the glass forming ability parameter, K_{gl} , and the shifting of various symmetrical bending vibrational frequencies with increase in concentration of Cr₂O₃. Various absorption bands with varying peak intensities were observed from optical absorption studies of these glasses for different concentrations of Cr₂O₃. From the dielectric studies of these glasses, various dielectric parameters viz., dielectric constant (ϵ'), loss ($\tan \delta$), and ac conductivity (σ) were determined as a function of frequency (10^2 Hz to 10^5 Hz) and temperature (30°C to 200°C). In addition, dielectric breakdown strength at room temperature was determined to estimate the insulating characteristics of these glasses. Pseudo Cole-Cole plot method was used to describe the dielectric relaxation effects in these glasses. Quantum mechanical tunnelling model was used to describe the temperature independent part of the conductivity of these glasses.

Index Terms- lead-tellurite glasses, Hruby's parameter, optical absorption, dielectric parameters, dielectric relaxation.

I. INTRODUCTION

The study of dielectric properties, such as dielectric constant ϵ' , loss $\tan \delta$ and ac conductivity σ_{ac} over a wide range of frequency and temperature and the dielectric breakdown strength of the glasses helps in assessing their insulating character; these studies may also help in understanding the structure 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 [1-5]. Tellurite glasses are best known due to their superior physical properties such as high density, high refractive index, low melting and softening temperatures and high infrared transmission. In view of these 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 were also judged as very good materials for hosting lasing ions like chromium / rare-earth ions, since these glasses provide a low phonon energy environment to minimize non-radiative losses. A number of recent investigations on optical and mechanical properties of these glasses mixed with different modifiers are available in literature [6-15]. Among various tellurite glass systems, the alkali free ZnF₂-TeO₂ glasses are observed to be relatively moisture resistant and possess a low rate of crystallization. The present study is intended to report the dielectric properties of this glass system mixed with PbO as modifying oxide. Addition of this modifier into the glass matrix produce low rates of crystallization, since PbO has the ability to form stable glasses due to its dual role; one as glass former, if Pb-O is covalent and the other as modifier, if Pb-O is ionic [16]. Most of the studies available on tellurite glasses are on optical [17-20] (such as Raman spectra, infrared spectra, optical absorption, luminescence etc.) and elastic properties [21, 23]. Though some studies on electrical properties [24-26] (mostly on dc conductivity especially of some binary tellurite systems) exist in the literature, much devoted studies particularly on dielectric properties such as dielectric relaxation, ac conductivity and breakdown strength of tellurite glass

systems of this type are not available. Such studies of dielectric parameters over a wide range of frequency and temperature of the glasses help in assessing their insulating character and in understanding the structure of the glass up to some extent [1-5]. Chromium ion has a strong influence over the electrical properties of the glasses, for the simple reason that it exists in different oxidation states viz., Cr³⁺ (acts as modifier with CrO₆ structural units) and Cr⁶⁺ (acts as network former with CrO₄²⁻ structural units). The content of chromium in different states with different structural units in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strengths, mobility of the modifier cation etc. Extensive investigations on the optical absorption, luminescence and ESR spectroscopy of Cr³⁺ ion in a variety of inorganic glasses were prepared in the recent years in view of their importance in the development of tunable solid-state lasers and new luminescence materials [27, 28].

It is the aim of this investigation to have a comprehensive understanding over the influence of chromium ions on the insulating character of ZnF₂-PbO-TeO₂ glasses from a systematic study on dielectric constant ϵ' , loss $\tan \delta$, ac conductivity σ_{ac} in the frequency range 10^2 - 10^5 Hz and in the temperature range 30-200°C and in addition the dielectric breakdown strength in air medium. Further, using the results of these studies an attempt has been made to throw some light on the structural modifications (with the aid of data on optical absorption and infrared spectral studies) that take place in the glass network due to varying concentrations of Cr₂O₃.

II. EXPERIMENTAL PROCEDURES

A. Preparation techniques of glasses

For the present investigation, the composition 40ZnF₂-10PbO-(50-x)TeO₂: Cr₂O₃; is taken with x = 0.05, 0.1, 0.2, 0.3 and 0.4, all in wt.% and the glasses are, respectively, labelled as PT (0.05), PT (0.1), PT (0.2), PT (0.3) and PT

(0.4). Melt-quench method was used to cast the glass materials from appropriate amounts of respective analar grade reagents. The glassy nature of the quenched materials was checked by using X-ray diffraction technique.

B. Property measurements

The density d of the glasses was determined to an accuracy of 0.001 by the standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid. The glass transition temperatures T_g , crystallization temperature T_c , and melting temperature T_m of these glasses were determined (to an accuracy of $\pm 1^\circ\text{C}$) by differential scanning calorimetry traces, recorded using Universal V23C TA Differential Scanning Calorimeter with a programmed heating rate of 15°C per minute in the temperature range $30\text{--}700^\circ\text{C}$. The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range $350\text{--}800\text{ nm}$ using Shimadzu UV-VIS-NIR (model 3100) spectrophotometer. Infrared transmission spectra for these glasses were recorded using a Perkin Elmer Spectrometer in the wave number range $400\text{--}4000\text{ cm}^{-1}$ by KBr pellet method. 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 $10^2\text{--}10^5\text{ Hz}$ and in the temperature range $30\text{--}200^\circ\text{C}$. The dielectric breakdown strength for all the glasses was determined at room temperature in air medium using a high ac voltage breakdown tester (ITL Model AAH-55, Hyderabad) operated with an input voltage of $220\text{--}250\text{ V}$ at a frequency of 50 Hz ; it was ensured that all the glasses used for this study were of almost identical thicknesses.

III. RESULTS

Fig. 1 shows the differential scanning calorimetric traces of $\text{ZnF}_2\text{--PbO--TeO}_2$ with different concentrations of Cr_2O_3 . The glasses exhibit an endothermic change between 315°C and 335°C , which can be attributed to the glass transition temperature T_g . At still higher temperature T_c , an exothermic peak due to the crystal growth followed by another endothermic effect at a temperature T_m due to the re-melting of the glass are also observed. From the measured values of T_g , T_c and T_m , the parameter, $K_{gl} = (T_c - T_g)/(T_m - T_c)$, known as Hruby's parameter, that gives the information on the stability of the glass against divitrification, is evaluated and its variation with the concentration of Cr_2O_3 is presented as an inset in Fig. 1. The K_{gl} parameter shows an increasing trend beyond 0.3% of Cr_2O_3 . Table 1 shows the data on analysis of differential thermal calorimetric studies on $\text{ZnF}_2\text{--PbO--TeO}_2\text{:Cr}_2\text{O}_3$ glasses.

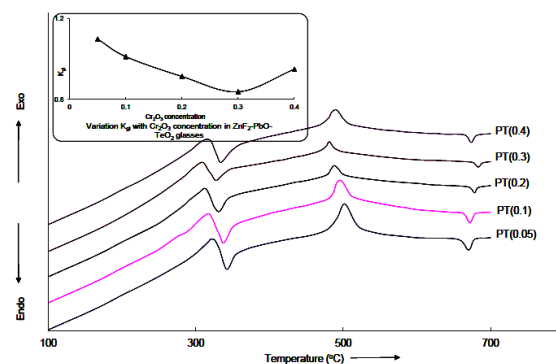


Fig. 1. DSC patterns of Cr_2O_3 doped $\text{ZnF}_2\text{--PbO--TeO}_2$ glasses. Inset shows the variation of K_{gl} parameter with different concentration of Cr_2O_3 doped $\text{ZnF}_2\text{--PbO--TeO}_2$ glasses

Table 1
Summary of data on optical absorption spectra of $\text{ZnF}_2\text{--PbO--TeO}_2\text{:Cr}_2\text{O}_3$ glasses

Glass	Band positions			D_q (cm^{-1})	B (cm^{-1})	Nepheluric ratio, β
	$^4A_2 \rightarrow ^4T_1(F)$	$^4A_2 \rightarrow ^4T_2$	$^4A_2 \rightarrow ^4T_1(P)$			
PT	462	661	346	1512	717	0.781

Fig. 2 shows the optical absorption spectra containing different concentrations of Cr_2O_3 , recorded at room temperature in the wavelength region $350\text{--}800\text{ nm}$.

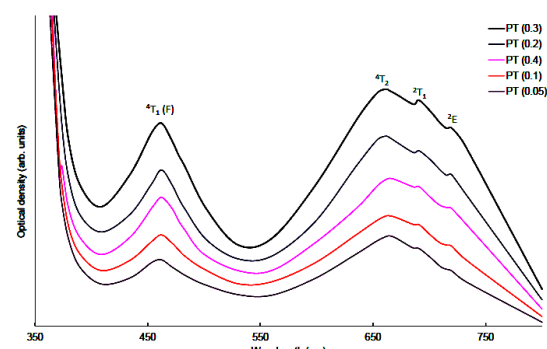


Fig. 2. Optical absorption spectra of $\text{ZnF}_2\text{--PbO--TeO}_2\text{:Cr}_2\text{O}_3$ glasses; all the transitions are from the ground state 4A_2

The spectra show two prominent absorption bands with the peaks at 451 nm (peak 1) and 654 nm (peak 2); with the increase in the concentration of Cr_2O_3 , the peak positions remain unchanged but the intensity associated with these peaks increased up to 0.3 wt. \% and beyond that it is decreased. Further, an additional kink (whose intensity is found to increase with the increase in the concentration of Cr_2O_3 at the expense of other two prominent peaks) has also been observed.

The optical absorption spectrum has been analyzed using Tanabe Sugano diagrams and the absorption peaks are assigned to $^4A_2 \rightarrow ^4T_1(F)$ (peak 1) and $^4A_2 \rightarrow ^4T_2$ (peak 2) transitions of Cr^{3+} ions. The value of crystal field splitting energy D_q evaluated using the energies of these transitions is found to 1512 cm^{-1} . Similarly the value of inter electronic repulsion parameter B (Racah parameter) is found to be 717 cm^{-1} . Our calculations also predict a third band due to the $^4A_2 \rightarrow ^4T_1(P)$ transition in the absorption spectra of this glass; this band could not be observed as its wavelength lies well below the cut-off value. In addition, two weak bands due to the spin forbidden transitions $^4A_2 \rightarrow ^2T_1$ and $^4A_2 \rightarrow ^2E$ have also been located in the spectra of these glasses [29]. These observations indicate the presence of chromium ion mainly in $\text{Cr}^{3+}(d^3)$ state with octahedral environment up to 0.3 wt. \% concentration of Cr_2O_3 . The additional kink observed at about 370 nm in the spectra of the glasses containing higher concentrations of Cr_2O_3 (> 0.3) is attributed to CrO_4^{2-} (T_d) ions [30].

Infrared transmission spectra of ZnF₂-PbO-TeO₂ glasses containing Cr₂O₃ along with the IR spectrum of the crystalline TeO₂ (C-TeO₂) is presented in Fig. 3.

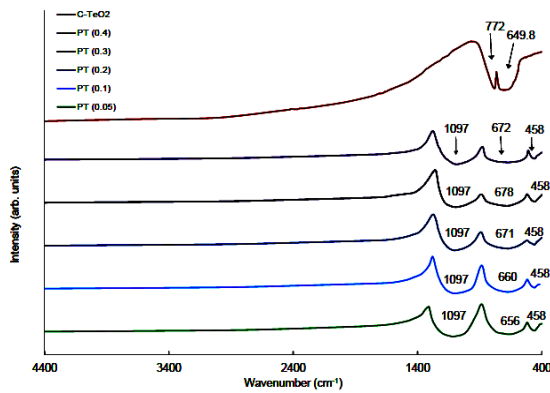


Fig. 3. IR spectra of ZnF₂-PbO-TeO₂:Cr₂O₃ glasses along with that of crystalline TeO₂ (C-TeO₂)

The spectrum of crystalline TeO₂ has exhibited two fundamental bands at 772 cm⁻¹ (ν_1 (A₁) – equatorial band) and at 650 cm⁻¹ (ν_2 (A₂) – axial band, band 2) of TeO₂ [31]. However, in the spectrum of ZnF₂-PbO-TeO₂ glass, the equatorial band is observed to be missing and only the band due to $\nu_{TeO_2ax}^S$ vibrations with C_{2v} symmetry is observed. In addition, a band presumably due to PbO_nF_m [32] complexes is detected (in the range 1085-1100 cm⁻¹, band 3) in the spectrum. Further, the IR spectrum has exhibited absorption band (band 1) at 458 cm⁻¹ due to PbO₄ structural vibrations [33]. When the glass is doped with Cr₂O₃, the intensity of the axial band is found to decrease with the shifting of meta-centre towards slightly higher wave number up to 0.3% concentrations of Cr₂O₃, beyond these concentrations the intensity and the peak position of this band seems to exhibit a reverse tendency.

Fig. 4 represents the variation of dielectric constant (ϵ') with the concentration of Cr₂O₃ for ZnF₂-PbO-TeO₂ glasses at 1 kHz frequency, while the inset of the same figure presents the variation of dielectric constant (ϵ') at 0.3 wt. % of Cr₂O₃ of the glass at different frequencies.

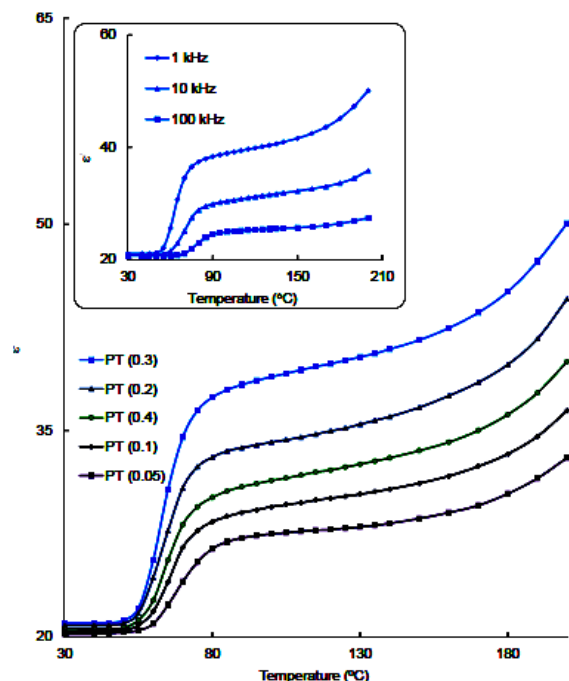


Fig. 4 Variation of dielectric constant with temperature for Cr₂O₃ doped ZnF₂-PbO-TeO₂ glasses at 1 kHz. Inset shows the variation of dielectric constant with temperature for 0.3 wt. % of Cr₂O₃ doped ZnF₂-PbO-TeO₂ glass at different frequencies.

The maximum value of ϵ' is observed 0.3 wt. % of Cr₂O₃ at all frequencies and beyond these concentrations the value of dielectric constant is found to decrease. The variation of dielectric loss, tan δ , 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 different concentrations of Cr₂O₃ on the relaxation strength of these glasses can be clearly understood from Fig.5 in which tan δ is plotted against temperature at different concentrations of Cr₂O₃ containing ZnF₂-PbO-TeO₂ glasses at 10 kHz frequency. The inset of the same figure presents the temperature dependence of tan δ containing a particular concentration (0.3 wt.%) of Cr₂O₃ at different frequencies.

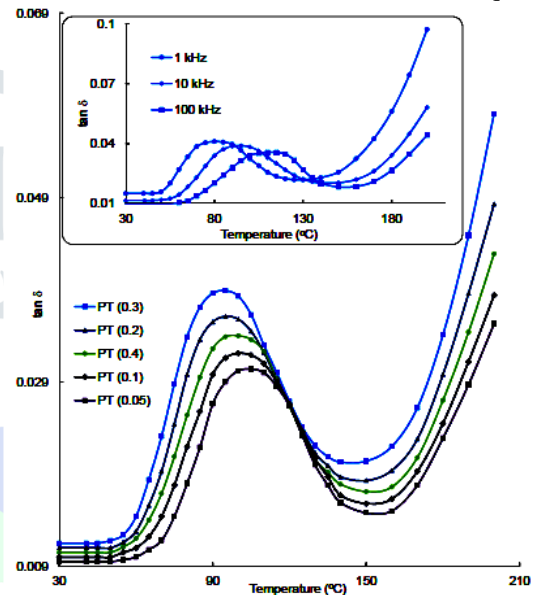


Fig. 5 Variation of dielectric loss with temperature for Cr₂O₃ doped ZnF₂-PbO-TeO₂ glasses at 10 kHz. Inset shows the variation of dielectric loss with temperature for 0.3 wt. % of Cr₂O₃ doped ZnF₂-PbO-TeO₂ glass at different frequencies.

The region of relaxation is observed to shift towards higher temperatures (with narrowing relaxation peaks) with increase in the concentration of Cr₂O₃ beyond 0.3, and below this concentration, the relaxation peaks are found to be relatively broader (Table 2).

Table 2 Temperature region of relaxation and spreading factor of ZnF₂-PbO-TeO₂ glasses

Concentration of Cr ₂ O ₃	Temperature region of relaxation (°C)	Spreading factor, β
0.05	91-121	0.41
0.1	80-111	0.44
0.2	88-118	0.49
0.3	80-111	0.51
0.4	86-115	0.45

The relaxation effects of these glasses were analyzed by pseudo Cole-Cole plot method (instead of conventional Cole-Cole plot method between $\epsilon''(\omega)$ and $\epsilon'(\omega)$ at a fixed temperature) suggested by Sixou [35] in which $\epsilon'(\omega, T)$ vs. $\epsilon''(\omega, T)$ are plotted at a fixed frequency. The nature of variation of $\epsilon'(T)$ and tan δ with temperature for these glasses indicates that, the Cole-Davidson equation

$$\epsilon''(\omega, T) = \epsilon''_{max} \frac{\omega^{\alpha} \tau^{\alpha}}{1 + \omega^{\alpha} \tau^{\alpha}} \quad (1)$$

can be safely applied. Separating real and imaginary terms of equation (1) and rewriting with explicit temperature dependence of terms:

$$\epsilon'' = \frac{A_0 \omega \tau \exp(-W_d/kT)}{1 + \omega^2 \tau^2} \quad (2)$$

and

$$\epsilon' = \frac{A_0}{1 + \omega^2 \tau^2} \quad (3)$$

Where,

$$\epsilon' = \epsilon_s - \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \quad (4)$$

In equation (4), A_0 is a constant and W_d is the activation energy for the dipoles. The plot between $\epsilon''(T)$ and $\epsilon'(T)$ given by equations (2) and (3) at a fixed frequency is often called a pseudo Cole-Cole plot which cuts ϵ' axis at ϵ_s (high temperature dielectric constant) and ϵ_∞ (low temperature dielectric constant). The plot cuts ϵ' axis (as per Sixou [35]) at low temperature side at angle of $(\pi/2)\beta$, where β is spreading factor for relaxation times. The spreading factor β is estimated from the pseudo Cole-Cole plot of 0.3 wt.% of Cr_2O_3 doped ZnF_2 -PbO- TeO_2 glass is 0.51; the value of β is found to increase slightly up to 0.3 concentrations of Cr_2O_3 and beyond these concentrations a reverse trend is observed (Table 2).

Further, the value of $(\tan \delta)_{max. avg}$ has exhibited the highest value at 0.3% concentration

Using the equation:

$$f = f_0 \exp(-W_d/kT) \quad (5)$$

The effective activation energy W_d , for the dipoles is calculated for the glasses; the value of activation energy is found to be minimum for 0.3% of concentration.

The ac conductivity σ is calculated at different temperatures using the equation:

$$\sigma = \omega \epsilon_0 \tan \delta \quad (6)$$

(where ϵ_0 is the vacuum dielectric constant) for different frequencies and the plot of $\log \sigma$ against $1/T$ is shown in Fig. 6 at 100 kHz. From these plots, the activation energy for conduction in the high temperature region over which a near linear dependence of $\log \sigma$ with $1/T$ could be observed, is calculated and presented in Table 3. The activation energy is found to be minimum at 0.3% of concentration.

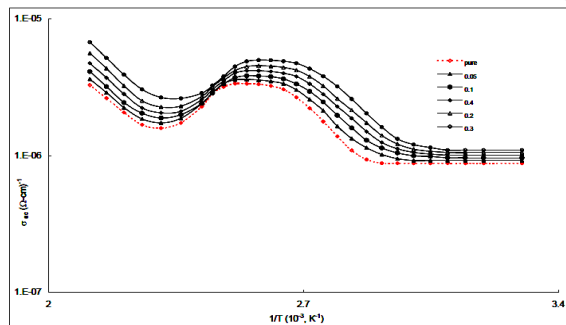


Fig. 6. A comparison plot of ac conductivity with 1/T for Cr_2O_3 containing ZnF_2 -MO- TeO_2 glasses at 100 kHz

Table 3
Data on density of energy states, activation energy for conduction and dielectric breakdown strength of ZnF_2 -PbO- TeO_2 glasses

Concentration of Cr_2O_3	Dielectric breakdown strength (kV/cm)	Activation energy for conduction (eV)	S_{exp}
0.05	11.7	0.24	0.91
0.1	11.6	0.23	0.86
0.2	11.2	0.22	0.84
0.3	10.9	0.21	0.82
0.4	11.4	0.22	0.85

Concentration of Cr_2O_3	Density of energy states $N(E_s)$ in 10^{21} ($eV^{-1}cm^{-3}$)		S_{pollak}
	(Austin and Mott)	(Butcher and Hyden)	
0.05	1.96	0.82	1.99
0.1	2	0.84	2.03
0.2	2.1	0.87	2.13
0.3	2.14	0.89	2.17
0.4	2.05	0.86	2.08

IV. DISCUSSION

Earlier neutron scattering experiments [36, 37] and Raman spectral studies [38, 39] on TeO_2 glasses containing different modifiers have revealed that the basic building block of TeO_2 glass structure is a trigonal bipyramid commonly called TeO_4E , where one of the three equatorial directions is occupied by the $5s^2$ electronic pair (E) of the tellurium atom with two equatorial bonds of lengths 1.91 Å and two axial bonds of lengths 2.08 Å [40-42]. The environment of these Te atoms is completed by two other longer interactions of lengths 2.9 Å and the three dimensional close packing is constituted from vertices sharing TeO_4 groups ($Te_{eq}-O_{ax}-Te$) reinforced by weaker Te-O interactions of lengths 2.9 Å [40, 43]; this structure leads to long chains of tetrahedrons where the long chain molecules are entwined and the introduction the chromium ions causes cross linking of the glass structure. If we consider a network modifier, PbO, to be incorporated between the long chain molecules in the vicinity of chromium ion, then the symmetry and or covalency of the glass at the chromium ions should be different for different modifiers. In general PbO act as modifier; oxygen ions break the Te-O-Te bonds while Pb^{2+} ions occupy interstitial positions. However, PbO participate in the glass network with PbO_4 structural unit when lead ion is linked to four oxygens in covalency bond configuration. The presence of PbO_4 unit in the present glass network can be established from the observation of vibrational bands in IR spectra of these glasses; further, there may also be a possibility for the formation of PbO-Te linkages.

Chromium seems to exist in both Cr^{3+} and Cr^{6+} states in ZnF_2 -PbO- TeO_2 glass network; Cr^{3+} ion enters the network as modifier whereas Cr^{6+} ion enters as network former with CrO_4^{2-} structural units [44, 45]. As a modifier chromium ion may enter the glass network by breaking up local symmetry and introduces coordinated defects known as dangling bonds in these glasses. During this process there can be different ways of formation of dangling bonds in the present glasses: (i) the stable $Te-\bar{O}$ and (ii) unstable $Te-\bar{O}$ bonds which will later be modified to $Te-\bar{O}$ (or simply TeO_{3+1}) owing to the contraction of one $Te-\bar{O}$ and the elongation of another $Te-\bar{O}$ bond. Further, the elongation of Te-O bond of TeO_{3+1} and its cleavage finally lead to the formation of trigonal prismatic TeO_3 units. Thus, the structure of the present glass network consists of bonding defects like TeO_{3+1} , TeO_3 units, free Pb^{2+} ions, free F^- ions and non-bridging oxygens. The concentrations of such bonding defects in the glass network depend upon the concentration of Cr^{3+} and Cr^{6+} ions.

The decrease in the intensity of $^4A_2 \rightarrow ^4T_1(F)$ and $^4A_2 \rightarrow ^4T_2$ bands and a simultaneous increase in the intensity of the kink at about 370 nm in the optical absorption spectra of glasses from (0.3) to (0.4) indicates a gradual conversion of Cr^{3+} ions (from octahedral environment) to Cr^{6+}

(tetrahedral environment) with CrO_4^{2-} structural units that take part in the network forming positions. The nephelauxetic ratio has also been evaluated using the formula $\beta = B(\text{complex})/B(\text{free ion})$ for the glass and its value is found to be 0.735. The glasses containing ZnO as modifier are more covalent in nature where as PbO modifier glasses are more ionic [16]. The observed decrease in the intensity of symmetrical axial band and the

shifting of its meta-centre towards slightly higher wave number in the IR spectra of the glass containing Cr_2O_3 up to 0.3 % indicates an increasing concentration of Cr^{3+} ions that act as modifiers which disturb the local symmetry in these glasses. The increase in the intensity of this band beyond these concentrations of Cr_2O_3 obviously suggests an increasing presence of Cr^{6+} ions that take part network forming positions with CrO_4^{2-} structural units.

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 ϵ' and $\tan \delta$ of these glasses, we notice, a large increase of these parameters with temperature beyond the relaxation region; such behaviour can only be attributed to space charge polarization due to the bonding defects of the type mentioned earlier in this glass [46, 47]. 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 [48]. Among the three constituents viz. ZnF_2 , PbO , and TeO_2 of this glass, the bonds of tellurium with oxygen are known to be polar in nature [49] and hence, it is reasonable to attribute the observed dipolar effects in this glass to the TeO_2 molecules [47, 50]. The spreading of relaxation time in this glass 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 [51].

The conduction phenomenon in this glass in the high temperature region can be explained based on mixed conduction mechanism [52]. The conductivity variation with the concentration of Cr_2O_3 at higher temperature (Fig. 10) show an increasing trend (zone I) up to 0.3 wt.% of Cr_2O_3 and beyond these concentrations conductivity is found to decrease (zone II). The conduction in the zone I (where σ_{ac} increases with Cr_2O_3) is identified due to mobility of ions whereas the zone II is identified as electronic conductive zone [51].

An attempt has been made to explain the temperature independent part of the conductivity (low temperature side) in the present $\text{ZnF}_2\text{-PbO-TeO}_2\text{:Cr}_2\text{O}_3$ glass system based on the Quantum mechanical tunnelling (QMT) model. In general, the ac conductivity of the amorphous material where charge carriers experience an approximately random potential energy on diffusing is found to obey the equation [53]:

$$\sigma(\omega) = A\omega^s \quad (7)$$

With $s < 1$ (up to the frequency of 1 MHz) which is considered to signify the coupling of ion's movement with its environment. The values of s obtained from the plot of $\log \sigma(\omega)$ vs. $\log \omega$ at a temperature of 320 K are presented in Table 3.

According to QMT model, only those pairs of carriers separated by hopping distance R_i , given by:

$$R_i = (1/2\alpha) \ln \left(\frac{V_{ph}}{\omega} \right), \quad (8)$$

contribute significantly to the conduction. With this, the equation for ac conductivity due to quantum mechanical tunnelling is given by [53]:

$$\sigma = \frac{N(E_F) \alpha^2 v_{ph} \eta}{\omega} \exp \left[-\frac{2\alpha R_i}{\hbar} \right] \quad (9)$$

Where $N(E_F)$ is the density of the energy states near the Fermi level, α is the electronic wave function decay constant, v_{ph} is the phonon frequency and η is a constant and its value is given by $\pi/3$ (Austin & Mott [53]), $3.66\pi^2/6$ (Butcher & Hyden [54]), $\pi^4/96$ (Pollak [55]).

Among various mechanisms of conduction in the amorphous materials (such as band conduction, conduction in extended states, conduction in localized states near the band edge and conduction in localized states near the Fermi level), the conduction in the localized states near the Fermi level occurs when ac conductivity is nearly temperature independent and varies linearly with frequency. The conduction in present glass in the low temperature region (up to 320 K) can safely be attributed to take place by the mechanism. The value of $N(E_F)$, i.e., the density of energy states near Fermi level, for a frequency of 10^5 Hz and at 320 K taking α equal to 0.40 \AA^{-1} (obtained by plotting $\log \sigma_{ac}$ against R_i) and $v_{ph} \sim 5 \times 10^{12}$ Hz, is computed using equation (9). With the value of numerical constant η suggested by different investigators and presented in Table 3. The value of $N(E_F)$ is found to decrease from glass (0.3) to (0.4) concentration. Furthermore, the range of $N(E_F)$ values obtained $\sim 10^{21} \text{ eV}^{-1}/\text{cm}^3$; such values of $N(E_F)$ suggest the localized states near the Fermi level [53].

When the dielectric is placed in an electric field, the heat of dielectric loss is liberated. If the applied field is an alternating field, then the specific dielectric loss i.e., the loss per unit volume of the dielectric is given by [56],

$$\rho = E^2 \omega \epsilon' \epsilon_0 \tan \delta \text{ W/m}^3 \quad (10)$$

This equation indicates that smaller the values of $\epsilon' \tan \delta$ of the glass at a given frequency, the lower are the losses. In a dielectric across which the voltage is 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 equation (10).

CONCLUSIONS

The summary of conclusions drawn from the study of dielectric properties of $\text{ZnF}_2\text{-PbO-TeO}_2\text{:Cr}_2\text{O}_3$ glasses together with optical absorption and IR spectral studies are as follows:

The optical absorption and IR spectral studies indicate the presence of chromium ions predominantly in Cr^{3+} state which take modifier positions if Cr_2O_3 is present in lower concentrations up to 0.3 wt % .When the concentration of Cr_2O_3 is in higher quantities, these ions exist in Cr^{6+} state that take network forming 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 ac conduction are found to decrease with the increase in Cr_2O_3 concentration up to 0.3 wt. % indicating an increase in the concentration of Cr^{3+} ions that act as modifiers. Moreover, when Cr_2O_3 is present in higher concentrations, we observe that the values of the dielectric parameters to decrease with increase in Cr_2O_3 ; such changes have understood due to increase in the concentration of Cr^{6+} ions that take part in network forming positions. The temperature independent part of the conductivity could successfully be explained based on the Quantum mechanical tunnelling model.

The dielectric loss variation with the temperature has exhibited dielectric relaxation effects; these effects are described by pseudo Cole-Cole plot method.

Finally the studies on dielectric properties along with optical absorption and IR of ZnF₂-

PbO-TeO₂:Cr₂O₃ glasses indicate that when the concentration of Cr₂O₃ in the glass network is ≤ 0.3 wt % , chromium ions exist in Cr³⁺ state, take modifier positions and weaken the glass network; when Cr₂O₃ concentration is > 0.3 wt % , a part of chromium ions exist in Cr⁶⁺ state, take the network forming positions and strengthen the structure of the glass.

REFERENCES

- [1] M.D. Ingram, Phys. Chem. Glasses 286 (1987) 215-34.
- [2] A.A. Bahgat, M.M. El-Samanoudy, A.I. Sabry, J. Phys. Chem. Solids 60 (1999) 1921.
- [3] R. Mallawani, El. Mater. Chem. Phys. 37 (1994) 224.
- [4] V. Ravikumar, N. Veeraiah, J. Phys. Chem. Solids 59 (1998) 91.
- [5] G. Srinivasarao, N. Veeraiah, J. Solid State Chem. 166 (2002) 104.
- [6] G. El-Damrawi, Phys. Stat. Sol. 177 (2000) 385.
- [7] M. Pal, Y. Tsujigami, A. Yoshikado, H. Sakata, Phys. Stat. Sol. 182 (2000) 727.
- [8] D.K. Durga, N. Veeraiah, J. Mater. Science 36 (2001) 5625.
- [9] M.M. Elkholy, Phys. Chem. Glasses 42 (2001) 49.
- [10] B.V.R. Chowdari, P. Pramoda Kumari, J. Phys. Chem. Solids 58 (1997) 515.
- [11] R.A. Montani, S.E. Giusia, Phys. Chem. Glasses 42 (2001) 12.
- [12] G. El-Damrawi, S. Abd-El-Maksoud, Phys. Chem. Glasses 41 (2000) 64.
- [13] H.H. Qiu, M. Kudo, H. Sakata, Mater. Chem. Phys. 51 (1997) 233.
- [14] D. Lezal, J. Pedlikova, P. Kostka, J. Bludska, M. Poulain, J. Zavadil, J. Non-Cryst. Solids 284 (2001) 288.
- [15] M.A. Sidkey, R.A. El-Mallawany, A.A. Abousehly, Y.B. Saddeek, Mat. Chem. Phys. 74 (2002) 222.
- [16] M. R. Reddy, S. B. Raju, N. Veeraiah, J. Phys. Chem. Solids., 61 (2000) 1567.
- [17] A. Kanoen, S. Alaya, H. Maaret, Phys. Stat. Sol (B) 162 (1990) 523.
- [18] A. Abdel-Kader, R. Mallawany, M. El, Elkholy, H. Farang, Mater. Chem. Phys. 36 (1994) 3.
- [19] J.S. Wang, E. Snitzer, J. Lum. 60 (1994) 9.
- [20] A. Ahmed, J. Non-cryst. Solids 70 (1989) 17.
- [21] S. Hart, J. Mater. Sci. (GB) 18 (1993) 1264.
- [22] P.E.S. Kartha, S.J. Lakshman Kumar, V.C. Podaki, E.S.R. Gopal, J. Acc. Soc. VII (1983) 15.
- [23] V. Kozhukharov, H. Burger, S. Neovs, B. Sidzhimov, Polyhedron 5 (1986) 91.
- [24] M.N. Khan, M.A. Hassan, C.A. Hogath, Phys. Stat. Sol. (A) 104 (1998) 505.
- [25] R.N. Hampton, W. Hong, G.A. Saunmders, R.El. Mallawany, J. Non-Cryst. Solids 194 (1987) 307.
- [26] R.El. Malla Wany, Mater. Chem. Phys. 37 (1994) 224.
- [27] T.N.R. Kutty, Mat. Res. Bull 25 (1990) 485.
- [28] A. Van Die, A.C.H.I. Leenaers, W.F. Van Der Weg, J. Non-Cryst. Solids 99 (1988) 32.
- [29] E. Baiocchi, A. Monyrnrto, M. Bettinelli, J. Non-Cryst. Solids 46 (1981) 203.
- [30] A. Paul, Trans. Indian Ceram. Soc. 39 (1980) 71.
- [31] K. Hirao, S. Todoroki, N. Soga, J. Non-Cryst. Solids 175 (1994) 263.
- [32] D.K. Durga, P. Yadagiri Reddy, N. Veeraiah, J. Lumin. 53 (2002) 99.
- [33] G. Srinivasarao, N. Veeraiah, Eur. Phys. J. AP. 16 (2001) 11.
- [34] P. Subbalakshmi, N. Veeraiah, Indian J. Eng. Mater. Sci. 8 (2001) 275.
- [35] P. Sixou, P. Damsas, D. Gillot, J. Chem. Phys. 64 (1967) 834.
- [36] N. Mochida, K. Takahashi, K. Nakata, Yogyo Kyokai Shi 86 (1978) 316.
- [37] G.A. Clare, C.A. Wright, N.R. Sinclair, F.L. Galeener, E.A. Geissberger, J. Non-Cryst. Solids 111 (1989) 123.
- [38] S. Neov, J. Phys. C 2 (1979) 2475.
- [39] A. Berthereau, Y. LE Luyer, R. Olazcuaga, Mater. Res. Bul. 29 (1994) 933.
- [40] T. Sekiya, N. Mochida, A. Ohtsuka, J. Non-Cryst. Solids 144 (1992) 128.
- [41] V. Kozhukharov, H. Burger, S. Neov, B. Sidzhimov, Polyhedron 5 (1986) 771.
- [42] O. Lindqvist, Acta. Chem. Scand 22 (1968) 977.
- [43] D. Godeke, M. Muller, C. Russel, Glass Sci. Tech. 74 (2001) 177.
- [44] O. Guldal, C. Apak, J. Non-Cryst. Solids 38 (1980) 251.
- [45] G.A.N. Fuxi, D.E.N.G. He, L.I.U. Huiming, J. Non-Cryst. Solids 52 (1982) 135.
- [46] V. Ravikumar, M. Rami Reddy, N. Veeraiah, Phys. Status. Solidi. (a) 147 (1995) 601.
- [47] V. Ravikumar, N. Veeraiah, S. Buddhudu, J. Phys III France 7 (1997) 951.
- [48] G. Srinivasarao, N. Veeraiah, J. Phys. Chem. Solids 63 (2002) 705; J. Solid. State Chem. 166 (2002) 104.
- [49] R.T. Sanderson, Inorganic chemistry (New Delhi: Affiliated East West Press Pvt., Ltd.) 194 (1971).
- [50] A. Singh, V.K. Dhawan, Philos. Mag. B48 (1983) 215.
- [51] S.R. Elliot, Adv. Phys. 36 (1987) 135.
- [52] R.A. Montani, S.E. Giusia, Phys. Chem. Glasses 42 (2001) 12.
- [53] I.G. Austin, N.F. Mott, Adv. Phys. 18 (1969) 657.
- [54] P. Butcher, K. Hyden, J. Phil. Mag. 36 (1977) 657.
- [55] M. Pollak, Phil. Mag. 23 (1971) 519.
- [56] B. Tareev, Physics of dielectric Materials, Mir Publishers, Moscow. (1979).