

## Optical and Dielectric Properties of Cr<sup>3+</sup> & Cu<sup>2+</sup>:P<sub>2</sub>O<sub>5</sub>-ZnO-LiF Glasses

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### ABSTRACT

The present paper reports on the results concerning structural, thermal, optical (absorption & emission), dielectric and ac conductivity properties of host glass in the chemical composition of 50P<sub>2</sub>O<sub>5</sub>-30ZnO-20LiF (PZL), and two different transition metal ions doped glasses such as (0.5 mol%) Cr<sup>3+</sup>:49.5P<sub>2</sub>O<sub>5</sub>-30ZnO-20LiF and (0.5 mol%) Cu<sup>2+</sup>:49.5P<sub>2</sub>O<sub>5</sub>-30ZnO-20LiF glasses have successfully been prepared by a melt quenching technique. Thermal analysis has been carried out on the host (PZL) precursor chemical mix in evaluating weight loss from its TG profile and glass transition temperature (T<sub>g</sub>) and crystalline temperature (T<sub>c</sub>) from its DTA profile. The presence of Cr<sup>3+</sup> and Cu<sup>2+</sup> has been confirmed from their EDX profiles and absorption spectra. From the absorption spectrum of Cr<sup>3+</sup>: PZL glass, a couple of bands at 460 nm (<sup>4</sup>A<sub>2g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(F)) and 664 nm (<sup>4</sup>A<sub>2g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F)) have been displayed where as a broad absorption band at 824 nm (<sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub>) is observed from Cu<sup>2+</sup>: PZL optical glass. The nature of local symmetry and structural information of the neighboring atoms of dopant ions (Cr<sup>3+</sup> & Cu<sup>2+</sup>) in the host matrix have been understood by evaluating the crystal field strength (Dq) and Racah (B & C) parameters. The emission spectrum of Cr<sup>3+</sup>: PZL glass exhibits emissions at 442 nm, 490 nm, 590 nm and 650 nm with an excitation at λ<sub>exci</sub> = 368 nm. While in case of Cu<sup>2+</sup>: PZL glass, three emission bands are located at 436 nm, 542 nm and 652 nm with an excitation at λ<sub>exci</sub> = 312 nm have been observed. The frequency dependence of ac conductivity (σ<sub>a.c</sub>) and dielectric parameters (ε' and tanδ) in the frequency range 1 Hz to 1MHz at room temperature for these glasses has been studied. The low frequency dispersion in the profiles of dielectric constant and loss tangent would be resulting in because of space charge polarization effect at the electrode-electrolyte interface and it is also noticed that σ<sub>a.c</sub> increases in accordance with frequency change.

**Keywords:** Optical glasses and Dielectric properties.

### I. INTRODUCTION

The oxide glasses containing transition metal (TM) ions are of great interest, because these ions exist in multivalent oxidation states in glassy matrix exhibiting interesting behaviors like optical, semiconducting and magnetic properties [1-3]. Among different types of glasses, the phosphate glasses are considered to be significant in nature because of their possessing unique performance displaying high transparency, good thermal expansion coefficient, lower refractive index, with an extended transmission ability from near UV to middle IR demonstrating their suitability as luminescent potential optical materials [4-11]. In such glasses, chemical durability has been found to be enhanced with an addition of modifier salts like LiF, ZnO, etc. LiF increases the UV extension ability and ZnO improves the thermal stability with ensured chemical durability. Optical, electronic and magnetic properties of these glasses depend on the relative proportion of different valence states of the transition metal/ rare earth ions. In the present work, we have taken up a glass in a general composition of

50P<sub>2</sub>O<sub>5</sub>-30ZnO-20LiF to incorporate with Cr<sub>2</sub>O<sub>3</sub> and CuO ions based on their usefulness as optical materials [12, 13].

Bright and prominent bluish green colour could be found due to the presence of Cu<sup>2+</sup> ions from the point of view of ligand field theory. The electronic structure of the copper atom is [Ar] 3d<sup>10</sup> 4s<sup>1</sup>; and its stable ionic states are Cu<sup>+</sup> and Cu<sup>2+</sup>; the cuprous (Cu<sup>+</sup>) ion, having its five d- orbitals occupied, thus prevents display of colouring, while Cu<sup>2+</sup> ions create colour centres with absorption bands in NIR wavelength region; although Cu<sup>2+</sup> ion doped materials would be in blue and sometimes in green colour in its visual appearance [14, 15]. The chromium ion, Cr<sup>3+</sup> (d<sup>3</sup>), gives rise to the free ion terms of <sup>4</sup>F, <sup>4</sup>P, <sup>2</sup>G and several other doublet states, of which <sup>4</sup>F is the ground state. In an octahedrally coordinated system in the weak fields, <sup>4</sup>F splits as <sup>4</sup>A<sub>2g</sub>(F), <sup>4</sup>T<sub>2g</sub>(F) and <sup>4</sup>T<sub>1g</sub>(F) whereas <sup>4</sup>P transforms as <sup>4</sup>T<sub>1g</sub>(P). In the doublet states, <sup>2</sup>G splits as <sup>2</sup>A<sub>1g</sub>(G), <sup>2</sup>E<sub>g</sub>(G), <sup>2</sup>T<sub>1g</sub>(G) and <sup>2</sup>T<sub>2g</sub>(G). The weak field terms <sup>4</sup>A<sub>2g</sub>(F), <sup>2</sup>E<sub>g</sub>(G), <sup>2</sup>T<sub>1g</sub>(G) and <sup>2</sup>T<sub>2g</sub>(G) correspond to the lowest strong field configuration (t<sub>2g</sub>)<sup>3</sup>. The states

${}^4T_{1g}(F)$  and  ${}^4T_{2g}(F)$  correspond to  $(t_{2g})^2(e_g)^1$  and  ${}^4T_{1g}(P)$  corresponds to  $(t_{2g})^1(e_g)^2$ . The ground state is  ${}^4A_{2g}(F)$  at all strengths of the crystal field. Thus, only three spin allowed transitions arise from  ${}^4A_{2g}(F)$  to  ${}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F)$  and  ${}^4T_{1g}(P)$  states in addition to several spin forbidden transitions [16, 17]. Latter on dielectric and conductivities studies were carried for the host, chromium and copper ion containing glasses at room temperature in the frequency range of 1Hz - 1MHz.

## II. EXPERIMENTAL STUDIES

By employing melt quenching method, host glass with and without transition metal ions as dopants in the following chemical composition were prepared:

- (i) 50 P<sub>2</sub>O<sub>5</sub> - 30 ZnO - 20 LiF (host glass)
- (ii) 0.5 mol % (Cr<sub>2</sub>O<sub>3</sub>): 49.5P<sub>2</sub>O<sub>5</sub>-30ZnO-20LiF
- (iii) 0.5 mol % (CuO): 49.5P<sub>2</sub>O<sub>5</sub>-30ZnO-20LiF

NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, ZnCO<sub>3</sub>, LiF, Cr<sub>2</sub>O<sub>3</sub> and CuO of analytical grade were used as starting chemicals. All the chemicals were weighed in 10 g batch each separately, thoroughly mixed using an agate mortar and a pestle and then each of those was transferred into porcelain crucible and heated in an electric furnace for melting them for an hour at 950 °C. These melts were stirred occasionally in obtaining a homogeneous and to reduce bubble formation. Such melts were later on poured in rectangular blocks and quenched to obtain glasses in rectangular designs and a thickness of 0.5 cm and these glasses were further characterized. For an easy reference the prepared glasses were labeled as host PZL, Cu<sup>2+</sup>: PZL, Cr<sup>3+</sup>: PZL.

XRD profiles were recorded for the glass samples on a Seifert X-ray Diffractometer (model 3003TT) with Cu K<sub>α</sub> radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 KV and 20 mA with a Si detector and  $2\theta = 10^\circ$  and  $60^\circ$  at the rate of two degrees per minute. Simultaneous measurement of TGA and DTA was carried out on a Netzsch STA 409 at a heating rate of 10 °C/min with N<sub>2</sub> as the purging gas. The elemental analysis for the prepared glasses was done using EDAX technique. Absorption spectra of glasses were measured on a Varian-Cary-Win Spectrometer (JASCO V-570). The emission spectrum of 0.5 mol% CuO and 0.5 mol% Cr<sub>2</sub>O<sub>3</sub> doped glasses were measured in a steady state mode on a SPEX Fluorolog-3 (Model-II) Fluorimeter. Dielectric and conductivity measurements were carried using a two electrode cell configuration at room temperature over a frequency range of 1 Hz – 1 MHz at ac voltage strength of 0.5 V<sub>rms</sub> on a Phase Sensitive Multimeter (PSM 1700) in LCR mode.

## III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD profile of the host PLZ glass, exhibiting a broad diffusion peak between  $2\theta$  values of  $20^\circ$ - $30^\circ$ , confirming amorphous nature of the prepared glasses. Similar nature has been observed in the case of transition metal ions doped PZL glasses.

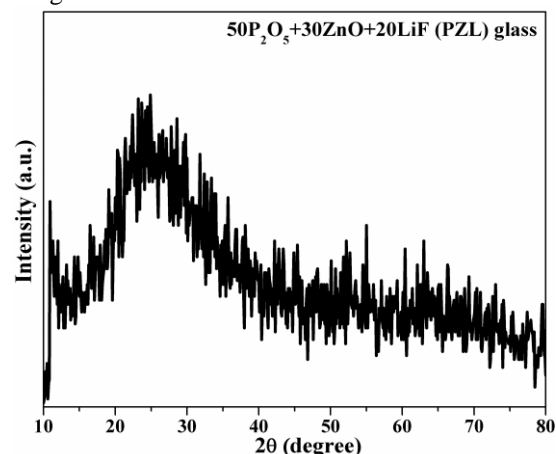


Fig.1: XRD profile of host P<sub>2</sub>O<sub>5</sub>-ZnO-LiF (PZL) glass.

From Fig.2, TG profile reveals that the weight loss takes place in a multi step process in the measured range from 30 °C – 700 °C. The total weight loss in the sample has been found to be 55 % due to decomposition of H<sub>2</sub>O and CO<sub>2</sub> and above 460 °C no major weight loss has been noticed due to the formation of pure compound.

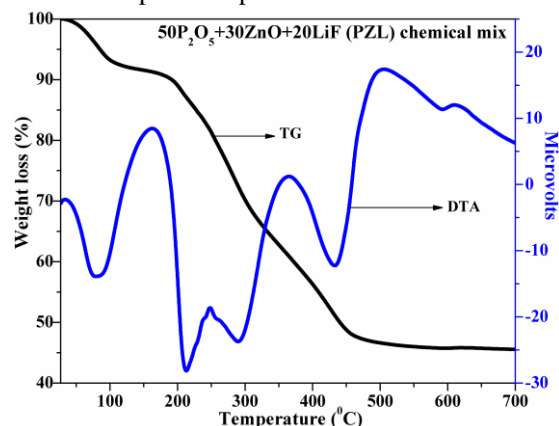
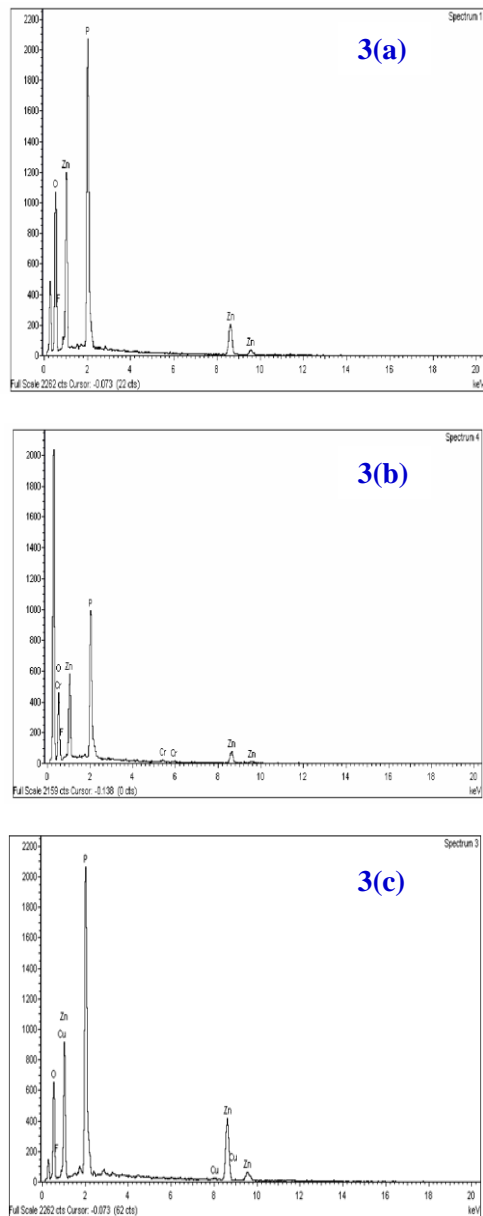


Fig.2: TG-DTA profiles of P<sub>2</sub>O<sub>5</sub>-ZnO-LiF (PZL) glass precursor chemicals mix.

The DTA profile of host precursor chemicals mix shows an endothermic peak at 162 °C which is attributed to the partial melting of small percentage of impurities and due to phase changes in P<sub>2</sub>O<sub>5</sub>. The glass transition temperature (T<sub>g</sub>) and crystalline temperature (T<sub>c</sub>) are noticed at 375 °C and 500 °C.

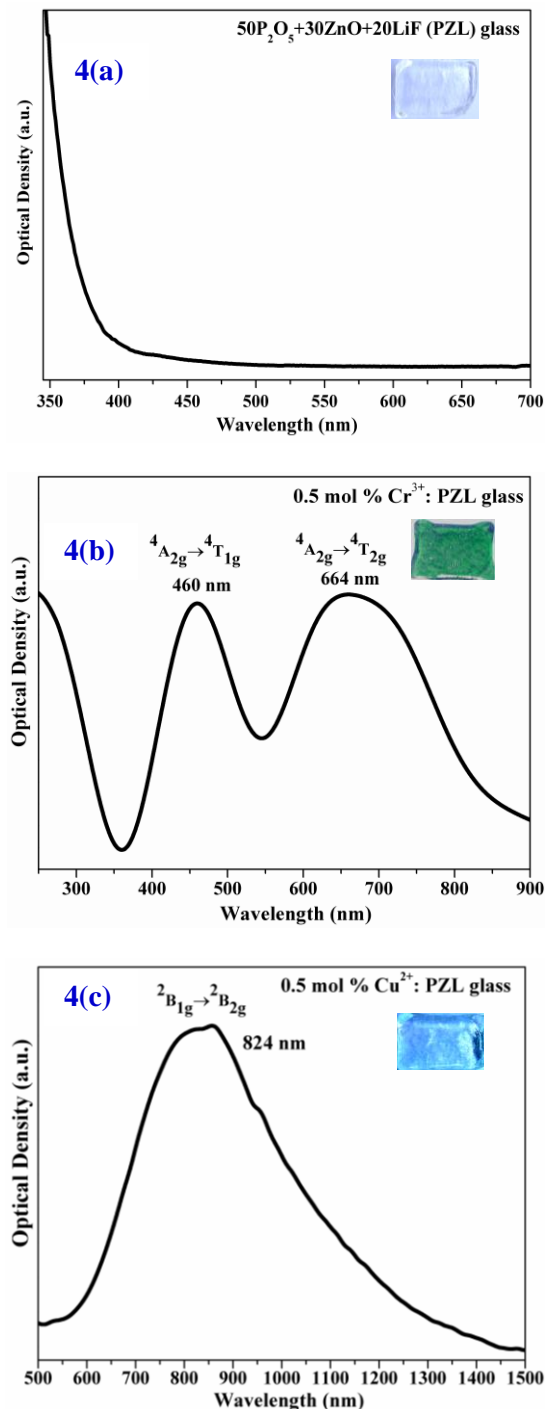
The presence of transition metals (CuO & Cr<sub>2</sub>O<sub>3</sub>) in the chemical composition of the host glass are verified separately from their EDAX analysis as shown in Figs.3 (a, b & c).



**Fig.3:** EDAX profile of (a) host PZL, (b) Cr<sup>3+</sup>: PZL and (c) Cu<sup>2+</sup>: PZL glasses.

In Fig.4 (a, b & c), optical absorption of the host (PZL) and the Cr<sub>2</sub>O<sub>3</sub>: PZL and CuO: PZL glasses are shown. The absorption edge for the host glass lies in the UV region. From the absorption spectrum of Chromium ion containing glass, a couple of bands at 460 nm and 664 nm assigned to the spin allowed optical d-d transitions of <sup>4</sup>A<sub>2g</sub> (F) → <sup>4</sup>T<sub>1g</sub> (F) and <sup>4</sup>A<sub>2g</sub> (F) → <sup>4</sup>T<sub>2g</sub> (F) respectively, which are characteristic bands of Cr<sup>3+</sup> ions in octahedral

symmetry [18, 19]. With regard to absorption spectrum of the glass containing Copper ion, it has been noticed that a broad band arises in Vis-NIR region around 824 nm assigned to the characteristic electronic transition of <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub>. This confirms that copper ions in the glass matrix exhibit Cu<sup>2+</sup> oxidation state due to their octahedral coordination [20, 21].



**Fig.4:** Optical absorption spectra of (a) host PZL, (b) Cr<sup>3+</sup>: PZL and (c) Cu<sup>2+</sup>: PZL glasses.

In order to have a better understanding of the nature of local symmetry, distortions and structural information on the neighboring atoms of dopant ions ( $\text{Cr}^{3+}$  &  $\text{Cu}^{2+}$ ) from the absorption spectrum, crystal field strength  $Dq$  and Racah parameters  $B$  &  $C$  (electron–electron interaction parameters) are obtained [22, 23]. From Fig. 4(b) the crystal field strength parameter ( $Dq$ ) gives the energy difference between ground state and first excited state of  $\text{Cr}^{3+}$ ,  ${}^4A_{2g}$  and  ${}^4T_{2g}$  respectively, and the equation is of the form:

$$10Dq = E({}^4A_{2g}) - E({}^4T_{2g}) \quad \dots (1)$$

$\Delta E$  is the energy difference between two peaks of  $\text{Cr}^{3+}$ , at  ${}^4T_{1g}$  and  ${}^4T_{2g}$  respectively, and the equation is given by:

$$\Delta E = E({}^4T_{1g}) - E({}^4T_{2g}) \quad \dots (2)$$

The Racah parameter  $B$  (electrostatic parameter which is a measure of the inter-electronic repulsion) is calculated from the following formula:

$$\frac{B}{Dq} = \frac{\left(\frac{\Delta E}{Dq}\right)^2 - 10\left(\frac{\Delta E}{Dq}\right)}{15\left(\left(\frac{\Delta E}{Dq}\right) - 8\right)} \quad \dots (3)$$

The energy of the  ${}^4T_{2g}$  depends on the  $Dq$  and  $B$ , the  $Dq$  value calculated for  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transition from eq. (1) is  $1506.02 \text{ cm}^{-1}$  and the energy difference  $\Delta E$  from eq (2) is found to be at  $6678.9 \text{ cm}^{-1}$ . Substituting the obtained values of  $Dq$  and  $\Delta E$  in the eq (3),  $B$  is evaluated to be  $693 \text{ cm}^{-1}$ . The value of  $C$  is evaluated from the equation given below:

$$C = \frac{\left[ E({}^2E) - 7.9B + 1.8B^2/Dq \right]}{3.05} \quad \dots (4)$$

here  $E({}^2E) = 14044.9 \text{ cm}^{-1}$  taken from the earlier reports [23], using the values of  $Dq$ ,  $\Delta E$  and  $B$ ,  $C$  is evaluated to be  $4691.8 \text{ cm}^{-1}$ . The value of  $Dq/B \ll 2.3$ , then  $\text{Cr}^{3+}$  ions lies in weak crystal field sites or else if  $Dq/B \gg 2.3$ , then  $\text{Cr}^{3+}$  ions lies in strong crystal field sites and for intermediate crystal fields  $Dq/B \approx 2.3$ . For the present glass system the value of  $Dq/B$  ( $4.43$ )  $\gg 2.3$ , implies that  $\text{Cr}^{3+}$  ions lies in strong crystal field sites. From Fig. 4(c), crystal field strength ( $Dq$ )  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  is calculated from:

$$10Dq = E({}^2B_{1g}) - E({}^2B_{2g}) \quad \dots (5)$$

It is found to be  $1213.5 \text{ cm}^{-1}$ .  $\Delta E$  and  $B$ ,  $C$  could not be calculated, as the absorption spectrum of

$\text{CuO}$ : PZL glass could exhibit only a broad band covering Vis-NIR region.

Figs. 5 (a & b) show the excitation and emission spectra of 0.5 mol%  $\text{Cr}_2\text{O}_3$ :  $49.5\text{P}_2\text{O}_5$ - $30\text{ZnO}$ - $20\text{LiF}$  glass. The excitation spectrum exhibits a band at 368 nm, which has been used in the measurement of emission spectrum of  $\text{Cr}^{3+}$  glass. From the emission spectrum of  $\text{Cr}^{3+}$ : PZL glass, four emission bands at 442 nm (blue region), 490 nm (yellow), 590 nm (orange) and 650 nm (red) respectively have been observed[24].

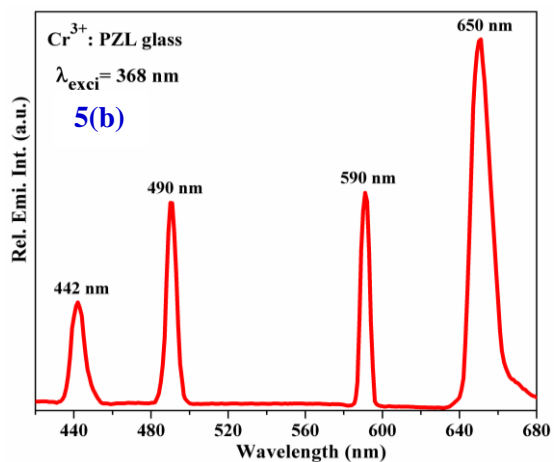
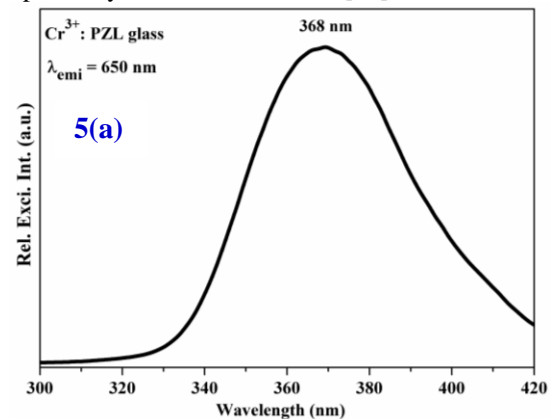


Fig.5: (a) Excitation and (b) emission spectra of  $\text{Cr}^{3+}$ : PZL glasses.

The excitation and emission spectra of 0.5 mol%  $\text{CuO}$ :  $49.5\text{P}_2\text{O}_5$ - $30\text{ZnO}$ - $20\text{LiF}$  glass are presented in Figs. 6 (a & b). The emission spectrum with an excitation at 312 nm is shown in Fig. 6(b), reveals three emissions at 436 nm (blue), 542 nm (green), and 652 nm (red) respectively of  $\text{Cu}^{2+}$  ion glass [25, 26].

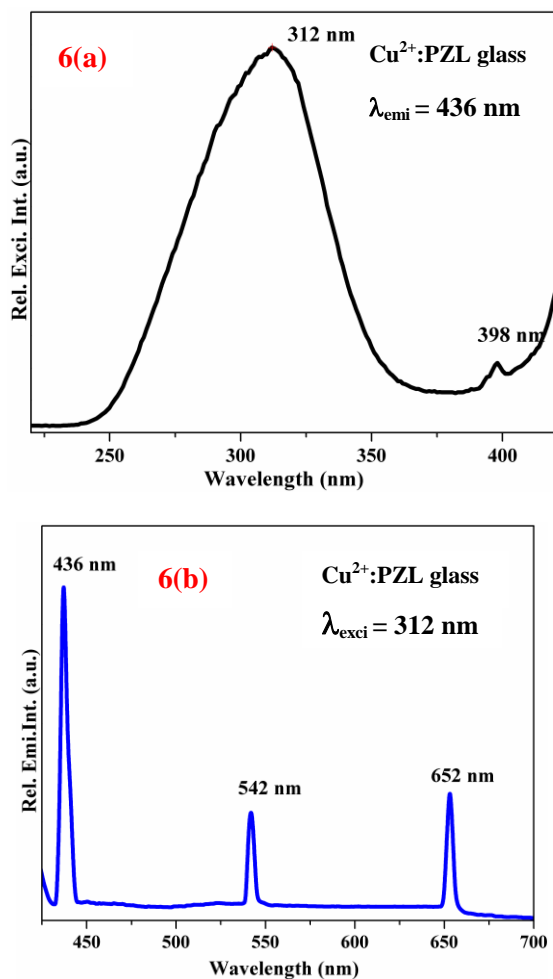


Fig.6: (a) Excitation and (b) emission spectra of Cu<sup>2+</sup>: PZL glasses.

Dielectric properties arise due to ionic diffusions with in a conducting material when electric field is applied. The charge carriers in the glass cannot move freely through a glass matrix but they can be displaced and polarized as response to an applied alternating field. In the dielectric studies, the complex permittivity of the system is calculated using the impedance data [27]:

$$\epsilon^* = \frac{1}{(j\omega C_o Z^*)} = \epsilon' - j\epsilon'' \quad \dots (6)$$

where Z\* is the complex impedance, C<sub>o</sub> is the capacitance of free medium. The real part of permittivity (dielectric constant) ε' represents the polarizability of the material, while the imaginary part (dielectric loss) ε'' represents the energy loss due to polarization and ionic conduction. The dielectric parameters (dielectric constant (ε'), dielectric loss tangent (tan δ)) and ac σ<sub>ac</sub> conductivities are calculated using the formulae [27]:

$$\epsilon' = \frac{Cd}{\epsilon_o A} \quad \dots (7)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad \dots (8)$$

$$\sigma_{ac} = \omega \epsilon_o \epsilon'' \quad \dots (9)$$

where C is the capacitance of the glass sample, ε<sub>o</sub> is the permittivity of the free space (8.85x 10<sup>-12</sup> F/m) and A is the cross-sectional area of electrode.

The variation of dielectric constant (ε') at room temperature in the frequency range 1Hz-1MHz for host (PZL), Cu<sup>2+</sup>: PZL and Cr<sup>3+</sup>: PZL glasses are shown in Fig.7(a). All the three profiles have exhibited same trend of rapid decrease in dielectric constant with an increase in the frequency and finally reaching to a constant value.

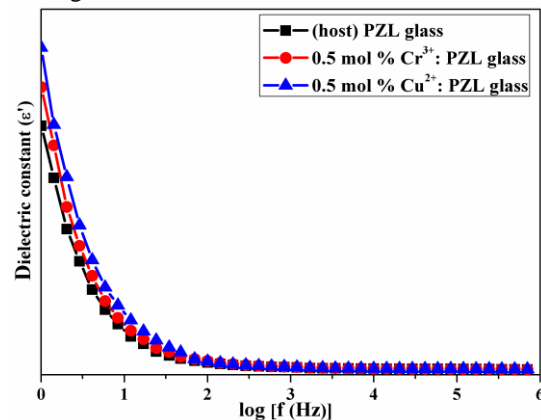
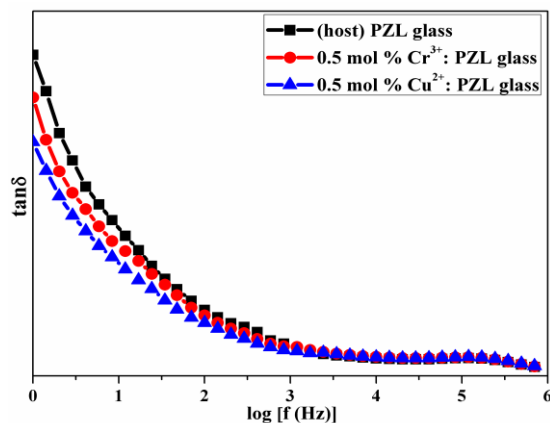


Fig.7 (a): Variation of dielectric constant (ε') as a function of log (f) at room temperature for host PZL, Cu<sup>2+</sup>: PZL and Cr<sup>3+</sup>: PZL glasses.

At low frequencies, dielectric constant profile exhibits a high dispersion, because the ions are not in a position to diffuse themselves along with the electric field direction and as a result, charges accumulate in space charge region at the electrode-electrolyte interface due to net polarization effect. At higher frequencies, the periodic reversal of electric field at interface occurs so fast that no excess ions accumulate in the electric field direction [28] and hence, the dielectric constant is lowered by weakening of ion-ion interaction in the dipoles and as a result their contribution to the polarization would be reduced.

The dielectric loss tangent (tanδ) is the phase difference due to the loss of energy within the sample. The contribution to the dielectric loss is mainly attributed to thermally activated relaxation of freely rotating dipoles trying to align themselves in the applied field direction.

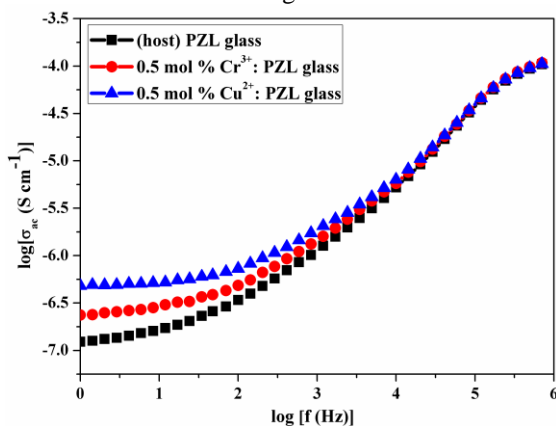


**Fig.7 (b):** Variation of dielectric loss ( $\tan\delta$ ) as a function of  $\log(f)$  at room temperature for host PZL,  $\text{Cu}^{2+}$ : PZL and  $\text{Cr}^{3+}$ : PZL glasses.

In Fig.7(b), the dependence of dielectric loss tangent ( $\tan\delta$ ) as a function of frequency for host (PZL),  $\text{Cu}^{2+}$ : PZL and  $\text{Cr}^{3+}$ : PZL glasses are shown. From figure it is observed that dielectric loss of the three studied glass system decreases with an increase in frequency due to mobility of conducting species. The higher the mobility of conducting species, the higher would be the dielectric loss component [29]. The frequency ( $\log f$ ) dependent ac conductivity ( $\log\sigma_{ac}$ ) profiles for host (PZL),  $\text{Cu}^{2+}$ : PZL and  $\text{Cr}^{3+}$ : PZL glasses shown in Fig.8 are analyzed on the basis of Jonscher universal power law [30]:

$$\sigma(\omega) = \sigma_{dc} + A\omega^s \quad 0 < s < 1 \quad \dots (10)$$

where  $\sigma_{dc}$  is the dc conductivity of the samples, A is temperature dependent constant,  $\omega = 2\pi f$  is the angular frequency of the applied field and  $s$  is the power law exponent in the range  $0 < s < 1$ , represents the degree of interaction between the mobile ions. The frequency dependence of conductivity is sum of the dc conductivity due to movements of free charges and polarization conductivity (ac conductivity) due to movements of bound charges.



**Fig.8:** Dependence of ac-conductivity ( $\log\sigma_{ac}$ ) as function of  $\log(f)$  at room temperature for host PZL,  $\text{Cu}^{2+}$ : PZL and  $\text{Cr}^{3+}$ : PZL glasses.

In Fig.8, from the profiles of frequency dependence of ac conductivity, it is observed that, the glass system with and without  $\text{CuO}$  and  $\text{Cr}_2\text{O}_3$  as dopant ions exhibit same trend of increasing in ac conductivity as a function of frequency. It is also observed that in the low frequency region, ion conductivity low and frequency independent, which could be attributed to the polarization effects at the electrode-electrolyte interface, the accumulation of ions due to slow periodic reversal of the electric field. In the intermediate frequency region, conductivity is a frequency independent due to a short range transport of ions in response to electric field. In the high frequency region, conductivity curves were tending to merge into a single curve becoming strongly frequency dependent. These curves show almost a linear behaviour which follows a power law relation in the higher frequency region:

$$\sigma(\omega) = A\omega^s \quad s < 1 \quad \dots (11)$$

The exponent  $s$  can be measured by taking slope of  $\log\sigma_{ac}$  versus  $\log f$  for the curves from the

$$\text{equation } S = \frac{d(\text{Ln}\sigma_{ac}(f))}{d(\text{Ln}(f))}$$

range of 0.7 to 0.9 which explains the interaction between the mobile ions [31].

#### IV. CONCLUSION

In summary, it is concluded that we have prepared transparent and stable optical glasses in the chemical composition of  $50\text{P}_2\text{O}_5\text{-}30\text{ZnO-}20\text{LiF}$  (host),  $0.5 \text{ mol } \% \text{ Cr}_2\text{O}_3$ :  $49.5\text{P}_2\text{O}_5\text{-}30\text{ZnO-}20\text{LiF}$  and  $0.5 \text{ mol } \% \text{ CuO}$ :  $49.5\text{P}_2\text{O}_5\text{-}30\text{ZnO-}20\text{LiF}$  glasses by employing melt quenching technique. Weight loss in the host precursor chemical mix is noticed from its TG profile whereas glass transition ( $T_g = 375 \text{ }^\circ\text{C}$ ) and crystalline ( $T_c = 500 \text{ }^\circ\text{C}$ ) temperatures have been identified from their DTA profile. Amorphous nature of host glass has been confirmed from its XRD profile and EDAX profiles of doped and undoped (host) PZL glass provide evidence for elemental analysis for all three chemical compositions glasses studied. The absorption spectra of  $\text{Cr}_2\text{O}_3$ : PZL and  $\text{CuO}$ : PZL glasses confirm that chromium exists in  $\text{Cr}^{3+}$  state while copper exists in  $\text{Cu}^{2+}$  state in an octahedral site. From absorption spectra, local symmetry and structural information of the neighbouring atoms of dopant ions ( $\text{Cr}^{3+}$  &  $\text{Cu}^{2+}$ ) have been explained from their crystal field strength (Dq) and energy level structures addressing Racah (B & C) parameters. Both excitation and emission spectra these two doped optical glasses have also been analysed. The dielectric properties ( $\epsilon'$  &  $\tan\delta$ ) of these glasses are found to be decreasing with an increase in frequency due to accumulation of charges at the electrode-electrolyte interface hence results in with polarization effect.

Due to the adding of transition metal ions ( $\text{Cr}^{3+}$  or  $\text{Cu}^{2+}$ ) into the chosen host glass matrix, their ac ( $\sigma_{ac}$ ) conductivities are found to be significantly enhanced in comparison with the host (PZL) glass. Thus, we suggest that the present study has provided us progressive outlook tend in carrying out further exploration on these glasses to dope them with several other transition metal ions as dopants to evaluate their optical, dielectric and conductivity performances for applications purpose.

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