

RESEARCH ARTICLE

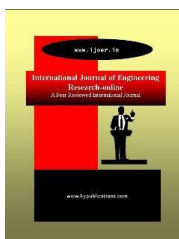
Dielectric studies of $K_2O-Al_2O_3-P_2O_5$ glasses doped with CuON. KRISHNA MOHAN^{1*}, K. SAMBASIVA RAO²¹Dept of Physics, Akkineni Nageswara Rao College, Gudivada, A.P²Dept of Physics, J.K.C College, Guntur, A.P.

*E-Mail : nkm68@rediffmail.com

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ABSTRACT

The present study is to investigate the dielectric properties of $K_2O-Al_2O_3-P_2O_5$ glasses doped with varying concentrations of CuO. These glasses were fabricated using conventional melt quenching technique. P_2O_5 glasses, with addition of The present study are to investigate the dielectric properties of $K_2O-Al_2O_3-P_2O_5$ glasses doped with varying concentrations of CuO. These glasses were fabricated using conventional melt quenching technique. P_2O_5 glasses, with addition of alkali oxide like K_2O is to make the glasses more moisture resistant. Copper ions have strong bearing on electrical, optical and magnetic properties of glasses. Very few studies are available on electrical properties of these glasses and most of them are restricted to the d.c.conductivity measurements. The clear objective of this study is to have a comprehensive understanding over the influence of of copper ions on the insulating character of $K_2O-Al_2O_3-P_2O_5$ glass system, by a systematic study of dielectric properties (dielectric constant ϵ' , loss $\tan \delta$ and a.c. conductivity σ_{ac} over a moderately wide range of frequency and temperature.

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1. Introduction

P_2O_5 glasses have attracted extensive investigation in recent years, in view of their potential applications in a number of solid state ionic devices. Copper ions have strong bearing on electrical, optical and magnetic properties of glasses. These ions subsist in different surroundings (ionic, covalent) in glass matrices. The content of copper in different environments exist in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the position of the copper ion and the physical properties of the glass is highly interesting Cu^{2+} ions are well-known paramagnetic ions and it is also quite likely for copper ions to have link with phosphate groups; strengthen the glass structure and may raise the chemical resistance of the glass.

Thus the clear objective of this study is to have a comprehensive understanding over the influence of of copper ions on the insulating character of $K_2O-Al_2O_3-P_2O_5$ glass system, by a systematic study of dielectric

properties (dielectric constant ϵ' , loss $\tan \delta$ and a.c. conductivity σ_{ac} over a moderately wide range of frequency and temperature .

2. Experimental

For the present study, a particular composition $25K_2O-15Al_2O_3-(60-x) P_2O_5:xCuO$ with four values of x (ranging from 0 to 0.6 mol%) is chosen. The details of compositions of the glasses investigated are:

G₀: 25 K₂O-15 Al₂O₃-60 P₂O₅

G₂: 25 K₂O-15 Al₂O₃-59.8 P₂O₅: 0.2 CuO

G₄: 25 K₂O-15 Al₂O₃-59.6 P₂O₅: 0.4 CuO

G₅: 25 K₂O-15 Al₂O₃-59.5 P₂O₅: 0.5 CuO

G₆: 25 K₂O-15 Al₂O₃-59.4 P₂O₅: 0.6 CuO

The glasses used for the present study are prepared by the melting and quenching techniques. The starting materials used for the preparation of the present glasses were analytical grade reagents (99.9 % pure) of K₂CO₃, Al₂O₃, P₂O₅, and CuO. The compounds of required compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible. The furnace used was a PID temperature controlled furnace. The glasses were melted at about 900 - 950 °C for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (containing smooth polished inner surface) held at room temperature. The samples were subsequently annealed at 350 °C in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying the dielectric properties are 1cm x 1cm x 0.2cm. Thin coating of silver paint was applied on either side of the glasses, to serve as electrodes.

The density (d) of the glasses was determined by the standard principle of Archimede's using o-xylene (99.99 % pure) as the buoyant liquid. From the measured values of density (d) and calculated average molecular weight (\overline{M}), various physical parameters such as metal ion concentration (N_i), mean ion separation (r_i), which are useful for understanding the physical properties of these glasses were evaluated using standard formulae.

The dielectric measurements on the K₂O- Al₂O₃-P₂O₅: CuO glasses were carried out on HP 4263B LCR Meter in the frequency range $10^2 - 10^5$ Hz in the temperature range 30 – 300° C.

3. Results

3.1 Physical parameters: From the measured values of density (d) and calculated average molecular weight (\overline{M}), various physical parameters such as copper ion concentration N_i and mean copper ion separation r_i of these glasses are evaluated using the conventional formulae and are presented in Table 1 .

Table 1: Various physical parameters of K₂O- Al₂O₃-P₂O₅glasses doped with CuO

Glass	Avg. Mol. weight (\overline{M})	Density d (g/cm ³)	Cr ion conc. Ni (10^{21})	Inter ionic distance r_i (A ^o)	Polaron radius r_p (A ^o)
G ₀	121.74	3.765	--	--	--
G ₂	121.92	3.77	3.73	6.45	2.59
G ₄	122.1	3.776	7.45	5.12	2.06
G ₅	122.19	3.778	9.31	4.75	1.91
G ₆	122.28	3.781	11.21	4.47	1.8

3.2 Dielectric Properties

The dielectric constant ϵ' , at room temperature (≈ 30 °C) and at 100 kHz of pure K₂O- Al₂O₃-P₂O₅ glasses is measured to be 6.67 and this value is found to increase with the decrease in frequency. With the addition of CuO, the value of ϵ' is observed to increase up to 0.4 mol % beyond that it is found to decrease with considerable frequency dependence, exhibiting larger values at lower frequencies. The dielectric loss,

$\tan\delta$, at room temperature with the concentration of CuO has exhibited a similar behaviour. Fig. 1 and Fig. 2 represent the variation of dielectric constant and loss (for different concentrations of CuO) with frequency measured at room temperature. The temperature dependence of ϵ' at different frequencies for glass G_2 is shown in Fig.3; ϵ' is found to increase with temperatures slowly up to about 100°C and beyond this temperature it increases rapidly especially at lower frequencies. Fig 4 shows a comparison plot of the temperature dependence of ϵ' for $K_2O-Al_2O_3-P_2O_5$ glasses doped with different concentrations of CuO measured at 1 kHz. The rate of increase of ϵ' with temperature is found to be the largest for the glasses containing 0.4 mol % of CuO. A summary of data on the dielectric constant and loss of $K_2O-Al_2O_3-P_2O_5: CuO$ glasses are presented in Table 2 and Table 3.

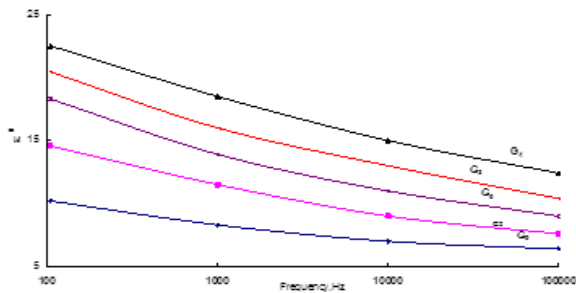


Fig. 1 Variation of dielectric constant with frequency at room temperature for $K_2O-Al_2O_3-P_2O_5$ glasses doped with different concentrations of CuO.

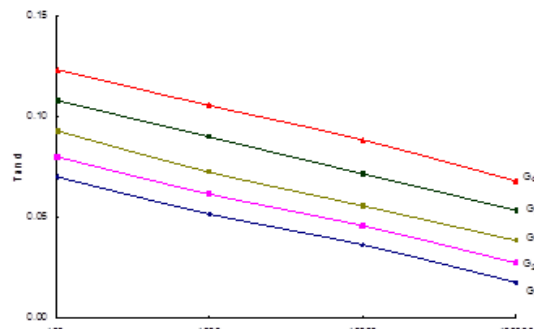


Fig. 2 Variation of dielectric loss with frequency at room temperature for $K_2O-Al_2O_3-P_2O_5:CuO$.

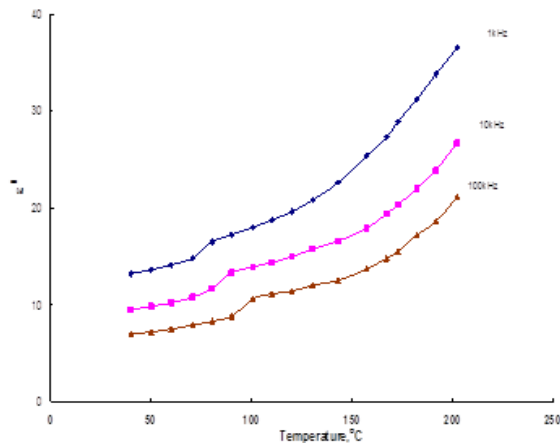


Fig.3 Variation of dielectric constant with temperature for glass G_2 at different frequencies

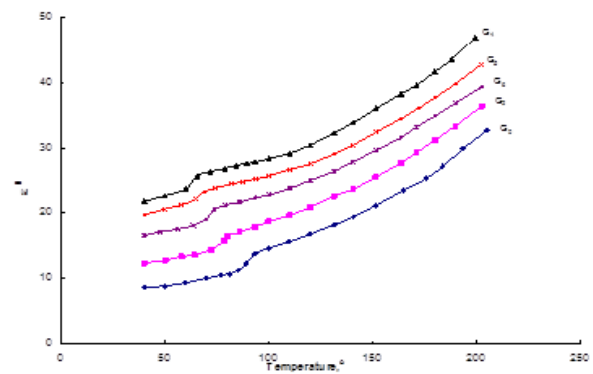


Fig.4 variation of dielectric constant with temperature at 1 kHz for different concentrations

Table 2: Summary of Data on dielectric constant of $K_2O-Al_2O_3-P_2O_5: CuO$ Glasses

Glass	1 kHz			10 kHz		
	30°C	100 °C	200 °C	30 °C	100 °C	200 °C
G_0	8.5	14.4	32.23	7.32	12.54	27.36
G_2	11.7	18.5	35.45	8.88	13.82	26.52
G_4	18.8	28.22	44.1	15.11	17.45	32.44
G_5	16.4	25.56	41.50	12.98	13.78	29.12
G_6	13.4	22.78	39.22	11.12	12.89	28.89

Table 3 : Summary of data on dielectric loss of K₂O- Al₂O₃-P₂O₅:CuO Glasses

Glass	(Tan δ _{max}) _{avg}	Temp. region of relaxation °C	Activation energy for dipoles(e V)	β
G ₀	0.09	76-96	2.65	0.54
G ₂	0.12	74-94	2.60	0.58
G ₄	0.19	70-92	2.46	0.66
G ₅	0.16	77-94	2.50	0.61
G ₆	0.14	78-90	2.55	0.59

The temperature dependence of dielectric loss tan δ of pure and CuO doped K₂O- Al₂O₃-P₂O₅:glasses have exhibited distinct maxima and with increasing temperature the frequency maximum shifts towards higher frequencies, indicating the dielectric relaxation character of dielectric loss of these glasses. With the increase in the concentration of CuO beyond 0.4 mol %, the relaxation intensity is found to decrease.

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

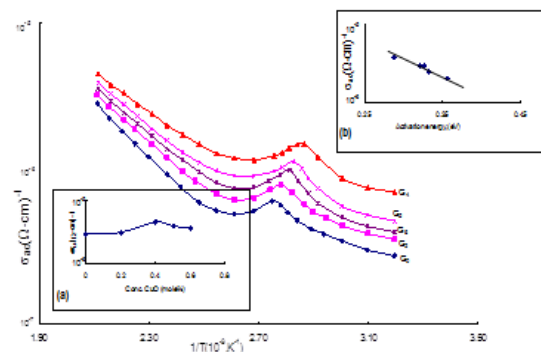
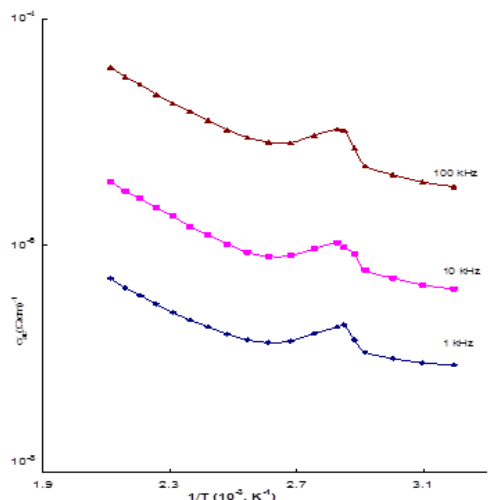
$$\sigma_{ac} = \omega \epsilon' \epsilon_0 \tan \delta ,$$

(where ε₀ is the vacuum dielectric constant) for different frequencies and the plots of log σ_{ac} against 1/T are shown in Fig. 5 for glass G₆ at different frequencies; Fig. 6 shows the variation of σ_{ac} with 1/T for glasses doped with different concentrations of CuO measured at 10 kHz. The conductivity is found to increase with the concentration of CuO up to 0.4 mol % and there after it is found to decrease (inset (a) Fig. 6).

Table 4: Summary of data on a.c. conductivity of K₂O- Al₂O₃-P₂O₅:CuO Glasses

Glas	N(E _f) in 10 ²¹ eV ⁻¹ /cm ³			A.E for conduction (eV)
	Austin	Butcher	Pollak	
Glass G ₀	--	---	----	0.35
Glass G ₂	1.52	0.63	1.548	0.31
Glass G ₄	2.64	1.10	2.687	0.27
Glass G ₅	1.66	0.69	1.683	0.32
Glass G ₆	1.59	0.67	1.621	0.34

From these plots, the activation energy for conduction in the high temperature region over which a near linear dependence of log σ_{ac} with 1/T could be observed, is evaluated and presented in Table 4; the activation energy is found to vary linearly with the conductivity (inset (b) of Fig. 6).



3.3 Discussion

The important results of present study on dielectric properties $K_2O-Al_2O_3-P_2O_5: CuO$ glasses are summarized below:

The dielectric constant ϵ' at room temperature (30 °C) and at 100 kHz of the pure glass is measured to be 6.67 and the value is found to increase with the decrease in frequency. The dielectric loss at room temperature for pure glasses exhibited similar behaviour. With the introduction of CuO (0.2 mol %) in to $K_2O-Al_2O_3-P_2O_5: CuO$ glass matrix, the values of dielectric constant and loss are found to increase and continued to increase upto 0.4 mol % and beyond this concentration dielectric constant and loss are found to decrease with increase in the concentration of CuO. The variation of dielectric constant of $K_2O-Al_2O_3-P_2O_5: CuO$ glasses with temperature shows a considerable increase especially at lower frequencies. The variation of dielectric loss of pure and CuO doped $K_2O-Al_2O_3-P_2O_5$ glasses with temperature exhibited dipolar relaxation effects. The ac conductivity σ for CuO doped glasses has been observed to increase up to 0.4 mol % and there after the conductivity is found to decrease. The activation energy for ac conduction is estimated to be the lowest for glass G₄.

The properties of glasses depend not only upon its composition but also to a considerable degree upon its structure. Deep and important changes can occur as a result of structural transformation. $K_2O-Al_2O_3-P_2O_5: CuO$ glasses have a complex composition and are an admixture of network formers, intermediates and modifiers.

The alkali oxide i.e. K_2O acts as a modifier (normally the oxygen's of K_2O break the local symmetry while K^+ ions occupy interstitial positions) and introduces co-ordinated defects known as dangling bonds along with non-bridging oxygen ions. P_2O_5 is a well-known network former with PO_4 structural units with one of the four oxygen atoms in PO_4 tetrahedron is doubly bonded to the phosphorus atom with the substantial π -bond character to account for pentavalency of phosphorous [1]. The PO_4 tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygen. Neighbouring phosphate chains are linked together by cross bonding between the metal cation and two non-bridging oxygen atoms of each PO_4 tetrahedron. In general the P-O-P bond between PO_4 tetrahedral is much stronger than the cross bond between chains via the metal cations [2]. CuO is yet another modifier entering in to $K_2O-Al_2O_3-P_2O_5$ glass network. There is also a possibility for Cu^{2+} ions to be reduced in to Cu^+ ions as reported in a number of other glass systems [3], since $Cu^{2+} + e^- = Cu^+$ takes place only with $E^0 = 0.153V$ [4]. When CuO enters as modifier in the glass network, the π - bond of P = O may be ruptured with the creation of new non-bridging oxygen ions.

The dielectric constant of a material is due to electronic, dipolar and space charged polarizations. The space charge contribution depends on the purity and perfection of the glasses. Its influence in general is negligible at very low temperature and noticeable in the low frequency region. The dipolar orientation effects can sometimes be seen in the glasses even upto 106 Hz. Recollecting the data, the slight increase in the dielectric constant and loss at room temperature, particularly at low frequencies for pure and CuO doped – $K_2O-Al_2O_3-P_2O_5$ glasses may be ascribed to defects produced in the glass network which contribute to the space charge polarization.

The temperature has a complicated influence on the dielectric constant. Generally, increase in the temperature of glasses decreases the electronic polarization. The increase of ionic distance due to the increase in temperature, influence the ionic and electronic polarizations. The decrease in the electronic dielectric constant for many solids is found to be less than 3 % for temperature changes of about 400°C. Similarly, it appears that the changes in the ionic polarization are not large. Even the presence of dipoles and their contribution to dielectric constant, we know from Debye's theory ϵ' is inversely proportional to temperature. As such it is expected that dielectric constant of CuO doped of $K_2O-Al_2O_3-P_2O_5$ glasses should not change considerably with temperature. However, we find a large increase of ϵ' and $\tan\delta$ (beyond relaxation region); such a behaviour can only be attributed to the space charge polarization due to bonding defects of the type

mentioned earlier in the glasses [5-10]. The change in ϵ' and $\tan\delta$ with temperature are smaller at higher frequencies as this type of polarization decreases appreciably with frequency.

Variation of ϵ' and $\tan\delta$ with temperature is observed to be the highest for the glasses containing 0.4 mol % concentration of CuO. This indicates an increase in the distortion in of $K_2O-Al_2O_3-P_2O_5$ glass network, thus resulting the enhancement of the space charge polarization, which ultimately causes larger increase of ϵ' and $\tan\delta$ values, as observed. Obviously this is due to increasing modifying action of CuO similar to Al_2O_3 . As modifiers, these oxides enter the glass network by breaking up P-O-P bonds and introduce dangling bonds. The bonding 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 of the glasses dielectric parameters [11]. When the concentration of CuO is greater than 0.4 mol % in these glasses, we have observed the dielectric constant and loss to decrease. At such concentrations it seems that there is a possibility for the reduction of Cu^{2+} ions into Cu^+ ions. These Cu^+ ions may be blocked in tetrahedral coordination [12] in the glass network and make network more stable leading to a decrease in the dielectric parameters.

The conduction phenomenon in these glasses in the high temperature region can be explained on the basis of mixed conduction mechanism [13]. In fact, the interrelation and reduction processes could occur only if the material simultaneously exhibits a mixed conductivity, i.e., both ionic and electronic [13]. The conductivity variation with the concentration of CuO at higher temperature shows an increasing trend up to 0.4 mol.% of CuO and beyond this concentration conductivity is found to decrease. The conduction in the up to 0.4 mol.% (where σ_{ac} increases with CuO) is identified due to mobility of ions where as the beyond 0.4 mol.% is identified as electronic conductive zone [13]. It may be stated here that the highest conductivity and the lowest activation energy observed for the glass G_4 is obviously due to the highest concentration of free charge carriers, which may find easy paths for migration in the high disordered network.

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 the localized states near the Fermi level), the conduction in the localized states near Fermi level occurs when a.c. conductivity is nearly temperature independent and varies linearly with frequency. The conduction in the present $K_2O-Al_2O_3-P_2O_5:CuO$ glasses in the low temperature region (up to 350 K) can safely be attributed to take place by this mechanism.

Finally, the analysis of the results on dielectric properties of $K_2O-Al_2O_3-P_2O_5:CuO$ indicate that, there is an increasing rigidity of glass network when the concentration of CuO is more than 0.4 mol% in the glass network.

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