



Dielectric and optical properties of CuO containing sodium zinc phosphate glasses

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Abstract

Dielectric and optical properties of $45P_2O_5\text{-}34ZnO\text{-}(20-x)Na_2O\text{-}1Al_2O_3\text{-}xCuO$ glasses ($0 \leq x \leq 5$) were investigated. The frequency and composition dependencies of the dielectric parameters were analysed and discussed. The values of real part of dielectric constant (RPDC) lie between 748 to 1169 for $RPDC_{Max}$, and 654 to 1031 for $RPDC_{Min}$. The range of values of imaginary part of dielectric constant (IPDC) extends from 39.4 to 57.5 for $IPDC_{Max}$ and from 27.3 to 40.1 for $IPDC_{Min}$. It was observed that each of these parameters begins to decrease with increasing CuO content, but further addition of CuO causes their rise. Thus, small amount of CuO causes a decrease in both RPDC and IPDC until CuO content reaches 2 mol%, thereafter, they nearly return to their original values at 5 mol% of CuO. Similar behaviour was observed for AC conductivity. Transmittances of the investigated glasses were also measured and used to estimate their optical absorption coefficients and optical band gaps. The optical energy gap is ~ 4 eV for the samples with up to 4 mol% CuO, while it is somewhat higher (~ 5 eV) for the glass with 5 mol% CuO.

Keywords: copper phosphate glass, glass technology, conductivity, dielectric properties, optical properties

I. Introduction

Electrical and optical properties of various inorganic glasses containing different transition metal ions have been severely investigated [1–4]. Phosphate glasses are both scientifically and technologically important materials because they generally offer some unique physical properties better than other glasses, such as high thermal expansion coefficients, low melting and softening temperatures, high electrical conductivity, ultraviolet (UV) transmission and optical characteristics [5–11]. The oxide glasses containing transition metal ions are of great interest because of their semiconducting properties. Chemical durability of phosphate glasses is greatly improved by addition of ZnO because Zn^{2+} ion acts as an ionic cross linker between different phosphate anions, inhibiting hydration reaction [12]. ZnO acts as a glass modifier, where Zn^{2+} occupies interstitial sites in glass network [13].

The CuO containing glasses are important from the technological point of view because they exhibit semi-conducting properties and several other potential applications [14–23]. The electronic structure of the copper atom is $[Ar] 3d^{10} 4s^1$; the cuprous ion, having occupied d -orbitals, does not produce colouring [24], while Cu^{2+} ions create colour centres with an absorption band in the visible region [25] and produce blue and green glasses.

In view of the high scientific and technological importance of elucidating the dielectric (DE) behaviour of materials, studying the electrical properties of materials in an applied AC electric field has been the focus of numerous papers. In these papers, measurements have been carried out in wide frequency and temperature ranges for many types of materials [26]. Based on the dielectric measurements, two fundamental electrical characteristics of a material could be pinpointed: i) the nature of the material as an insulating medium that exhibits its capability to store electric charges, and ii) the nature of the material as a conductive medium that exhibits its capability to transfer the electric charge. Elec-

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trical conduction in these glasses occurs by the hopping of electrons from Cu^+ to Cu^{2+} . The study of dielectric properties over a wide range of frequencies and temperatures of the glass materials not only helps in accessing the insulating character and understanding the conduction phenomenon but to a large extent also gives information on the structural aspects of the glasses [27–30]. It has been observed that even in very small quantities, these metal ions (such as copper) dissolved inadvertently in the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{ZnO}$ glass matrix make these glasses coloured leading to the strong influence on their dielectric properties and optical transmission. So, it is very important to obtain information on the dielectric constants of these glasses before and after introducing the Cu^{2+} ions in them. Thus, the aim of the current paper is mainly oriented to investigate the optical and dielectric properties of the CuO doped $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{ZnO}-\text{Al}_2\text{O}_3$ glasses.

II. Experimental

Copper phosphate glasses with composition $45\text{P}_2\text{O}_5-34\text{ZnO}-(20-x)\text{Na}_2\text{O}-1\text{Al}_2\text{O}_3-x\text{CuO}$, where $x = 0, 1, 2, 3, 4$, and 5, were investigated. The chemical composition of each composite was carefully weighted, well mixed and ground in a porcelain mortar. The investigated glasses were prepared by conventional melting method in porcelain crucibles. For each composite, the mixed powders were heated in a muffle furnace up to 1000°C and kept for about one hour with clockwise shaking to ensure high homogeneity. Thereafter, the melts were cast in steel mould. The cast glasses were quenched at 300°C in another muffle furnace.

Bruker-D8 Advance Diffractometer (Bruker, UK) in flat plate geometry, using Ni filtered $\text{Cu K}\alpha$ radiation, was used to check the formation of any crystalline phase that confirmed the amorphous nature of the glasses under investigation. The optical measurements were carried out using JASCO-V-670 Spectrophotometer with wavelength range extending from 190 to 3200 nm. Five samples were ground and finely polished to be slab-like with flat faces that suit the dielectric measurements. For such a slab, a thin coating of silver paint was applied on to two opposite larger-area faces to serve as electrodes. With the aid of point contacts, two metal electrodes were contacted to the centres of the silver-printed faces. The contacts were confirmed using the I - V measurements. The DE measurements were carried out in a vacuum. A sample was mounted on the finger of the holder inside the Optistat-DN2 (Oxford Nanoscience Corporation) that was evacuated to about 10^{-5} torr using turbo pumping station (Pfeiffer HiCube 80 Eco). The dielectric measurements were carried out using HIOKI LCR HiTester, Model 3532-50 with frequency range 42 Hz to 5 MHz ($\pm 0.005\%$).

III. Results and discussion

3.1. Dielectric properties

Dielectric (DE) parameters (e.g. the dielectric constant ϵ' , the dielectric loss ϵ'' , the dissipation factor $\tan \delta$ and the alternating current conductivity σ_{AC}) were evaluated in the working frequency range (from 1.05 to 100 kHz) and for all investigated composites. The frequency dependence plots of these DE parameters are illustrated in Figs. 1–4.

The complex dielectric constant of a material is generally formulated with two parts: $\epsilon = \epsilon' + j\epsilon''$; where ϵ' is the real part of dielectric constant (RPDC) that is a measure of the energy stored from the applied electric field in the material and identifies the strength of alignment of dipoles in the dielectric. On the other hand, ϵ'' is the dielectric loss or the imaginary part of dielectric constant (IPDC) that is the energy dissipated in the dielectric that is associated with the frictional dampening, which prevents the displacement of bound charge from keeping in phase with the field change. Both RPDC and IPDC were evaluated by measuring the equivalent parallel capacitance C_p and the equivalent parallel resistance R_p of the samples under investigation, using the following equations [31]:

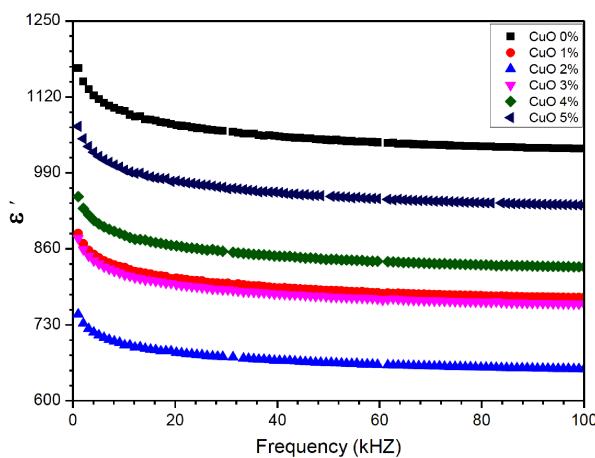


Figure 1. Frequency dependence of RPDC for investigated samples

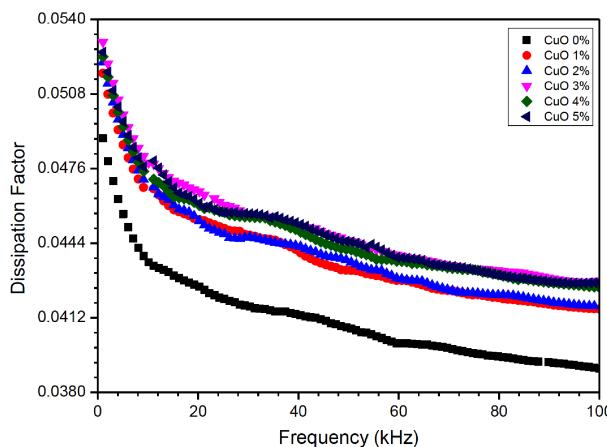


Figure 2. Frequency dependence of IPDC for investigated samples

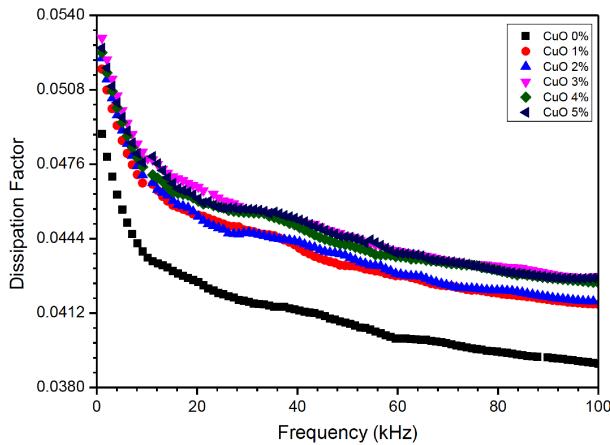


Figure 3. Frequency dependence of dissipation factor for investigated glass samples

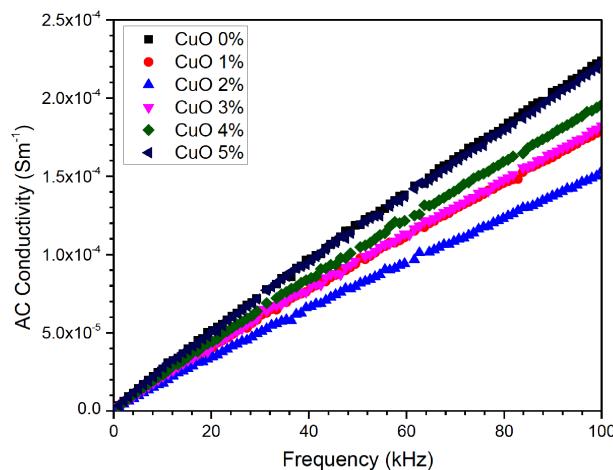


Figure 4. Frequency dependence of AC conductivity for investigated samples

$$\epsilon' = \frac{C_p \cdot d}{\epsilon_0 \cdot A} \quad (1a)$$

$$\epsilon'' = \frac{\epsilon'}{\omega \cdot C_p \cdot R_p} \quad (1b)$$

where C_p is the capacitance of the sample, d is the thickness, A is the area and ϵ_0 is the absolute permittivity of the vacuum having a value of 8.854×10^{-12} F/m. Based on the values of RPDC and IPDC, the dissipation factor or loss factor tangent ($\tan \delta$) gives the phase difference due to the loss of energy within the structure ($\tan \delta = \epsilon''/\epsilon'$) [32].

As a result of applying an AC electric field to a dielectric medium, electrical displacement (polarization) occurs for the charge carriers that causes a decrease in the RPDC with increasing frequency of the field. The decrease of the dielectric constant with increasing frequency can be attributed to the contribution of many components of electrical polarization that are well specified as electronic (P_e), ionic (P_i), dipolar (P_d), and space charge polarization (P_s) [33,34]. For a dielectric

material, the algebraic summation of all aforementioned components can be expressed as the total polarization P [33]:

$$P = P_e + P_i + P_d + P_s \quad (2)$$

The total polarization P is related to the relative dielectric constant ϵ' through the following equation [24]:

$$P = \epsilon_0(\epsilon' - 1)E = \epsilon_0 \cdot \chi \cdot E \quad (3)$$

where ϵ_0 is the permittivity of vacuum, χ is the electric susceptibility, and E is the applied AC electric field. Equation (3) shows the direct relation between relative dielectric constant and polarization. In accordance with this equation, one could predict the magnitude of the polarization in a dielectric material as the relative dielectric constant is well known for this material. The relative dielectric constant ϵ' determines the maximum energy that can be stored in the material. However, the relative loss factor ϵ'' evaluates the absorption of electrical energy by a dielectric material that is subjected to an alternating electromagnetic field. Furthermore, the dissipation factor $\tan \delta = \epsilon''/\epsilon'$ determines how well a material can absorb the electromagnetic field [33,35].

Elucidation of the electrical conduction of semiconductor materials in an applied AC electric field gives information about the nature of charge transport and states in the forbidden gap [36]. So, the values of the alternating current conductivity (σ_{AC}) for all samples under investigation were calculated based on the measured values of the aforementioned DE parameters and using the following relation [37]:

$$\sigma_{AC}(f) = 2\pi \cdot f \cdot \epsilon_0 \cdot \epsilon' \cdot \tan \delta \quad (4)$$

where f is the measuring frequency of the applied AC electric field and $\tan \delta$ is the dissipation factor that describes the phase difference between the current and voltage with respect to the applied AC electric field.

Figure 1 illustrates the frequency dependence of RPDC for all investigated samples. It is evident that RPDC sharply decreases with the increase in frequency in the low frequency region 1.05–8.12 kHz, and hence this parameter is strongly dependent on the frequency at the low frequency region. However, in the high frequency region (8.12–100 kHz) this parameter starts falling slightly with increasing frequency for all investigated samples. Dielectric properties arise due to the ionic diffusion within a conducting material when electric field is applied. The charge carriers in a glass cannot move freely through the glass matrix, but they can be displaced and polarized as response to an applied alternating field. An intensive decrease in the RPDC is clear at lower frequencies for all investigated samples. This could be due to the presence of the large capacitance at the electrode-electrolyte interface, which apparently reduces the AC current [38]. However, the relative low values of RPDC at higher frequencies suggest possible importance of these glasses for the construction of

photonic and NLO devices [39]. Consequently, RPDC profile at lower frequencies exhibits a higher 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 the net polarization effect. At higher frequencies, the periodic reversal of electric field at interface occurs quickly so no excess ions accumulate in the electric field direction [40] and hence, dielectric constant is lowered by weakening of ion-ion interactions in the dipoles and as a result their contribution to the polarization is reduced.

Changes in RPDC and IPDC of the investigated glasses with frequency exhibit effects of dielectric relaxation (Figs. 1 and 2). They are observed when the metallic ions are present in the divalent state [41]. These effects are observed for all samples due to the formation of dipoles from the divalent copper ions together with a pair of cationic vacancies. The considerable decrease in the dielectric constant and the loss at lower frequencies may be ascribed to the defects produced in the glass lattice which contribute to the space charge polarization that comes from mobility of ions and defects in the glasses [42]. Furthermore, the decreases in RPDC and IPDC with the increasing frequency could be explained by the fact that as the frequency is raised, the interfacial dipoles have less time to orient themselves in the direction of the alternating field [43–45].

Both IPDC and the dissipation factor, $\tan \delta$ (Figs. 2 and 3) exhibit higher dependency on frequency in the low frequency region, 1.05–8.12 kHz, than the real part of the dielectric constant. Thus, these parameters undergo sharp decrease with increasing the frequency in the low frequency region for all investigated samples. However, these parameters start falling slightly with increasing frequency in the frequency region from 8.12–100 kHz. Noticeably high values of $\tan \delta$ at low frequency range for all investigated samples may be due to the presence of some defects in the sample, such as oxygen vacancies, that play an important role in the conductivity [46]. The alternating-current conductivity is related to the dissipation factor by $\tan \delta \propto \sigma_{AC}/\omega$ [47]. The increase in the conductivity is smaller than that of frequency, and hence $\tan \delta$ decreases with the increasing frequency. It is evident from Fig. 3 that the dielectric loss of the investigated glasses decreases with increasing frequency due to the mobility of conducting species. The higher the mobility of conducting species, the higher would be the dielectric loss [48].

Figure 4 illustrates the frequency dependence of AC conductivity (σ_{AC}) in the frequency range extending from 1.05 to 100 kHz and for all investigated samples. It can be seen that the conductivity approximately linearly increases with frequency. Nearly the same behaviour was observed for sodium phosphate glass [49].

The measured total conductivity, σ , can be considered a summation of DC conductivity, σ_{DC} , and AC conductivity, σ_{AC} . The DC part is independent of fre-

quency, is dominant at lower frequencies and appears as a flat DC plateau in the low frequency region. The DC plateau, which is considered an indication of the DC conductivity domination, is observed at high temperature, but not at room temperature [49]. On the other hand, the AC conductivity is approximately independent of the frequency at lower frequencies, but more frequency dependent in high frequency region. The total conductivity follows the power relation [39]:

$$\sigma = \sigma_{DC} + A \cdot \omega^s \quad (5)$$

$$\sigma_{AC} = A \cdot \omega^s \quad (6)$$

where A is the pre-exponential factor and s is the power law exponent representing the degree of interaction between the mobile ions. In high frequency region, $A\omega^s \gg \sigma_{DC}$ so the total conductivity is equal to the AC conductivity [50].

The above equation is referred to as the universal dynamic pattern of AC electrical behaviour of conducting solids and liquids as proposed by Jonscher [51] based on the exponent s laying in the range $0 < s < 1$. It has been used mostly to characterize the electrical conduction in disorder ionic glasses, amorphous semiconductors and ionic conductors [52–54]. This power law is related to the dynamics of hopping transport between states in the forbidden gap. The exponent s is the measure of the degree of interaction with the environment. Experimental evidence of this behaviour is a power law of the AC conductivity $\sigma_{AC}(\omega) = A\omega^s$ observed within broad range of frequencies [55]. The interpretation usually involves analysis of the temperature dependence of $s(T)$ and composition dependence $s(x)$ that makes it possible to find the relevance of the hopping mechanism in terms of pair approximation [53]. Based on the aforementioned power law, the quantity $\ln(\sigma_{AC})$ was plotted as a function of $\ln(\omega)$ that is depicted in Fig. 5. The values of the exponent s for all investigated samples were evaluated by calculating the slopes of resultant straight

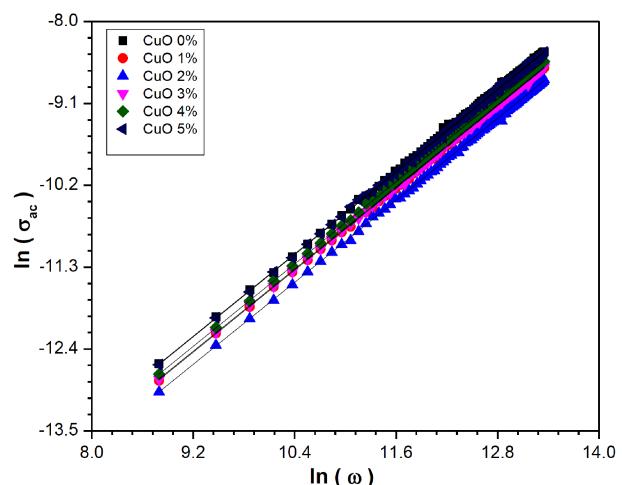


Figure 5. $\ln(\sigma_{AC})$ as a function of $\ln \omega$ for investigated

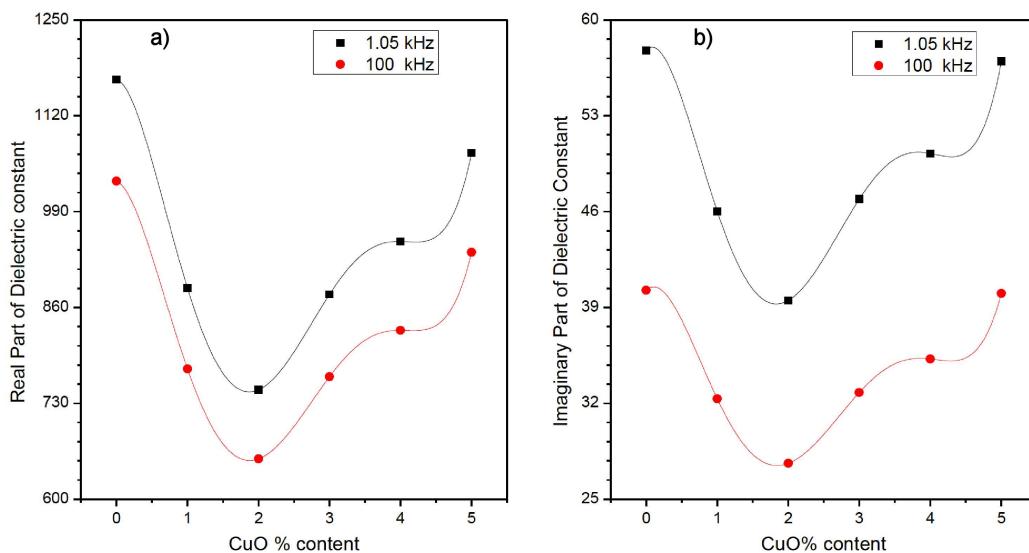


Figure 6. Influence of CuO addition on RPDC and IPDC for investigated glass samples

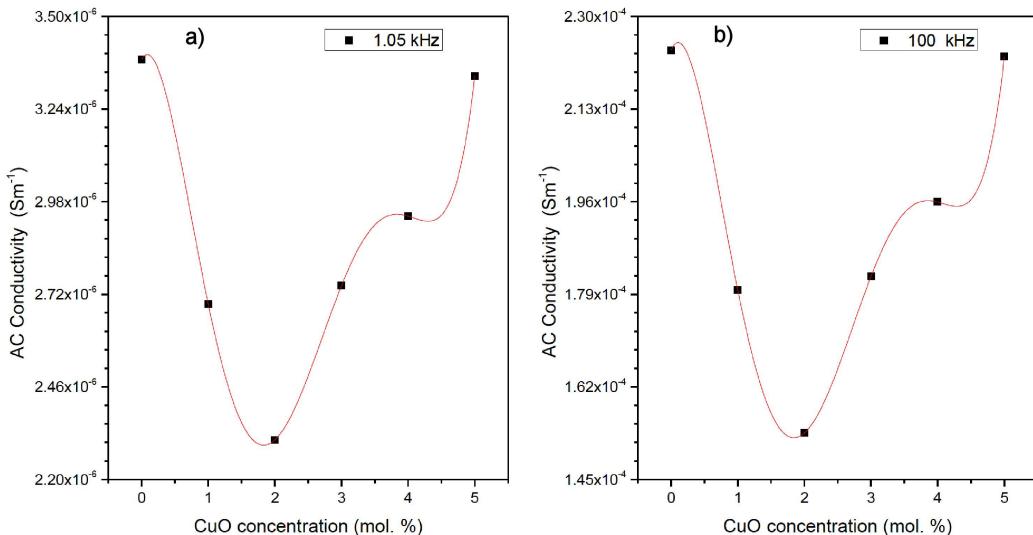


Figure 7. Change in AC conductivity with CuO content for investigated glass samples

lines. In the current work, the estimated values of the exponent s were found to be about 0.92 which is less than unity that represents the ion transport characterized by the forward-backward hopping process [56]. The linear behaviour of the $\ln(\sigma_{AC}) - \ln(\omega)$ relation indicates the presence of small polaron conduction mechanism between copper ions in the investigated glasses [57].

Figures 6a and 6b show the change of RPDC and IPDC with the concentration of CuO at frequencies 1.05 and 100 kHz. It is obvious that firstly each of these parameters begins to decrease with increasing CuO, but further addition of CuO causes their rise. Thus, small amount of CuO causes a decrease in both RPDC and IPDC until CuO content reaches 2 mol%, thereafter, they nearly return to their original values at 5 mol% of CuO.

Figures 7a and 7b show the dependence of AC conductivity on CuO concentration at frequencies 1.05 and

100 kHz, respectively. It is observed that the conductivity decreases with increasing CuO until 2 mol% and then it begins to rise with increasing CuO content. There are two contributions to the conductivity: electronic and ionic conductivity. The electronic conductivity comes from polaron hopping mechanism while the ionic conductivity is related to the existence of mobile ions. The ionic conductivity is therefore affected by the number of mobile ions and their mobility. For example, the conductivity of copper lithium phosphate glass increases by two or three orders of magnitude by replacing mobile Cu^{+} ions with more mobile Li^{+} ions [58]. Moreover, El-Desoky *et al.* [59] studied the influence of addition of iron ions into the sodium phosphate glasses on the electrical conductivity. They showed that the decrease of conductivity with increasing iron ions comes from the lower mobility of iron ions and their higher-polarizing power strength. Based upon the above discussion, the

decrease in the conductivity by increasing of CuO content may be due to: i) the replacement of lower ionic size sodium ions with larger copper ions, ii) the decrease of the concentration of Na₂O in contrast to the increasing of CuO content, iii) the higher polarizing strength power (the ratio of the cation valence to its diameter) of CuO than Na₂O and iv) the decrease of the molar volume with increasing CuO which reduces the mobility of mobile sodium ions. Topic *et al.* [60] stated that sodium ions in sodium iron phosphate glasses, having soda content below 20%, have less contribution to the conductivity since the hopping is dominant. Consequently, it is suggested that the ionic conductivity is negligible. However, addition of aluminum oxide (1 mol%) can make the ionic contribution to be observable where Al₂O₃ can increase molar volume leading to the increase in the mobility of sodium ions. On the other hand, further increase in CuO concentration makes increase in electrical conductivity as shown in Fig. 7. Both Na₂O and CuO act as modifiers in the glass network so each can open up the network creating dangling bonds and non-bridging oxygen ions by breaking the P–O–P bonds. These defects produce easy pathways for the migration of charge carriers [61]. The AC conductivity is more associated with the dipolar mechanism between the modifier ions and the non-bridging oxygen ions [62]. However, in lower CuO concentration, the ionic conductivity via Na⁺ predominates leading to decrease in the conductivity with decreasing Na₂O concentration. Further raise of the CuO concentration causes the presence of copper ions in two different valence states. This makes the small polaron hopping between Cu⁺ and Cu²⁺ to easily occur [63]. So, the electronic conductivity becomes dominant and the conductivity increases with increasing CuO concentration. As a result, these phosphate glasses can be considered as mixed ionic-electronic conductors.

3.2. Optical properties

The optical measurements are productive tools for understanding the band structure and evaluating the band gap width and optical parameters of both ordered and disordered materials. The optical absorption coefficient (α) is related to the transmittance (T) of a sample with thickness (d) through the relation:

$$\alpha = \frac{1}{d} \cdot \ln \frac{1}{T} \quad (7)$$

This relation was used to estimate the values of the absorption coefficient in the incident photon energy region from 3.6 to 5.50 eV (Fig. 8). It can be seen that the absorption coefficient exhibits a band tail at lower energies, and it represents a typical behaviour for all investigated samples. Tailing of the band states into the gap width may be induced by a large concentration of free carriers resulting from screened Coulomb interaction between carriers that perturbs the band edges. Thereafter, α steeply increases with increase in the photon energy near the fundamental edge. In the region of the

photon energy that has values greater than those of the exponential edge region, the absorption coefficient linearly increases with increasing the incident photon energy. It is evident from Fig. 8 that in the linear portion (high absorption region), the absorption coefficient undergoes a shift toward lower values of the photon energy with increasing the copper ions content. In the high absorption regions (linear increase of α with increase in the incident photon energy), the relationship between the absorption coefficient and the incident photon energy ($h\nu$) is governed by the relation [64,65]:

$$\alpha = A \frac{(h \cdot v - E_g)^n}{h \cdot v} \quad (8)$$

where, A is constant dependent on the transition probability, E_g is the width of the band gap and n is an index that characterizes the optical absorption processes in all investigated glasses. Analysis of the experimental results showed that a proportionality is revealed between the absorption coefficient and the frequency of the photon energy in the form $(h\nu - E_g)^n$. In accordance with Qasrawi [66], the exponent n equals to 2, 1/2, 3 or 3/2 for the indirect allowed, direct allowed, indirect forbidden or direct forbidden transition, respectively. The usual method for determining the type of the optical transition includes plots of $(\alpha h\nu)^{1/n}$ versus the incident photon energy $h\nu$. This proportionality gives a set of plots with four values of the exponent n : $(\alpha h\nu)^{1/2} - h\nu$, $(\alpha h\nu)^2 - h\nu$, $(\alpha h\nu)^{1/3} - h\nu$ and $(\alpha h\nu)^{2/3} - h\nu$. One of these plots satisfies the widest linearity of data, and hence its exponent determines the type of the optical transition. For all investigated glasses the exponent n indicates that the dominant transition is direct allowed one, and hence $(\alpha h\nu)^2$ was plotted against $h\nu$ (Fig. 9). The optical band gap was calculated for such a sample by linear fitting of the high absorption regions. For such glasses, the fitting intersects the $h\nu$ -axis at the value of the corresponding band gap width.

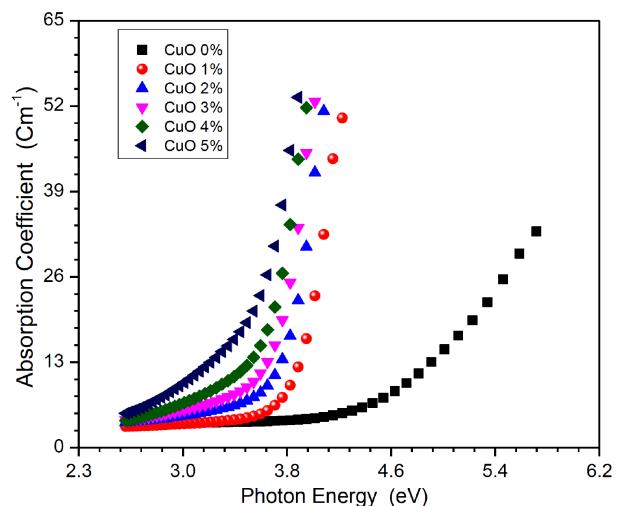


Figure 8. Absorption coefficient for investigated glass samples

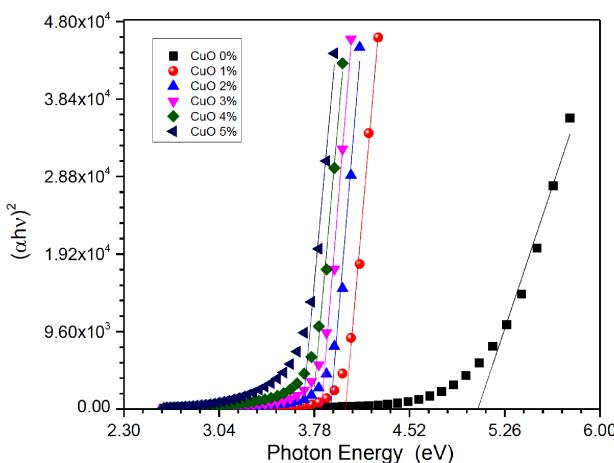


Figure 9. Plots showing $(\alpha h\nu)^2$ versus $h\nu$ for investigated glass samples

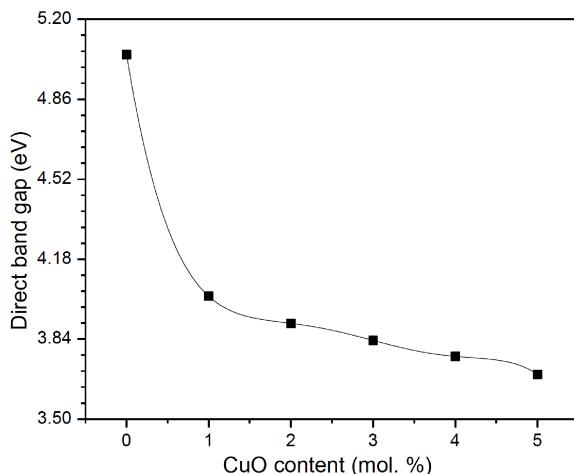


Figure 10. Optical band gap width versus to the copper ion content for investigated glass samples

In transition metal oxide glasses where small polaron conduction is supposed to occur, hopping is induced by the trapped electron absorbing a photon. Consequently, photon-induced hopping requires an energy of $\hbar\omega = 4E_H$, where E_H is the activation energy for conduction [67]. The optical energy gaps, for several binary phosphate glasses, are approximately equal to or greater than $4E_H$. Thus, using the reported activation energies for conduction in copper phosphate glasses, one would expect $E_{opt} \geq 4$ eV [68]. Alternatively, values reported by Hogarth *et al.* [69–74] are less than 4 eV that coincides with the data obtained in the present work. It is evident from Figure 10 that the E_{opt} values systematically decrease with increasing the copper ions content. The decrease of E_{opt} to lower energies with increase in the Cu^{2+} content is probably related to the progressive increase in the concentration of non-bridging oxygen. This makes it easier for the electrons to move through the material. It is reasonable to postulate that the optical energy gap of copper phosphate glass is due to the excitation of electrons from the hybridized $3d$ copper and $2p$ oxygen states to the conduction band near the

Fermi energy. The optical energy gap depends on the energy level of the upper valence band edge, which is determined by the separation of $3d$ copper and $2p$ oxygen states. For small separation between these states, hybridization of $3d$ copper and $2p$ oxygen states can occur easily, as it has been found in metallic or semiconducting copper oxides [75]. Hybridization broadens the valence band and moves the upper valence band edge to higher energy, resulting in a smaller energy band gap. Therefore, it may be plausible that the separation between $3d$ copper and $2p$ oxygen states, which depends on the chemical bonding characteristics in the glasses, determines the optical energy gap [68]. The variation of E_{opt} with glass composition can be explained as follows: the higher concentration of charged non-bridging oxygen ions with reducing P_2O_5 content causes an increase in $2p$ oxygen energy levels. This rise of $2p$ oxygen levels shortens the separation between $3d$ copper and $2p$ oxygen states, broadening the valence band, and thus diminishing E_{opt} [76]. Hence, with increasing the Cu^{2+} content, the optical energy gap is reduced since the separation between $3d$ copper and $2p$ oxygen becomes smaller. This is in accordance with the theoretical predictions that increased covalent character of the bonds causes a decrease in the absorption edge energy [76].

IV. Conclusions

The present study shows the effect of Cu^{2+} ion on the dielectric and optical properties of copper phosphate glasses (containing up to 5 mol% CuO). The measured dielectric parameters confirm presence of mixed conduction in these phosphate glasses. The values of real part of dielectric constant (RPDC) and imaginary part of dielectric constant (IPDC) were obtained. It is observed that each of these parameters begin to decrease with increasing CuO, but further addition of CuO makes their rise. Thus, small amount of CuO causes a decrease in both RPDC and IPDC until reaching 2 mol% CuO, thereafter, they nearly return to their original values at 5 mol% CuO. Transmittances of the investigated glasses were also measured and used to estimate their optical absorption coefficients and optical band gaps. The optical energy gap is ~ 4 eV for the samples with up to 4 mol% CuO, while it is somewhat higher (~ 5 eV) for the glass with 5 mol% CuO.

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