Thermal, mechanical and electrical properties of lithium phosphate glasses doped with copper oxide

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Abstract. Lithium phosphate glasses with the basic composition (P_2O_5 50 and Li_2O 50 mol%) series by the addition of copper oxide (0, 10, 15 and 20 g/100 g) were prepared by a melt quenching technique. Fourier-transform infrared (FTIR) absorption spectra and X-ray diffraction (XRD) analysis were used to characterize the glass samples. Thermal expansion and mass density were also measured. The different mechanical properties of the prepared glasses were measured by an ultrasonic non-destructive technique. Additionally, both frequency and temperature dependence of alternating-current conductivity were measured in the frequency range of 40 Hz–1 MHz and the temperature range of 308–488 K. Moreover, direct current conductivity was also measured for the same temperature range. FTIR measurements confirm the appearance of the bands of phosphate groups and the assumption of bonds formed between Cu and P. XRD spectra approve the amorphous nature of the studied glasses. Thermal expansion and mass density of the prepared samples show an increase in values by increasing the CuO content. The mechanical properties of the studied glasses (hardness (H_v), Young's modulus (E), elastic modulus (L), bulk modulus (K), shear modulus (G) and Poisson's ratio (ν)) were positively affected by the CuO content, reflecting a better packed structure. Furthermore, the electrical conductivity values of the prepared glasses are identified to increase with an increase in both temperature and CuO content. Such trends agree with the data obtained by thermal expansion and FTIR. The progressive addition of CuO is assumed to improve thermal, mechanical and electrical properties of the prepared lithium phosphate glasses.

Keywords. Lithium phosphate glass; copper oxide; thermal expansion; mechanical properties; electrical properties.

1. Introduction

Due to the numerous unique properties of phosphate glasses, they have diverse technological applications [1]. Phosphate glasses including copper have special interest due to their several properties. Optical, magnetic and electrical properties of copper-doped phosphate glasses permit a wide range of applications in solid state lasers, super-ionic conductors, colour filters and radiation sensors [2]. Lithium phosphate glass has low melting and low glass transition temperature. It also has high thermal expansion coefficient and high electrical conductivity which qualify glass to be used in laser host matrices, lithium micro-batteries and electro-optical systems [3–5]. Glasses containing lithium have potential applications in high energy density solid state batteries because Li_2O has high electro positivity which increases the glass conductivity. Different valence states of copper can exist in glass in many forms: cupric (Cu^{2+}), cuprous (Cu^+) and metallic copper (Cu^0) [6–8]. To investigate the nature of these glasses for their appropriate applications, the study of mechanical, electrical and physical properties is essential. High concentrations of transition metal oxides in glass make the glass

amorphous semiconductor. The main concept in the electronic conductivity of transition metal ions is the ability of ions to present in different valence states. The conductivity exists when the transmission of ions occurs from lower to higher valence states [9]. The addition of substantial quantity of alkali oxides like Li^+ to the glass network leads to an electronic ionic conduction [10]. Glasses containing CuO are essential from the scientific point of view to display semiconducting properties and several other prospective optical applications.

Many authors had studied the electrical properties of modified-phosphate glasses [11–13]. It has been noticed that ionic conductivity can be reached in many glass systems when different oxides are substituted or added instead of network formers. Also, ionic conductivity increases when any ionic conducting salt or alkali oxide is drugged in the glass matrix [14,15]. The attention to the ion conduction of phosphate glasses is developed due to many properties of these glasses like high thermal expansion coefficient, low glass transition and softening temperatures [16]. Copper phosphate glasses have many applications in electrical and optical properties. They can be used as super ionic conductors, heat absorbers,

Table 1. Chemical composition of the prepared glasses.

Mol%	Li ₂ O	P ₂ O ₅	CuO (g)
Base	50	50	—
Cu10	50	50	10
Cu15	50	50	15
Cu20	50	50	20

solid-state lasers and non-linear optics [17]. Ultrasonic spectroscopy depends on a repertoire of spectral signatures for a wide range of material and boundary conditions for both qualitative and quantitative microstructure characterization.

The structural and thermal properties of lithium phosphate glasses doped with various CuO contents have been studied in several articles. However, to the best of authors' knowledge, the effect of successive addition of CuO on the mechanical properties has not been reported in detail before. Accordingly, the ultrasonic technique was used to investigate elastic moduli: longitudinal modulus (L), shear modulus (G), Young's modulus (E), bulk modulus (B) and Poisson's ratio (ν). Furthermore, their electrical properties will also be measured with the aim of reaching a composition which can be applied in the industry.

2. Experimental

2.1 Glass preparation

All glass batches were prepared from chemically analytical materials as shown in table 1. Lithium oxide was obtained from lithium carbonate (Li₂CO₃) and phosphorous pentoxide was obtained from ammonium dihydrogen phosphate (NH₄H₂PO₄). Copper oxide (CuO) was correspondingly introduced from 10–20 g/100 g of the lithium phosphate glass. Every batch was accurately weighted, thoroughly mixed and added in a porcelain crucible, and melted in an electrical furnace at 1100°C for 2 h. Rotation for every 30 min was performed for complete homogenization. The melts were cast into preheated stainless steel moulds. The prepared glass samples were immediately transferred to a muffle furnace regulated at 300°C for annealing. The muffle containing the prepared samples after 1 h was switched off and left to cool to room temperature at a rate of 30°C h⁻¹. As the CuO content increased, the colour of the transparent glass changed from light to dark green due to the presence of Cu²⁺ ions.

2.2 FTIR spectroscopy

The Fourier transform infrared (FTIR) absorption spectra of the prepared glasses were recorded at room temperature in the range of 4000–400 cm⁻¹ by an infrared spectrophotometer

type (JASCO FT/IR-300E spectrophotometer, Japan), using the KBr disc technique. Two-milligrams of powdered glass were mixed with 200 mg of KBr and the mixture was subjected to a load of 5 tons per cm² in order to produce clear homogeneous discs. The infrared (IR) absorption spectra were recorded immediately after preparing the desired discs.

2.3 XRD analysis

For X-ray diffraction (XRD), the samples were crushed into fine powder using a pestle and mortar. XRD analysis was performed using a diffractometer with Cu radiation ($\lambda = 1.5405 \text{ \AA}$) operating at 40 kV and 30 mA at room temperature. Diffraction patterns were acquired on finely ground samples for 2θ values ranging from 5 to 80°.

2.4 Thermal expansion

The thermal expansion data were examined for the studied samples with dimensions $1.5 \times 0.5 \times 0.5 \text{ cm}$ using a computerized dilatometer type (NETSCH, 402 pc, Germany) with a heating rate of 5°C min⁻¹. The thermal measurements were carried out from room temperature up to the dilatometric softening temperature of the glass sample. The thermal expansion data show the glass transition temperature T_g and the softening temperature T_s and also the thermal expansion coefficient (α) values. All the samples were measured three times to estimate the average values and the errors.

2.5 Density

The bulk density of all the glass samples was determined according to Archimedes' method (ASTM: B962-13) using xylene as the immersion solution.

2.6 Mechanical properties of glass

Vickers microhardness (H_v) of 2.5 mm thick polished samples was measured with a Shimadzu-HMV (Japan) microhardness tester using 100 g load under ambient laboratory conditions with a constant indenter dwell time of 10 s. The microhardness was calculated using equation (1), finding the ratio of the applied load to the pyramidal contact area of the indentation according to ASTM:B933-09 [18,19].

$$H_v = 1.854 \frac{P}{D^2}, \quad (1)$$

where P is the indenter load in Newton and D is the length of the diagonal in mm.

The fracture toughness, K_{IC} , of the samples was determined from the indentation fracture using a Vickers microhardness tester. K_{IC} was calculated using equation (2) [19,20]:

$$K_{IC} = 0.016 H_v \frac{a^2}{c^{3/2}}, \quad (2)$$

where a is half the length of the diagonal of the indent and c is the crack length from the centre of the indentation to the crack end. The microhardness and fracture toughness values of the investigated materials were measured as the average of five readings along the cross-section surface for each sample.

The ultrasonic wave velocities (longitudinal and shear) propagated in the samples are obtained at room temperature using a pulse-echo technique MATEC Model MBS8000 DSP (ultrasonic digital signal processing) system with a resonating speed of 5 MHz. The values of Lamé's constants, i.e., λ and μ are obtained from the longitudinal (V_L^2) and shear (V_S^2) ultrasonic velocities as follows [21,22]:

$$\lambda = \rho(V_L^2 - 2V_S^2), \quad (3)$$

$$\mu = \rho V_S^2, \quad (4)$$

where ρ is the material bulk density in g cm^{-3} .

The values of the elastic moduli, longitudinal modulus (L), shear modulus (G), Young's modulus (E), bulk modulus (B) and Poisson's ratio (ν), were calculated from the following equations [21,22]:

$$L = \lambda + 2\mu, \quad (5)$$

$$G = \mu, \quad (6)$$

$$E = \mu \frac{3\lambda + 2\mu}{\lambda + \mu}, \quad (7)$$

$$B = \lambda + \frac{2}{3}\mu, \quad (8)$$

$$\nu = \frac{\lambda}{2(\lambda + \mu)}. \quad (9)$$

Compressive strength of the samples is measured according to ASTM E9.

Direct current (DC) electrical conductivity of measurements was performed as a function of temperature (308–488 K) using Keithley 616. Alternating-current (AC) electrical conductivity of measurements was performed as a function of both frequency (40 Hz–1 MHz) and temperature (308–488 K) using Hioki 3532.

3. Results and discussion

3.1 FTIR spectroscopy

IR spectroscopy is usually used to study the arrangement of the structural units of the studied glasses. The IR absorption spectra were recorded in the range of 4000–400 cm^{-1} as presented in figure 1. Phosphate glasses contain phosphate units which appear in the range of 1400–400 cm^{-1} . H_2O molecules or P–O–H vibrations appear at 3450, 2926 and 2855 cm^{-1} [23,24]. The P–O–H bridge or the carbonyl C=O stretching bonds found at 1644 cm^{-1} [25]. The band at 1406 cm^{-1} is due to water, hydroxyl or similar groups [26].

Figure 1. FTIR absorption spectra of the prepared glasses.

The properties of the phosphate glasses could be amended by the addition of halides or oxides of alkali, alkaline earth and transition metals into the glassy network. By oxide substitutions, the absorption band at 1264 cm^{-1} which corresponds to the PO_4^{3-} stretching vibration tends to move to a higher frequency with oxide substitutions. The band at 1098 cm^{-1} is due to $\nu_{\text{as}}(\text{PO}_3)$ which changes its amplitude when replacing Li_2O with Cu_2O . The two absorption bands at 1000 and 1100 cm^{-1} are attributed to P–O $^-$ symmetric and P–O $^-$ asymmetric, the phosphate-non bridging oxygen portion in PO_4 tetrahedra in a chain structure respectively. The band at 750 cm^{-1} is attributed to the P–O–P symmetric band. The peaks at 576 and 496 cm^{-1} are attributed to Cu–O vibrations confirming the phosphate–copper interaction [27].

An increase in the copper oxide content shows a slight shift of some band positions and sometimes changes in the relative intensities of the main bands. Information predicted from previous studies [28] leads to the following results:

- The intensity of the O–P–O band and other bands in the spectra does not significantly alter with composition, while the position of each band does shift slightly with a change in oxide composition. It is a typical band of the meta-phosphate glasses and a decrease in its intensity is detected with increasing the percentage of Cu_2O .
- The shifting of the two bands at 740 and 900 cm^{-1} of the P–O–P $_{\text{sym}}$ and P–O–P $_{\text{asy}}$ respectively to higher wavenumber may be due to the increase in the covalence character of these bands which indicates that the bonds are strengthened as Li_2O is replaced with Cu_2O [29].
- The band at about 900 cm^{-1} , which is assigned to P–O–P asymmetric, is slightly shifted to higher wavenumbers as Cu_2O content increases.

Figure 2. FTIR fitting pattern of base glass.

- (d) The band at 500 cm^{-1} which can be assigned to the deformation vibration of the PO_4^{3-} group is slightly shifted to higher wavenumbers as Cu_2O increases.

The existence of progressive ratios of CuO is observed to play an important role in the behaviour of lithium phosphate glasses beginning with a decrease in glass transition temperature. FTIR investigation reveals the formation of P-O-Cu bonds and shows the evolution of the phosphate skeleton. The formation of P-O-Cu bonds increases the cross-link density in the glass network and therefore increases the T_g of the glasses [29,30].

Deconvolution of the IR spectrum is necessary to analyse and illustrate the overlapping in FTIR spectra in a sensible manner [31]. We choose base glass with no copper oxide and glass Cu20 with the highest percent of copper oxide to illustrate the change in the spectrum. The connected spectral peaks in the region of $800\text{--}1500\text{ cm}^{-1}$ are highly increased in intensity with the same connected spectral features as shown in figures 2 and 3. It is clear that addition of copper oxide affects the spectrum by the appearance of new peaks as shown in figure 3 because of the formation of P-O-Cu^{2+} and P-O-Cu^+ bonds [32]. If copper ions are assumed to be cited in the modifying positions as alkali or alkaline earth ions with octahedral sites with terminal oxygens as the preferred nearest neighbours, then it affects the phosphate network by the replacement of P-O-P with P-O-Cu alongside the existence of metaphosphate groups [32].

3.2 XRD results

The amorphous phase of the samples was determined using the X-ray patterns. It comprised only broad humps, typical of vitreous solids as shown in figure 4. This proves the amorphous nature of the prepared glasses [9,33]. The vitreous nature of the glasses under study is established as the spectra

Figure 3. FTIR fitting pattern of Cu20 glass.

Figure 4. XRD pattern of the prepared glasses.

which are found to be free from any sharp Bragg peaks. This approves that the samples continue to be amorphous even after the introduction of different amounts of copper in the matrices of lithium phosphate glass.

3.3 Mass density and thermal expansion

It is obvious that CuO content affects the density values (ρ) of the studied glass as shown in table 2. The data of ρ

Table 2. Thermal expansion of the prepared glasses.

Sample no.	Density (g cm^{-3})	T_g ($^{\circ}\text{C}$)
Base	2.436	287
Cu10	2.635	292
Cu15	2.712	301
Cu20	2.858	309

increase from 2.436 g cm^{-3} for base glass to 2.858 g cm^{-3} for 20% CuO. The smallest alkali metal is lithium which can depolymerize phosphate chains to produce further non-bridging oxygens and permit more glassy structural volume [34]. The changes in density arise from the difference in the molecular weights of CuO and Li_2O and hence the substitution of Li_2O of a small radius by CuO of a large radius enlarges the glass network and makes structure rearrangement [35]. The T_g results shown in table 2 agree with the density results where the increase in copper addition increases T_g values, because of the change in phosphate chain nature i.e., length and bond strength [36,37]. The replacement of the P-O-Li^+ bond by P-O-Cu^+ or P-O-Cu^{2+} occur with maintenance of a similar portion of P-O-P bonds. The tight crosslinking between phosphate chains resulted from the replacement of the lithium oxygen bond which is less covalent by the copper oxygen bond resulted in an increase in T_g values [36]. Also, this crosslinking occur with addition of CuO results in obvious and remarkable changes in both softening temperature (T_s) and thermal expansion coefficients (α) as shown in table 3. The T_s values changed from 310°C for base glass to 320°C for glass Cu20. At the same time, the α values in different temperature ranges show a gradual decrease with an increase in CuO content.

3.4 Mechanical properties

In order to explore the abilities of phosphate glasses to be successfully applicable in various industrial fields, their properties should be tailored *via* modifying the composition and inserting beneficial elements within the amorphous network [38]. One promising way to modify the composition of phosphate glasses is by doping with metal oxides.

Figure 5. Effect of CuO contents on the microhardness and fracture toughness of lithium phosphate glass. **Figure 6.** Effect of CuO contents on the compressive strength of lithium phosphate glass.

Generally, such doping with metal oxides breaks P-O-P linkages and consequently, creates non-bridging oxygen atom. It is extremely important to note that the ionic cross-linking between the non-bridging oxygens of two phosphate chains is granted by modifying cations, which effectively improve the mechanical strength and chemical durability with an

Table 3. Density and glass transition temperature (T_g) of the prepared glasses.

Sample no.	T_s ($^{\circ}\text{C}$)	α (20–100 $^{\circ}\text{C}$) $\times 10^{-6}$	α (20–200 $^{\circ}\text{C}$) $\times 10^{-6}$	α (20–250 $^{\circ}\text{C}$) $\times 10^{-6}$
Base	310	5.06	9.45	11.61
Cu10	312	5.17	8.86	10.64
Cu15	318	3.58	5.65	9.25
Cu20	320	2.91	3.39	5.44

Figure 7. (a) Young's modulus (E), (b) elastic modulus (L), (c) bulk modulus (K), (d) shear modulus (G) and (e) Poisson's ratio (ν) as a function of CuO% contents.

increase in the bond strength of this ionic cross-link [39,40]. Based on the above mentioned considerations, CuO with different contents was added to phosphate-based glasses with the aim of enhancing their mechanical and electrical

properties. Microhardness (H_v), compressive strength, fracture toughness (K_{IC}), Young's modulus (E), longitudinal modulus (L), bulk modulus (K), shear modulus (G) and Poisson's ratio (ν) of all investigated specimens were measured

and illustrated in figures 5–7, respectively. As clearly seen from figures 5 and 6 that a significant increase in microhardness, fracture toughness and compressive strength is observed with an increase in CuO contents. As expected, glass sample contains the highest CuO contents recording the maximum values for these properties. Furthermore, the values of the elastic moduli: E , L , B , G and ν exhibit the same trend as hardness, toughness and compressive strength as they effectively increased by an increasing of CuO contents. These results are strongly correlated with the density values those discussed in the former section as the increasing of compactness of the glass structure is expected to play an increasingly important role in this enhancement of microhardness [41,42]. Furthermore, CuO possesses large charge which effectively promote its incorporation into the amorphous structure and forms cross-linking between the phosphate tetrahedra and accordingly, Cu–O–P bonds are created instead of P–O–P ones [28]. Therefore, the mechanical properties of these glasses are significantly improved.

The microhardness of the prepared glasses, in our work, is higher than that found in the literature. Rao and Shashikala [43] studied microhardness of $x\text{CaO}-(100-x)\text{P}_2\text{O}_5$ with $x = 30, 35, 40, 45$ and 50 mol% glass system and they found that the increasing of CaO, at the expense of P_2O_5 , led to a slight increase in the microhardness values from 3.37 to 3.62 GPa. Nabhan *et al* [30] prepared zinc–sodium–phosphate glasses doped with copper of the composition $40\text{ZnO}-(20-x)\text{Na}_2\text{O}-40\text{P}_2\text{O}_5-x\text{Cu}_2\text{O}$ where $x = 0, 2, 4, 6$ and 8 and then, they measured microhardness and family moduli (elastic, shear, etc.) for these samples. They reported that the microhardness of the examined samples exhibits a noticed increase with a progressive increase in Cu_2O contents ranging from 2.62 to 2.98 GPa while, the elastic modulus increases from 50.7 to 59.33 GPa and the shear modulus increases from 19.6 to 22.81 GPa.

3.5 Electrical properties

3.5a DC electrical conductivity: It is well-known that the conductivity of the materials is greatly affected by their structure. Both mobile ions and their concentrations are expected to play an increasingly important role in the occurrence of this effect. It is important to highlight that an increase in temperature and the concentration of mobile ions is responsible for more enhancement of the conductivity of the material [13]. Therefore, DC conductivity of the $50\text{Li}_2\text{O}-50\text{P}_2\text{O}_5$ glass sample with different CuO contents was measured at different temperatures as illustrated in figure 8. It is seen that an increase in CuO contents and temperature is responsible for a significant enhancement of the σ_{dc} of lithium phosphate glasses. The explanation of this positive result is that the doping of glasses with transition metals lead to the presence of mixed electronic–ionic electrical conduction, i.e., the existence of Cu^+ and Cu^{2+} ions encourages the replacement of P–O–P bonds with P–O– Cu^+ or P–O– Cu^{2+} which effectively improve conductivity of the investigated glass

Figure 8. Variation of the $\log \sigma_{dc}$ at different temperatures with CuO weight percent.

Figure 9. Temperature dependence of σ_{dc} of the base, Cu10, Cu15 and Cu20 glasses at different temperatures.

samples [40,44]. Mugoni *et al* [9] studied the conductivity of $(100-x)\text{Li}_2\text{O}-x\text{Cu}_2\text{O}-50\text{P}_2\text{O}_5$ glass series where lithium oxide has been substituted by copper oxide and reported that this substitution was responsible for significant reduction in conductivity values due to that lithium has much more mobile ions than copper. In contrast to these results, the addition of CuO contents to the above mentioned glass system effectively improves the conductivity of the prepared samples [45].

The obtained results suggest that the conductivity changes with temperature, as indicated in figure 7, according to Arrhenius equation [16]:

$$\sigma_{dc} = \sigma_0 e^{-E_{dc}/K_B T}, \quad (10)$$

Figure 10. Variation of activation energy, E_{dc} for Cu10, Cu15 and Cu20 glasses.

where E_{dc} is the activation energy for conduction, σ_0 is the pre-exponential factor, K_B is the Boltzmann constant and T is the absolute temperature in K.

Arrhenius plots of the variation of σ_{dc} for the prepared glass samples with temperature (308–488 K) and different CuO contents are shown in figure 9. It is worth noting that the slopes of the lines fitting the curves $\sigma_{dc} T$ vs. $1000/T$ are used to deduce the activation energy E_{dc} values. Notably, E_{dc} is important term that describes the average heights of the energy barriers that the ions have to overcome in their jumps [16].

It could be observed that conductivity of all glass specimens exhibits significant increase vs. an increase in temperature confirming the dependence of activation energy on the temperature (E_{dc}).

The activation energy as a function of CuO is shown in figure 10. From this figure, it is evidently noticeable that the increasing of CuO contents is responsible for a considerable decrease in the activation energy of all investigated samples. This observation can be interpreted in the manner that the increasing of CuO contents leads to more incorporation of Cu^+ ions into the glass network and consequently, it expands into voids in the structure reducing the pathways which in turn lowering the activation energy and contributing to easy migration of mobile Cu^+ ions [16,46].

Milanković *et al* [47] studied the effect of the replacement of ZnO with Li_2O ones in the $(100-x)Li_2O-xCu_2O-50P_2O_5$ ($0 < x < 40$) glass system on electrical conductivity at a temperature range of 298–473 K. The electrical conductivity of the glass sample increased from 1.04×10^{-4} to 2.18×10^{-4} at 298 K with an increase in Li_2O from 0 to 40 mol%. Moreover, an increase in temperature to 473 K is responsible for a further increase in electrical conductivity from 1.75×10^{-4} to $1.68 \times 10^{-3} S cm^{-1}$.

Figure 11. Variation of the log σ_{ac} of the (a) base and (b) Cu20 glasses vs. frequency (f) at different temperatures.

3.5b AC electrical conductivity: AC conductivity is an electrical factor that identifies the electrical conduction of a material in response to the applied electrical field [48]. It is worth mentioning that AC conductivity for the compositions of the lithium phosphate glass system is very advantageous for the assessment of non-linearity conductivity. Accordingly, the variation of AC conductivity (σ_{ac}) of base and Cu20 glass samples in the frequency range of 42 Hz–1 MHz at different temperatures, namely 308–488 K, was measured and represented in figure 11a and b. This figure reveals that AC conductivity is positively affected by the increasing of temperature as it records a significant increase in its values at all frequencies. Notably, this effect is known as thermal activation [49,50]. It is important to highlight that an increase in temperature leads to the occurrence of noticeable dispersion at a specific frequency which becomes prominent and shifts to a higher frequency region which is analysed by using Joncher's universal power law [40]

$$\sigma_{ac} = \sigma_{dc} + A\omega^s, \quad (11)$$

Figure 12. Temperature dependence of $\log \sigma_{ac}$ at different frequencies of the (a) base and (b) Cu20 glasses.

Figure 13. Activation energy of AC conductivity at different frequencies of the base and Cu20 glasses.

where σ_{dc} is the DC conductivity in the specific temperature range and frequency, A is the temperature-dependent parameter and s is the frequency exponent.

As clearly seen from the figure that there are two distinct regions: the first one is belonging to low frequencies at which the conductivity nearly remains constant. In other words, in this region, conductivity values are frequency independent. The explanation of this observation is that the conductivity arises from the hopping between the neighbouring particles. On the other hand, the second region is belonging to high frequencies and shows a successive increase in conductivity values with the increasing of frequency. Additionally, the increasing of temperatures leads to a measurable shift of conductivity towards higher frequencies. It is well-established that the frequency-dependent change is called conductivity relaxation phenomenon which agrees with the hopping relaxation model. Based on this model, charge carrier jumps to its neighbouring vacant site and contributes to σ_{dc} at low frequencies. However, the increasing of frequency is responsible for the likelihood of the correlated back and forth jumping and consequently, leads to the relaxation of the charge carriers [51,52].

Figure 12a and b illustrates the variations of $\ln(\sigma)$ vs. $1000/T$ at different frequencies for the base and Cu20 glass samples indicating an Arrhenius equation. The activation energy values corresponding to the crossover frequency have been estimated from the least squares straight-line fits as shown by solid lines in figure 13. It could be observed that the activation energy of all glasses shows recorded decrease with the increasing of frequency. The increase in the applied frequency and the improvement of mobile ion movement between the localized states are the most important reasons for such result [16,53].

Choudhary [40] prepared specimens of zinc-phosphate glasses doped with CuO and studied their electrical properties over a range of frequency from 100 Hz–1 MHz and at a temperature range of 323–573 K. The obtained results pointed out that the increasing of CuO content to 10% led to a remarkable increase in the electrical conductivity of the glass sample from 5.46×10^{-6} to 4.01×10^{-4} S cm $^{-1}$ at 323 K and 1 MHz. On the other hand, the increasing of temperature to 573 K is responsible for a further increase in electrical conductivity from 7.83×10^{-6} to 1.03×10^{-3} S cm $^{-1}$ at the same frequency.

4. Conclusions

The current study illustrates the effect of successive addition of CuO on the thermal, mechanical and electrical properties of lithium phosphate glasses of the main composition (P_2O_5 50 and Li_2O 50 mol%). FTIR showed different absorption bands due to phosphate groups and copper oxide. XRD confirmed the amorphicity of the prepared samples. Both thermal expansion and mass density increased with increasing the addition of CuO. The formation of P–O–Cu bonds increased the cross-link density in the glass network and therefore increases the glass transition temperature (T_g). Based on the variations in the T_g via structural modification, the glasses revealed to be

basically ionic conductors. The mechanical properties of glass samples increased with an increase in CuO. Electrical conductivity, in contrast to activation energy significantly increased with increasing the CuO content. These increases may be attributed to the possibility of ionic contribution to the electrical conductivity. The results revealed that the AC conductivity of all studied glasses intensely improved by increasing the frequency. This observation may be due to the increase in the mobility of charge carriers (ions). Furthermore, it is important to highlight that the low frequency region had no measurable effect on the activation energy of AC conductivity. On other hand, a further increase in the frequency led to a considerable decrease in their values.

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