

Effect of Cu ions on the Optical Properties of Glassy Filter System

M. Ibrahim, Dhia Aldin S. Mustafa, Y. H. Elbashar, M.Y. Hassaan, M. M. Elokr*

Department of physics, Faculty of Science, Al-Azhar University

**On leave from Republic of Iraq.*

Copper doped phosphate glass has been prepared by conventional melt quenching technique. The composition of the prepared system is 42 P₂O₅-39ZnO- 4CaO- (15-x) Na₂O- xCuO, where (x= 2, 4, 6, 8 and 10 mol %). The amorphous nature of the glassy system have been checked by X-ray diffraction (XRD). The density ρ has been measured by Archimedes method, using a toluene as the immersing liquid. The molar volume (M_v) has been calculated. It is observed that, the density of the prepared glasses increases by increasing copper oxide content and the molar volume M_v exhibit the same trend. The optical absorption spectra were measured in visible and near IR spectral regions. The data reveal that, such system exhibits band pass filtering effect. The height and width of absorption band were found to be copper concentration dependent.

1. Introduction

Phosphate glasses have several advantages over conventional silicate and borate glasses due to their peculiar physical properties such as high thermal expansion coefficient, low melting, softening temperature, high ultra-violet (UV) and far infrared transmission [1]. Copper-doped phosphate glasses exhibit interesting electrical and optical properties that make them suitable for use as super-ionic conductors, solid state lasers, and can be doped with high level by metal ions and remain amorphous [2]. The valence state of the copper ions in the glass band pass filters, and non-linear optical materials is usually divalent. The main advantage of a phosphate glass over other oxide glasses (e.g. silicate and borate) is the ability to accommodate high concentration of transition metals (TM). The valence state of (TM) depends on the type of inorganic precursor used to produce the glass: P₂O₅ or NH₄H₂PO₄. If P₂O₅ is used as precursor, the atmosphere is oxidative, and if NH₄H₂PO₄ is used as precursor, the atmosphere will act as reductive atmosphere [3]. Copper phosphate glasses exhibit an optical

absorption band in the visible-near infrared region and fundamental optical absorption edge in the ultraviolet region i.e. it can be used as band pass filter. It is well known that Cu^{2+} ion glass exhibits an optical absorption band in the visible region and creates colour in the glass. Copper can be present in glass in the form of Cu^{+2} ions, under strong reducing conditions, it exists as Cu^0 and Cu^+ . Copper oxides are the main constituent of blue and green glass. Their strong absorption in the long wavelength of the visible spectrum at about 800 nm is most likely due to Cu^{2+} ions which prevents the green signal during the foggy weather[4]. The optical absorption band arises from transitions associated with the internal d-d transition in Cu^{2+} . The absorption band positions in crystalline and amorphous is usually described by concepts of the crystal and ligand field theories[5]. UV optical absorption spectra of copper phosphate based glasses containing other oxides have been studied by Hogarth and Co workers[6]. They found that, the absorption edge varies with the glass composition. This behavior was explained as a result of the change of the ratio of Cu^{2+} and Cu_{tot} in the glass matrix. It was observed that, the optical energy gap increases as the $\text{Cu}^{2+}/\text{Cu}_{\text{total}}$ ratio increases. In addition fundamental optical absorption edge of amorphous systems are characterized by an exponential tail that occurs in the low-energy part of absorption edge, which is known as Urbach tail. The width of Urbach tail depends on the degree of disorder in glass matrix.

The aim of the present work is to investigate the structural features and optical absorption spectra of the glassy system:- $42[\text{P}_2\text{O}_5] + 39[\text{ZnO}] + 4[\text{CaO}] + (15-x)[\text{Na}_2\text{O}] + x[\text{CuO}]$, where $x = 2, 4, 6, 8$ and 10 mol %, which exhibit filtering effects. Copper redox states index, optical energy gap, E_g were obtained as a function of CuO content.

2. Experimental Technique

2.1. Glass Preparation:

Copper doped phosphate glasses $42[\text{P}_2\text{O}_5] + 39[\text{ZnO}] + 4[\text{CaO}]_{(15-x)} + [\text{Na}_2\text{O}] + x[\text{CuO}]$, where $x = 2, 4, 6, 8$ and 10 mol% were prepared. The oxide components were carefully weighted and well mixed in an agate mortar. The mixture was then heated in an electric furnace at 340°C for 1h to release gases, the temperature was then raised to 955°C for 30 min with continuous shaking to ensure high homogeneity. The mixing and heating steps are similar for all glasses, but the melting temperature and time for homogenization were different. Glasses were then annealed at 340°C for 3 hours to release any residual stress, and finally cooled to room temperature by shutting off the power to the furnace, that is cooling due to the furnace thermal inertia.

2.2. Glass Characterization

Different techniques have been used for characterizing the prepared samples: (XRD), density ρ , molar volume, M_v ($M_v = \text{molecular weight, } M_m / \rho$) and IR-VIS absorption. The amorphous nature of the prepared samples was proved by (XRD), where no peaks were observed indicating the amorphous nature of the prepared samples. The thickness of the glass samples were measured using a digital micrometer. Optical absorption spectra were measured using (JENWAY 6405 UV-VIS spectrophotometer). The measurements were carried out at room temperature in the wavelength range (200-1000 nm). The obtained densities of the prepared samples are shown in Fig. (1) and listed in Table (1). It is observed that ρ increases almost linearly by increasing CuO content. However, molar volume increases by raising CuO from 2% to 8% and attains almost constant value.

3. 3. Infrared (IR) Spectra:

For getting information about the structural units, FT-IR absorption spectra in the frequency range ($400\text{-}3500\text{ cm}^{-1}$) have been recorded using (FT-IR) Perkin Elmer Spectrometer type. Employing potassium bromid (KBr) pellet technique. In this technique the powdered sample mixed with KBr to obtain thin pellet for eliminating error caused by scattering. A fundamental advantage of this method is that KBr has no absorption bands in the studied spectral region [7].

3. Result and Discussion:

3. 1. X-ray Diffraction

The amorphous nature of the investigated samples were demonstrated by (XRD).

3.2. Density (ρ) and Molar Volume (M_v)

The dependence of density, and molar volume on CuO content for the investigated samples are shown in Fig. (1) and listed in Table (1). It can be seen that, both density and molar volume increases by increasing CuO content. The increase of density is most likely due to the replacement of Na ions by the heavier Cu ions. However, the increase in M_v can be accounted by considering the addition of Cu ions lead to enhance the formation of non-Bridging oxygen in the investigated system. Generally both density and molar volume have the same trend, where density and molar volume were found to increase by increasing CuO content. The obtained results were observed in other glassy system [8].

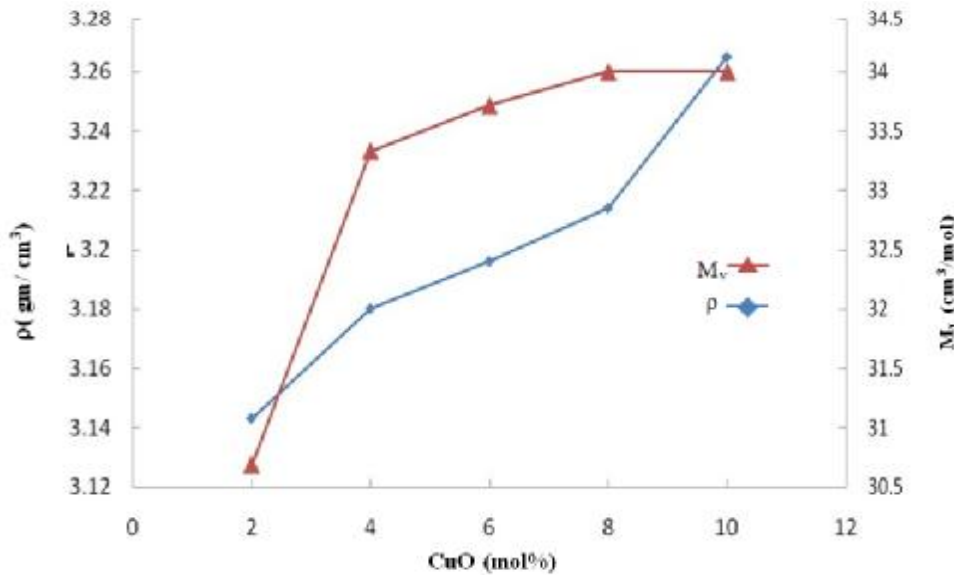


Fig.(1): The dependence of density(ρ) and molar volume(M_v) as a function of CuO content for the investigated samples.

Table (1): Estimated parameters of the prepared samples.

Sample	CuO (mol%)	ρ (gm/cm ³)	$M_{v=(M_m/\rho)}$ (cm ³ /mol)	M_m (gm)	E_g (eV)	E_c (eV)
S2	2	3.143	30.69	96.46	3.25	0.417
S3	4	3.18	33.33	106.14	1.59	0.313
S4	6	3.196	33.71	107.76	2.1	0.261
S5	8	3.214	34	109.38	2.17	0.23
S6	10	3.265	34	111	2.17	0.23

In general it is expected that the density and molar volume should opposite trend, but in the present glass samples, the behavior is different. However this anomalous behavior was observed in many glass systems, for example $\text{LiBO}_2\text{-TeO}_2$ [9] $\text{Li}_2\text{O TL}_2\text{O}_3\text{-B}_2\text{O}_3$ [10] $\text{TeO}_2\text{-Na}_2\text{O-B}_2\text{O}_3$ [11]. The molar volume behavior reveals that an increase in the content of Bi_2O_3 leads to the formation of non bridging oxygen(NBO) and expands the structure of the tight network of $\text{Li}_2\text{O}_{0.5}\text{B}_{1.5}\text{O}_{2.5}$ glass. The large values of the radii and the bond length of Bi_2O_3 compared to those of B_2O_3 , resulted in a formation of excess free volume, leading to increase the overall molar volume of these glasses. On the other hand the atomic weight of CuO ions (79.55) is higher than that of NaO (28.93) ions. This allows to conclude that, the copper ions probably reticulate the network of the glass (Fig,1).

3- IR Absorption Spectra:

Infrared spectroscopy is usually used to obtain the essential information concerning the arrangement of the structural units in the given system. It is assumed that the vibrations of structural units of the glass network are independent of the vibration of the other neighboring units [12]. Fig. (2) shows IR absorption spectra of the samples under study in the frequency range (400-3500 cm^{-1}). The broad absorption band observed in the frequency range (484-506 cm^{-1}) is usually considered as the micro structural changes occurred in addition to the reduction of the Cu^{+2} content in the samples [13]. The second band appeared at about (708-748 cm^{-1}), may be attributed to P-O-P groups. The same result was observed for other glass system [15]. The band located at about range (906-962 cm^{-1}) are usually assigned as P-O stretching in vibration $\text{CuO-P}_2\text{O}_5$. Absorption band observed in the range (1098-1114 cm^{-1}), is usually assigned due to the asymmetric stretching of PO_2 network groups [14].

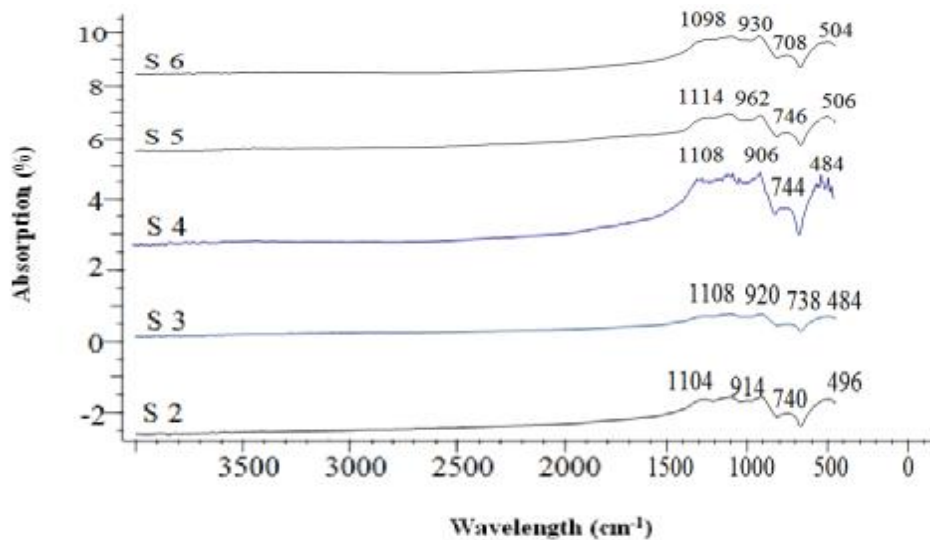


Fig. (2): The IR Spectra of different samples.

4. Optical Band Gap Determination:

The reflectance, R transmittance, T and absorbance, A were measured in the wavelength range (200-1000nm) for the investigated samples .

A well defined band is observed in the investigated samples. The height, width and area of the band depends on the CuO content. Fig. (3) shows the relation between transmittance, T and wavelength range ($\lambda = 200-1000$ nm) for the investigated samples. It can be seen that a broad band is observed nearly at

the wavelength range (200-500 nm), where the high almost decreases by increasing CuO content. This behavior can be attributed to the concentration of the Cu^{2+} ions. Fig.(4) shows the relation between high and weidth of the band against CuO content for the invastigated glassy samples. It can be seen that both high and width decreases by increasing CuO content. However, high has the highest value than those of the weidth.

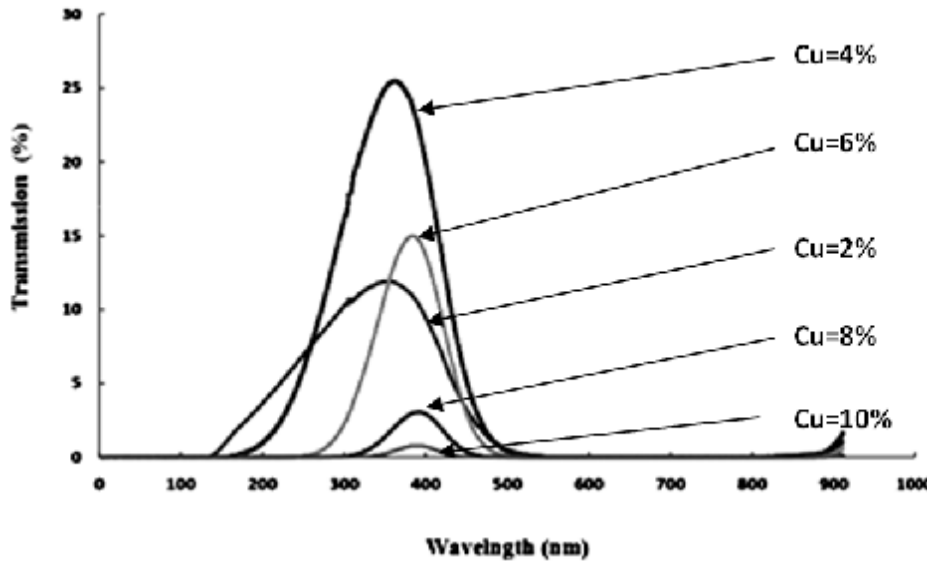


Fig.(3): Relation between transmittance, T and wavelength for the investigated samples.

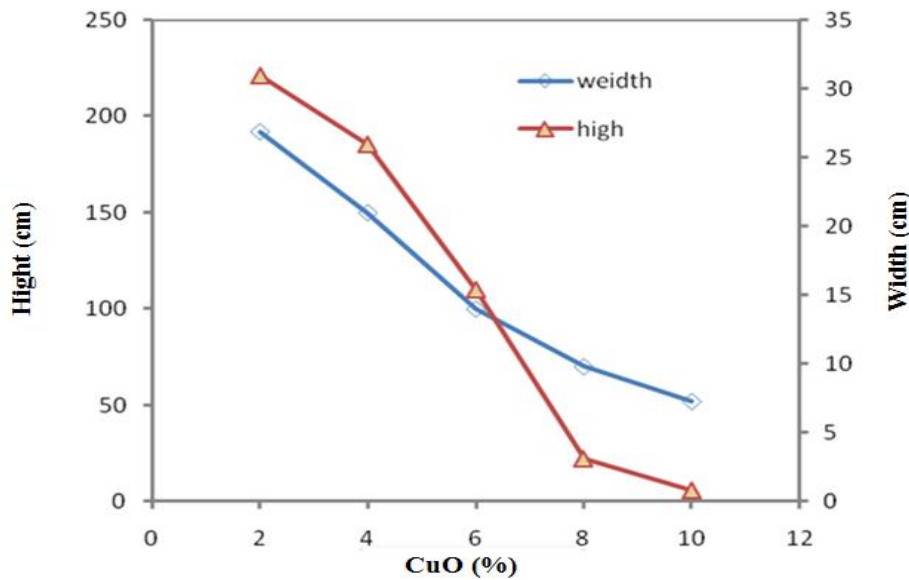


Fig.(4): Relation between the hight and width against CuO content.

If multiple reflections are neglected the transmittance, T of a sample is given by[15]:

$$T = (1-R)^2 \exp(-\alpha d) \tag{1}$$

Where, R is the reflectance, A is the absorbance, α is the absorption coefficient in cm^{-1} and d is the thickness. According to equation(1), α could be estimated.

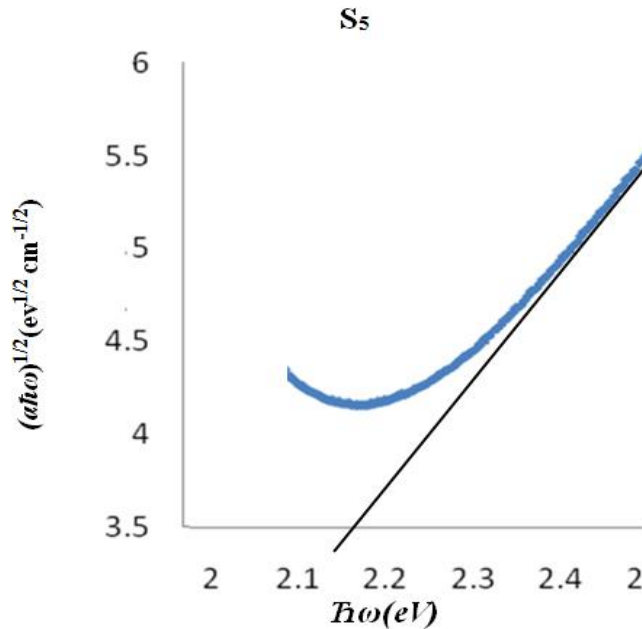


Fig.(5): Relation between $(\alpha\hbar\omega)^{1/2}$ and photon energy $(\hbar\omega)$ for sample (Cu=8 mol%) as illustrative example.

The optical energy gap values E_g were calculated according to the relation [16]: -

$$\alpha\hbar\omega = B(\hbar\omega - E_g)^r \tag{2}$$

where B is a constant, r is the parameter depend on the type of electronic transition during the absorption process and E_g is the optical energy gap. The parameter r take values 1/2, 3/2, 2, and 3 depending on the nature of electronic transition. For many glasses and amorphous materials [17], $r = 2$ was considered for indirect transitions in such materials, where wavevector k is no longer a good quantum number. This indicates that, the absorption is due to non-direct transition. Fig. (5) shows the relation between $(\alpha\hbar\omega)^{1/2}$ against photon energy $(\hbar\omega)$ in eV for Sample 5 as illustrative example. All other samples shows the same trend where $(\alpha\hbar\omega)^{1/2}$ exhibit liner dependence by increasing photon energy

($\hbar\omega$). Values of E_g can be obtained by extrapolating the linear curve to zero absorption. The obtained values of E_g are listed in Table (1). It can be seen that, values of E_g have 3.25 eV for sample with $x = 2$ mol %, then starts to decrease by increasing CuO content up to 4 mol%, then it starts to increase by increasing CuO content up to 8 mol % and finally it starts to be stable as increasing x up to 10 mol%. This behavior can be attributed to Cu ions which may act as a network modifier, copper can exist as Cu^{2+} and Cu^{+1} ions[18,19].

5. Band Tail Width Determination:

For many amorphous materials at low absorption range $\alpha=(10^3-10^4\text{cm}^{-1})$ Urbach assumed that, absorption coefficient, α , depends on the Photon energy ($\hbar\omega$) according to the relation[16]:

$$\alpha = \alpha_0 \exp(\hbar\omega/E_c) \quad (3)$$

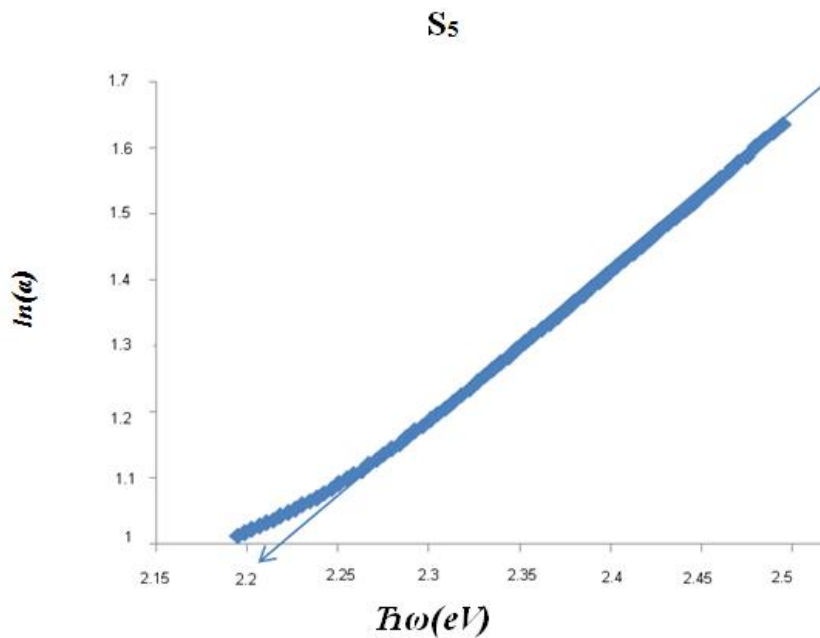


Fig. (6): Relation between ($\ln\alpha$) and photon energy ($\hbar\omega$) for sample(Cu=8 mol%) as illustrative example.

where α_0 is a constant and E_c is the width of the tail of localized states. Linear dependence of $\ln(\alpha)$ against ($\hbar\omega$) is presented in Fig. (6), where the values of E_c could be obtained. According to equation (2), values of E_c are calculated and listed in table (1) as a function of CuO content. Obtained results reveal that,

sample with $x=2$ mol% shows the highest value of $E_c(0.417$ eV), then it decreases as CuO content increases to about (0.23 eV) up to 8 mol%. Then it starts to be stable at $x=10$ mol%. This demonstrates that the degree of disorder depends on CuO content in our glass system.

Conclusion

Glassy system of composition $42P_2O_5-39ZnO-4CaO-(15-x)Na_2O-xCuO$, where $x=2, 4, 6, 8,$ and 10 mol%, has been prepared by melt quenching technique. The amorphous nature of the glassy system has been checked by X-ray diffraction (XRD). The density (ρ) and molar volume (M_v) have been estimated, where both the density (ρ) and molar volume (M_v) were found to increase. FTIR has been measured and the absorption bands have been assigned. The optical absorption showed transmission band in the region ($200-500\text{cm}^{-1}$) where the position, height, band width, and area of which, depend on the copper concentration. The indirect energy (E_g) were also estimated and it is found that the energy gap (E_g) depends on copper content.

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