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Towards Modeling of Copper-Phosphate Glass for Optical Bandpass Absorption Filter.

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ABSTRACT

Experimental studies of the optical band passes filter behavior of a new series of copper phosphate glasses have been carried out. The amorphous nature of the prepared samples was examined using XRD analysis. The effect of different contents of CuO on the thermal transition temperature (Tg) was investigated using differential thermal analysis (DTA). Density and its derivative parameters such as molar volume, copper ion concentration, and interionic distance have explored the effect of copper ions behave. The EPR spectra of copper phosphate glasses were measured at room temperature in order to examine the valance state of copper in the glass network. Finally, the optical filtering behavior of the prepared glasses was carried out using UV-Visible measurements. Optical band gap, Urbach energy, and refractive index, were studied to check the effect of Cu ion on the present glasses.

Keywords: copper phosphate glasses, optical filter, optical and structural properties, bandpass absorption glass filter

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INTRODUCTION

Optical glass filters are unique in their ability to transmit a very broad band of light [1, 2]. They are used for sorting, attenuation and spectral selection of a broadband source [3-6]. Lately, is considered one of the most important types of filters, which called bandpass filter. The competition between the interference and absorption filters was increased, but the technology of fabricating the transmittance bandpass filters is still very expensive and needs a lot of development in chemical composition to reach the optimum practical applications [7, 8]. Copper ion is one of the desired optical bandpass filter because of the Uniqueness optical transmission spectrum additionally its low glass transformation temperature [9].

Copper oxide in glass networks received numerous studies in order to explore its effect in different glass matrices [10]. The phosphate glass has marvelous properties such as low dispersion, high refractive index, low melting temperature, and galore economic [11, 12]. But the poor chemical durability of the phosphate glass is the main disadvantages of using this type of glass former [13, 14]. Hence, adding a good modifier such as transition metals oxide is an important factor to improve the chemical durability of phosphate glasses [13, 14]. The oxide metals such as zinc oxide play a good role for changing the properties of phosphate glass when it adds as a modifier. Zinc phosphate glass has a significant interest because it exhibits a high durability, low melting temperature with a lower glass transition temperature, and glass forming ability [15, 16]. On the basis of these aspects, the present work is focus on explore the influence of CuO on the optical properties of phosphate glasses in order to study their filtering behavior for visible light region.

EXPERIMENTAL

Samples with the chemical composition of $40P_2O_5$–40ZnO–(15-x) Na_2O–5CaO–xCuO, where x = 0, 2, 4, 6, 8, and 10 mol %, were prepared using the ordinary melt-quenching technique. The oxide components were carefully weighted and well mixed in an agate mortar. The mixture was then heated in an electrical furnace at 340^{o}C for one hour to release any gases, and then the temperature was raised to 1100^{o}C for one hour in order to melt the prepared mixtures with continuous shaking to ensure the homogeneity. The prepared samples annealed at 360^{o}C for 4 hours to release any residual stresses. Finally, the samples cooled to room temperature by shutting off the power of the furnace. After that, the obtained circular samples with thickness ranges between 0.97-1.73 mm were polished with high emery paper to prepare them for the measurements. X-ray diffraction measurements were carried out to check the amorphous nature of the prepared samples. Density was measured using normal Archimedes method and many structural parameters were estimated. The EPR spectra were recorded at room temperature for the prepared samples. Optical spectra were measured in UV-Visible region to study the filtering behavior of the present samples.

RESULTS AND DISCUSSION

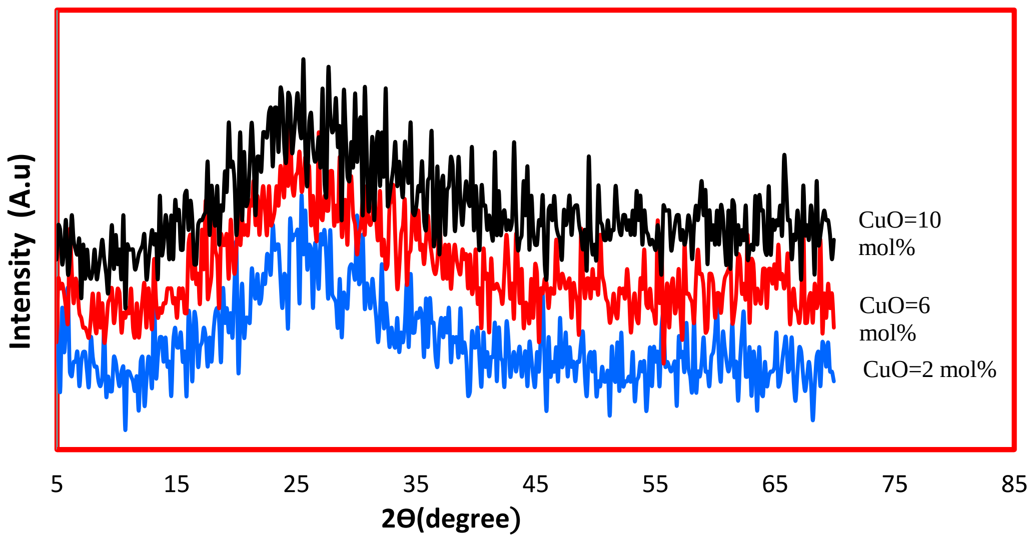

Figure 1: X-Ray diffraction patterns of the investigated samples

Figure (1) shows the X-ray diffraction (XRD) pattern, at room temperature, of the prepared samples. The broad halo which centered at $2\Theta=25^{o}$ for all the investigated samples reflect the characteristics of amorphous structure.

Effect of copper content on the glass transition temperature Tg for the investigated samples is shown in Figure (2). The increase in Tg could be attributed to increase in density of the sample with the increase of the copper content.

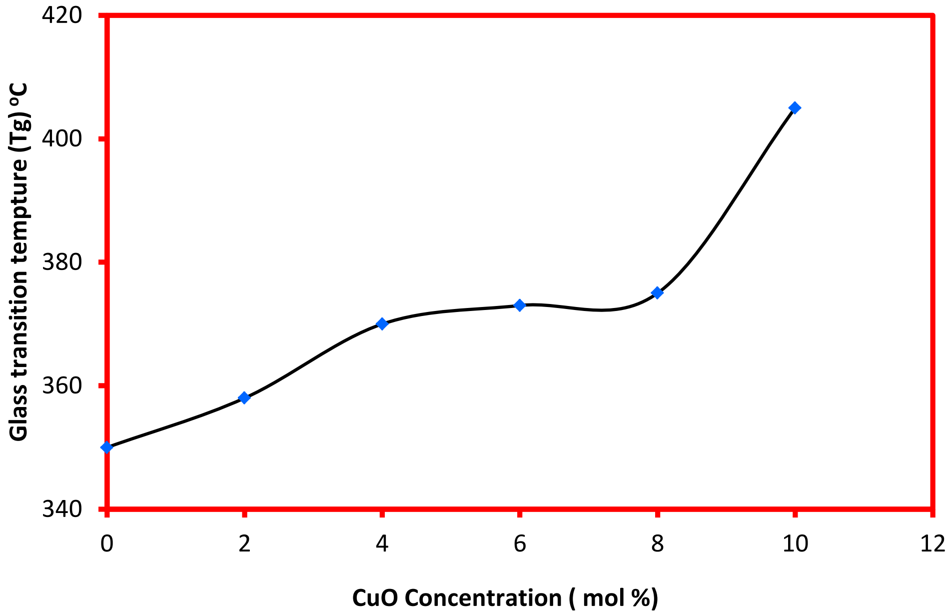

Figure 2: Variation of transition temperature with CuO content

Density (ρ) of the samples was measured by Archimedes principle using toluene as the immersion liquid. The molar volume was deduced based on the density data [17-20]. Figure (3) shows the measured densities and the estimated molar volume of the investigated glasses. With addition of CuO the density of mixed glasses is found to almost monotonic increase, such increase is attributed to the higher molecular weight of CuO compared to Na2O. The behavior of molar volume (MV) indicates that initially, at low CuO content, up to 2 mol %, no non-bridging oxygen was created in the glass network so molar volume decreases. However, beyond 2 mol%, copper leads to enhance the formation of non-bridging oxygen in the investigated system. Hence, the loose packing increases and then the molar volume increase.

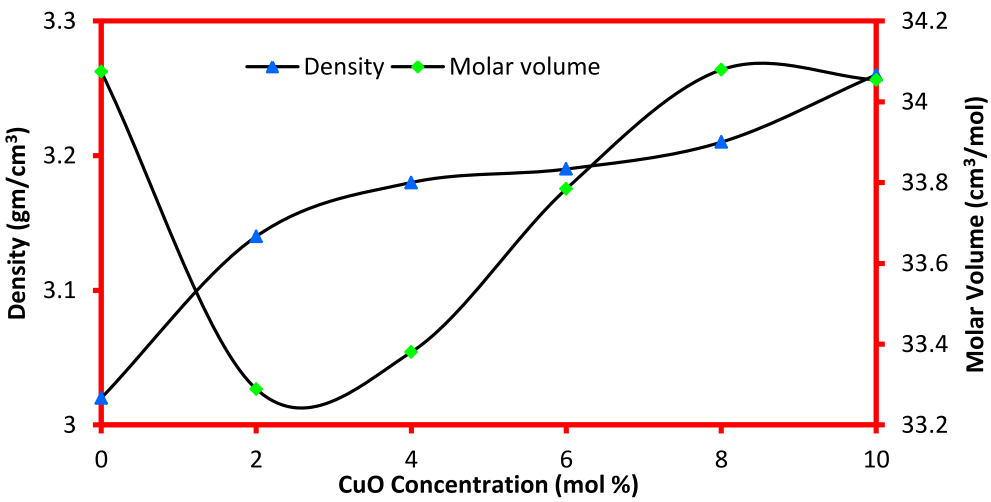

Figure 3: Density and molar volume as function in CuO content

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Helpful structural parameters such as, copper ion concentration (Ncu), interionic distance (ri), polaron radius (rp), field strength (F), oxygen packing density, oxygen molar volume, and number of boned per unit volume (n_b), which are very useful to describe the influence of copper ion on the structural units and transport properties of the glasses, are evaluated using the conventional formulae [20-24] and listed in table (1).

Table 1: Structural properties of the studied glasses

	CuO=0%	CuO =2%	CuO =4%	CuO =6%	CuO =8%	CuO =10%
N_{Cu} x 10^{22} (ions/cm^3)	0	3.619	7.217	10.697	14.139	17.687
r_i (Å)	0	3.023	2.402	2.107	1.92	1.781
r_p (Å)	0	1.218	0.968	0.849	0.7734	0.7178
OPD(g-atom/liter)	83.053	84.413	83.582	81.991	80.695	80.167
V_O (cm^3/mol)	19.811	19.354	19.407	19.642	19.813	19.799
F (cm^{-2})	0	5.470	8.667	11.267	13.57	15.754
n_b (cm^{-3})	6.54	6.694	6.676	6.596	6.539	6.544

The EPR spectra of pure and doped sample are shown in figure (4). No EPR resonance signal was detected in the spectra for free copper sample indicating the absence of paramagnetic centers in the prepared glasses. From the above arguments it clears that the observed EPR signal is only due to Cu^{2+} ($3d^9$) ions.

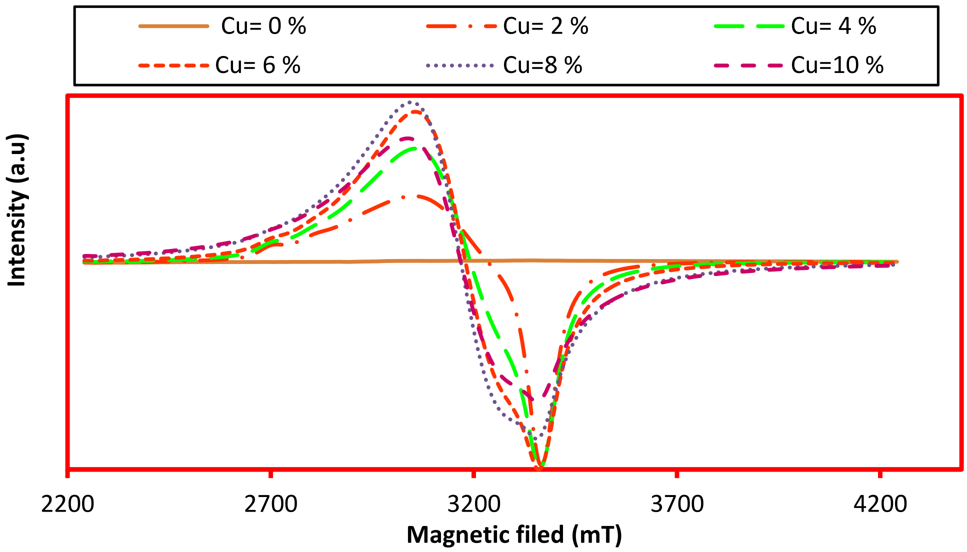

Figure 4: EPR spectra of obtained glass samples

From the spectra analysis, the spin Hamiltonian parameters are estimated and listed in table (2). The obtained values of parallel ($g_\parallel$) and perpendicular ($g_\perp$) component of 'g tensor and parallel ($A_\parallel$) and perpendicular ($A_\perp$) of hyperfine coupling tensor (A) reveal that $g_\parallel > g_\perp$ and $A_\parallel > A_\perp$, these values reveal that Cu^{+2} is in octahedral coordination with tetrahedral distortion. The obtained values suggest that Cu^{+2} is acted upon by compressed tetrahedral field. In such a case are should expect admixing of P states with (x^2-y^2) due to compression leading to increase of $g_\perp$ i.e. $g_\perp > g_\parallel$.

Table 2: Represent the values of EPR parameters

Cu Content	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$\Delta g_\parallel/\Delta g_\perp$
0	0	0	0	0	0
2	2.0845	2.270	597.3	564.9	0.918
4	2.145	2.273	512.6	351.4	0.945
6	2.162	2.268	498.6	347.3	0.953
8	2.182	2.270	460.8	351.4	0.961
10	2.189	2.284	454.1	345	0.958

The prepared base glass has been appeared purely colorless and then it becomes light green after that it is darkened at 10 mol% of CuO. The optical transmittance spectra of the studied glasses were recorded, at room temperature, for sake study the transmission/absorption band of the prepared glasses. It was found that all copper doped samples follow one common pattern where a well-defined transmitted band is observed (figure 5) i.e. all copper doped samples exhibit band pass filters behavior. The transmission bands are observed in the wavelength range 300-700 nm. The transmission spectrum of zero copper sample has not been shown any peak confirming that the radical effect of copper as a band pass filter.

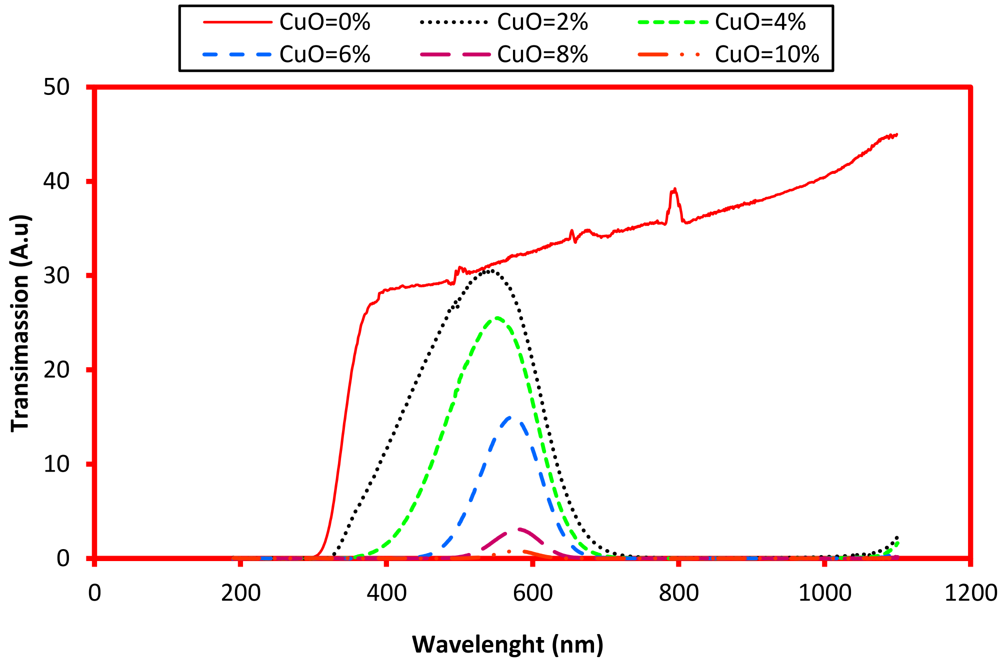

Figure 5: Optical transmittance of the investigated samples

The filter is usually characterized by three main features; namely the shift of central wavelength of maximum transmission λo, the bandwidth and the height of optical band, and the area of the band. In this regard, previously mentioned parameters were estimated and discussed. Figure (6) show the dependence of width and height of optical band on copper content. The data decrease by increasing copper content up to 10%. In other words, the increase of copper content improves the quality of the filter.

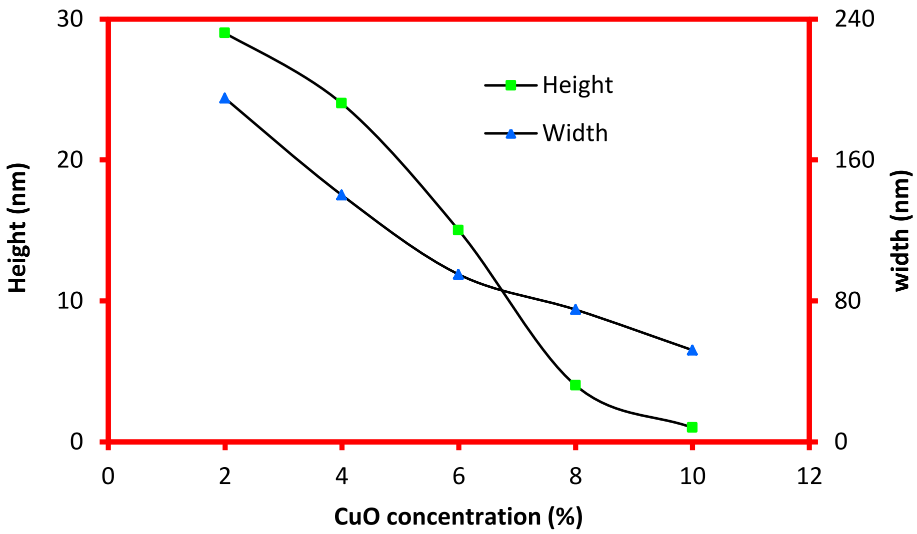

Figure 6: Relation between the height and width against CuO content

The variation of the wavelength of maximum transmission of different copper content for the present optical filter was shown in Figure (7). The obtained data reveal that λo increases almost linearly with increasing CuO content up to 8 mol%. Then it shows tendency to decreases up 10 mol%. This increase is attributed to the structural changes which will arise due to different site occupations, i.e., the increase Cu^{+2} ions interstitial in the glass network on the expense of Cu^{+1}.

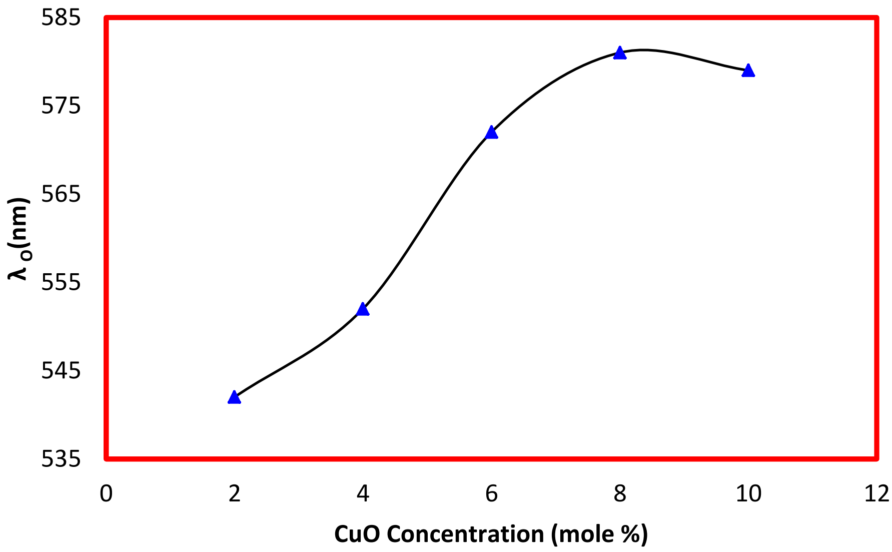

Figure 7: The wavelength of maximum transmission λ_o as a function of CuO content

The effect of CuO content on optical band gap and refractive index was shown in figure (8). The optical band gap (E_g) has been determined using the plot $(\alpha h\nu)^{1/2}$ versus the visible light photon energy ($h\nu$), from the linear extrapolation to zero ordinate the values of E_g was calculated [25-27]. Refractive index corresponding to optical band gap of the studied glasses was calculated using the following relation [25-27].

$$\frac{n^2-1}{n^2+1} = 1 - \sqrt{E_g/20} \qquad (1)$$

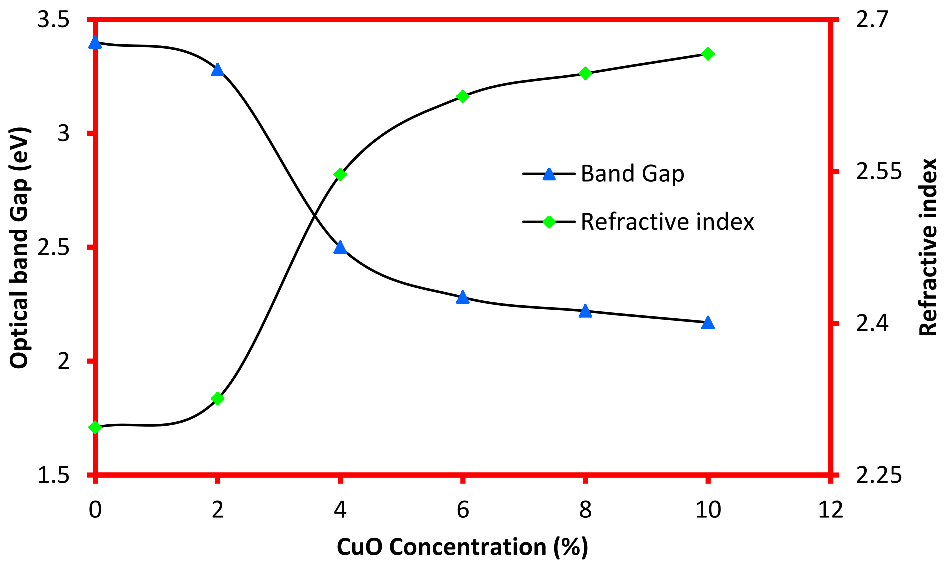

Figure 8: Relation between optical band gap and refractive index against CuO content

The optical band gap decrease and conversely refractive index increase with CuO content increase. A decrease of optical band gap to lower energies and increase of refractive index with an increase of copper oxide content were probably related to the progressive increase in the concentration of non-bridging oxygen, where this increase in turn gives the rise to a possible decrease in the bridging (P–O–P) oxygen. The NBOs cause an increase in the degree of localization of electrons thereby increasing the donor center in glass matrix. The higher concentration of donor center decreases the optical band gap and increases the refractive index, and shifts the absorption edge towards higher wavelength.

Generally, an increases in Urbach energy, which obtained from the reciprocal of the graph slope of logarithm of absorption coefficient ($\ln \alpha$) versus the photon energy ($h\nu$) [25-27]. It is increases the defects in glass network. But on the contrary, a decrease in the Urbach energy with copper content was found, as shown in Figure (9), which confirms that the number of defects decreases with copper content.

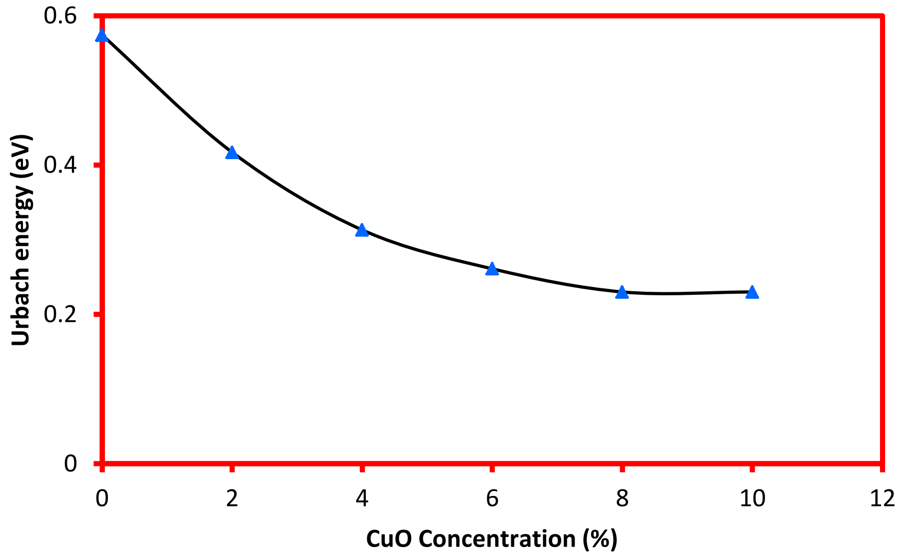

Figure 9: The variation of Urbach energy with CuO content

The values of molar refraction (R_M), molar electronic polarizability (α_m), and electronic polarizability of oxide ions (${\alpha_0}^{2-}$) were deduced using the equations [25-27] and listed in table (3).

Molar polarizability and electronic polarizability decreases initially up to 2 mol% then it starts increasing up to 10 mol% of CuO. This indicates that an addition of CuO content into the glass network breaks bridging P–O–P bonds and new non-bridging bonds formed. The non-bridging bonds have greater ionic character and lower bond energies. The metallization parameter values of the present glasses are found to be less than one. Hence, the present glasses systems with their metallization parameter values should exhibit insulating nature. These glass samples are poor electronic conductors and have shown ionic conductivity. The optical basicity of Na_2O is higher than that of CuO therefore basicity decreases with decrease of CuO in the host glass.

Table 3: Theoretical optical basicity (Λ_{Th}), Dielectric constant (ε), Metallization criterion (M), Molar electronic polarizability (α_m), and Electronic polarizability of oxide ion (${\alpha_0}^{2-}(n)$) of the investigated glasses

	ε	α_mx10^{24}	${\alpha_0}^{2-}(n)$	M	Λ_{Th}
Cu_2O=0%	5.276	7.948	2.906	0.412	0.700
Cu_2O=2%	5.408	7.242	2.641	0.445	0.695
Cu_2O=4%	6.485	8.545	3.125	0.339	0.690
Cu_2O=6%	6.885	8.855	3.239	0.315	0.685
Cu_2O=8%	7.005	8.991	3.288	0.302	0.680
Cu_2O=10%	7.108	9.042	3.305	0.290	0.675

CONCLUSION

Optical band pass filter of copper doped glasses was synthesized in the present study. The undoped glass was found to be colorless and transparent while the doped glasses changed from light green to dark

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green as the CuO content increased. The absence of sharp peaks in the X-ray diffraction pattern indicates the amorphous nature of prepared glasses. Density and glass transition temperature values are increased with the copper oxide increase while the molar volume decreases up to 2 mol % and increase again up to 10 mol% of copper oxide. The absorption/ transmission peak in optical spectra show the band pass filter behaving of the present glasses. Both width and height of confirm the optical band pass filter of the present glasses. The ESR spectral indicate that Cu^{+2} is in octahedral coordination with tetrahedral distortion.

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