Study of the Optical Properties for $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO Glass System

S. Al Ariki** [(1)]**, Y. H. Elbashar**[(2)]**, and A. El-Korashy** [(3)]***

[(1)]Physics Department, Faculty of Education, Thamar University, Tamar, Yemen
[(2)]Faculty of science Al-Azhar University, Physics Department, Nasr City, Cairo, Egypt
[(3)] British university in Egypt (BUE), Basic science Department, Faculty of Engineering, ElShorouk City, Cairo, Egypt
El-Korashy@Bue.edu.eg

Homogeneous glasses samples of compositions $42P_2O_5$-40ZnO-(16-x) K_2O-$2Bi_2O_3$-xCuO (where x = 1, 2 and 3 %) prepared by conventional a melt-quenched technique under controlled conditions. XRD study shows that the prepared samples are non-crystalline. The measured spectral transmittance and reflectance of the glasses were recorded in the range (200 – 900 nm). The optical band gap energy for glasses estimated from absorption data using the Mott and Davis relation. It is found that the band gap increases by increasing x. The mechanism of optical absorption found to be indirect. The band tail width also estimated and found to lay in the acceptable rang The Refractive index, which is measured and calculated. The absorption coefficient α(λ),extinction coefficient k(λ) were also estimated. The structure of the $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO glass systems was investigated by X-ray diffraction (XRD).

1. Introduction:

A host of borate rich glasses containing alkaline earth oxides along with ZnO, PbO, TeO_2 and Bi_2O_3 as glass modifiers are optimistic materials for their probable applications in the fields of optical communications (optical fibers), laser hosts, optical filters, γ-ray absorbers, photonic devices etc [1-5].

The changes in structural, physical, optical and electrical properties of various alkaline earth oxide glasses were reported by many researchers. Glasses containing heavy metal oxides exhibit good chemical durability and large refractive indices than conventional borosilicate glasses [6-13]. The metal oxides like ZnO, TeO_2, PbO and Bi_2O_3 .etc are well known conditional glass modifiers. Glasses containing these metal oxides exhibit good non-linear optical properties [4]. Metal oxides like PbO, ZnO behave as glass network formers (GNF) and also as glass network modifiers (GNM). Optical properties depend on role of the modeling oxide. Systematic study of the optical properties of glasses, including borate glasses is available in the literature. The present study is concerned with the study of the structural and optical properties of glass with a composition $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO (where x = 1, 2 and 3 %).

2. Experimental:

Glass samples $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO were prepared by the melt-quenching technique . The glassy sample weighted by using electric balance mixed well using an agate mortar. Then it was transferred to porcelain crucibles and was melted using an electric muffle furnace that was heated and exacted at temperature of 1200 C^0 for four hour. Melts were shacked from time to time to get complete mixing and homogeneity, then the melts were poured on stainless steel plate inside furnace with temperature~300°C for 30min and thin the furnace turned off, the glass samples remained in the furnace 24h as an annealing technique. The optical measurements for the glass sample, the transmittance T and reflectance R were determined using a computerized double beam spectrophotometer (Shimadzu UV-2101 PC). The measurements were carried out over wavelength rang of (200 to 900 nm). The amorphous nature of the samples was proved by X-ray diffraction. The X-ray diffractometer, Philips type 1710. The X-ray pattern was run with Cu target and graphite monochromator (λ=0.154 nm) at 40 kV and 30 mA, with a scanning speed of 3.76 deg/min. All the diffractograms were carried out at room temperature.

3. Theoretical Background

3.1. Absorption Coefficient α

The absorption coefficient α was calculated according to the relation:

$$T = (1- R)2\exp(-\alpha d) \qquad (1)$$

where T transmittance, R reflectance, d is the thickness and α absorption coefficient;

$$\alpha=\log[((1-R)^2/2T)+(1-R)^4/(4T^2+R^2)]^{1/2} \qquad (2)$$

3.2. Refractive Index n

A way from absorption, the refractive index n (λ) is given by:

$$n=[(1+R)/(1-R)+4R/((1-R)^2-k^2)]^{1/2} \quad (3)$$

where k is extinction coefficient

3.3. Extinction Coefficient k

When the absorption coefficient α is known, the extinction coefficient k can be found from the relation:

$$K= \alpha \lambda/4\pi \quad (4)$$

The real and imaginary parts of dielectric constants ε_1 and ε_2 can be calculated if the refractive index N (N=n+ik) are known using the relations:

$\varepsilon_1=(n^2-k^2)$ and $\varepsilon_2=2nk$

3.4. Urbach energy and Optical Energy gap

It is well known that the shape of the fundamental absorption edge in the exponential (Urbach) region yields information on the disorder effects, with incident photon energy less than gap, the increase in absorption coefficient is followed with an exponential decay of density of states of the localized into the gap and the absorption edge is known as Urbach edge. The lake of crystalline long –range order in amorphous/glassy materials is associated with a tailing of density of states. At lower values of the absorption coefficient ($1\ cm^{-1} < \alpha < 10^4 cm^{-1}$), the extent of the exponential tail of the absorption edge characterized by the Urbach energy is given by:

$$\alpha(\nu) = B \exp(h\nu / E_{tail}) \quad (5)$$

where $\alpha(\nu)$ is the absorption coefficient, B is constant and $h\nu$ is the photon energy, E_{tail} an energy interpreted as the width of the tails of the localized states in the normally for bidden band gap and which is also known as Urbach energy of the material. The origin of the exponential part in Eq.(5) arises from electronic transitions between localized states where the density of these states exponentially depends on energy. Davis and Mott [14] suggested that $\alpha(\nu)$, for indirect transition is given by:

$$\alpha(\nu) = C (h\nu - E_{opt})^2/h\upsilon \quad (6)$$

C is a constant and E_{opt} is the optical energy gap of the glass.

4. Result and Discussion:

4.1. X- Ray Diffraction:

The amorphous nature of the prepared glass samples was firstly examined by X-Ray diffraction (XRD) at room temperature. Fig.(1) shows XRD pattern of the prepared glasses. The XRD obtained pattern shows no sharp peaks indicating the non-crystalline nature of the prepared glasses[15-16].

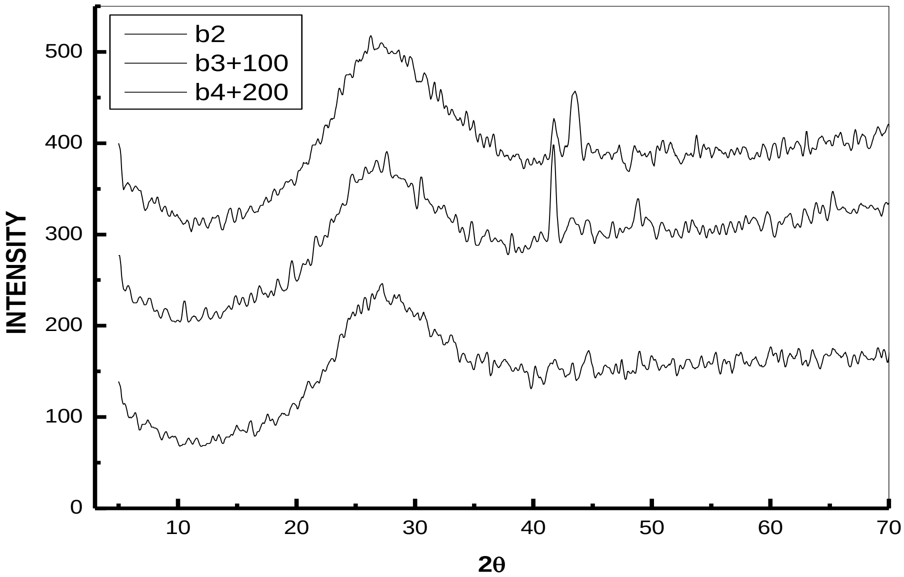

Fig. (1): X-ray diffraction for glass samples

The spectral dependence (in the wavelength range of (200 – 900 nm) of transmittance, T, and reflectance, R, for $42P_2O_5$-40ZnO-(16-x)K_2O-2Bi_2O_3-xCuO are given in Fig. (2,3). The obtained data were used to estimate the real and imaginary parts of dielectric constants ε_1 and ε_2 are listed in Table (1). The transmittance shows a maximum at~500nm for all samples the shape and width of which depend on the composite.

Table (1): Values of extinction coefficient k, refractive index n, real ε_1 and imaginary ε_2 parts at λ = 535 nm. Tauc energy gap E_g, Urbach parameter E_{till}

$42P_2O_5$-40ZnO-(16-x)K_2O-2Bi_2O_3-xCuO		
Cu_2O Compo-sition (mol%)	E_{till} (ev)	E_g (ev)
1	0.42	2.53
2	0.34	2.45
3	1.60	2.33

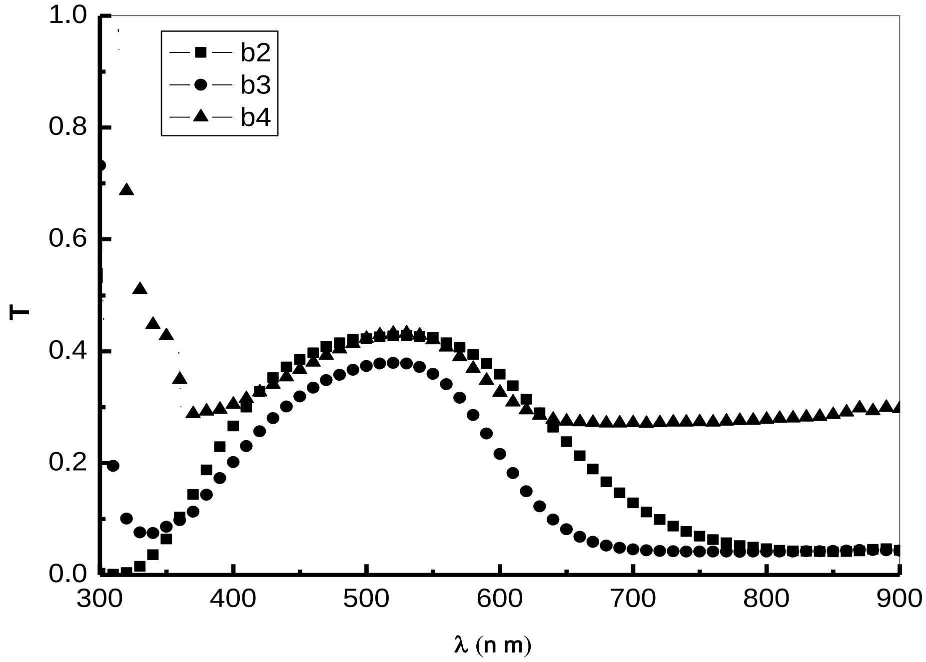

Fig. (2): Optical transmission T of $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO (where x = 1, 2 and 3 %) glasses

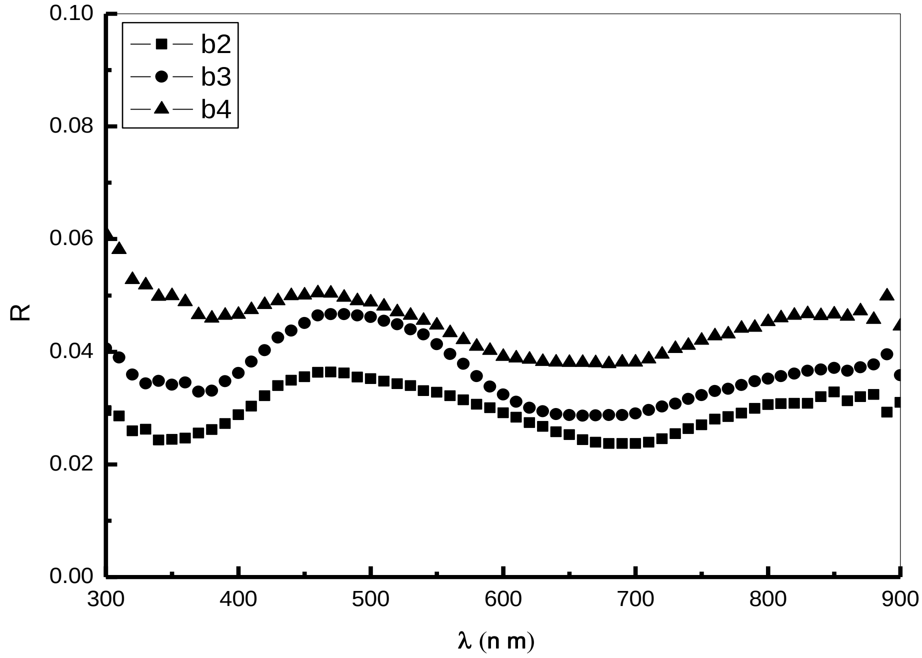

Fig. (3): Optical spectra reflectance R of $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO (where x = 1, 2 and 3 %) glasses

Figure (4) correspond to plots of (ln α) as a function of incident hν for the different compositions of the $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO glasses. The values of Urbach Etill were calculated by fitting the linear region of Fig.(4) by the method of least squares to the straight-line equation 5. As listed in Table (1). The obtained data reveal the band tail width decreases by increasing Cu content. In other words the addition of Cu reduces the degree of disorder.

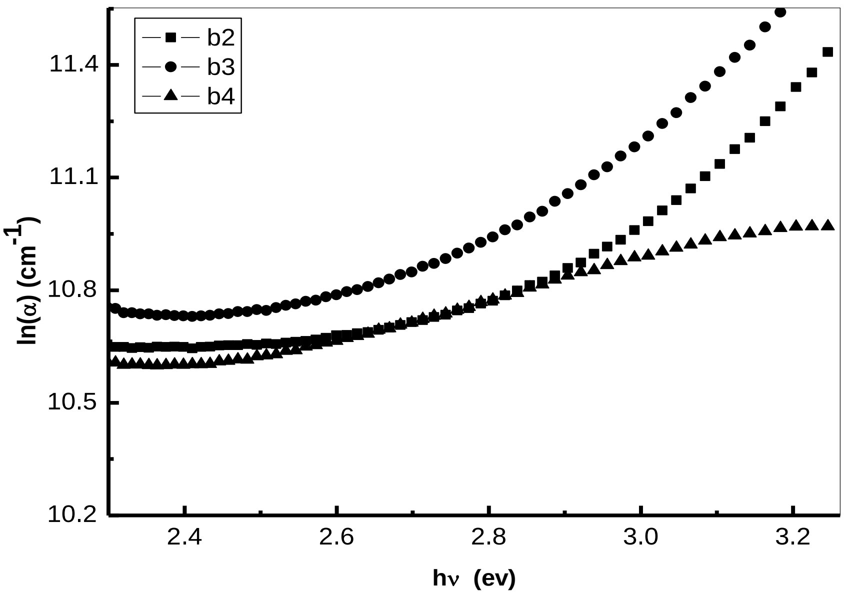

Fig. (4): The dependence of the absorption coefficient on the photon energy of $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO glass.

It is clear from Table (1) that the values of E_g of the glass samples decrease by increasing in Cu_2O content. It can be assumed that, as the cation concentration increases, the bridging oxygen (BO) develops bonds with Cu_2O, which in turn leads to the gradual breakdown of the glass network. The relation between $(\alpha\, h\nu)^{1/2}$ and the photon energy $h\nu$ (eV) was obtained and given in Fig. (5). The extrapolation of the straight line portion in Fig. (5) to cut the energy axis(x-axis) to zero absorption in the $(\alpha\, h\nu)^{1/2}$ versus $h\nu$ plot gives the optical energy gap Eg (eV). The values of Eg are given in Table1. It is clear from the table and Fig. (6) that the values of Eg of $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO glass samples decreased following an increase in Cu_2O content.

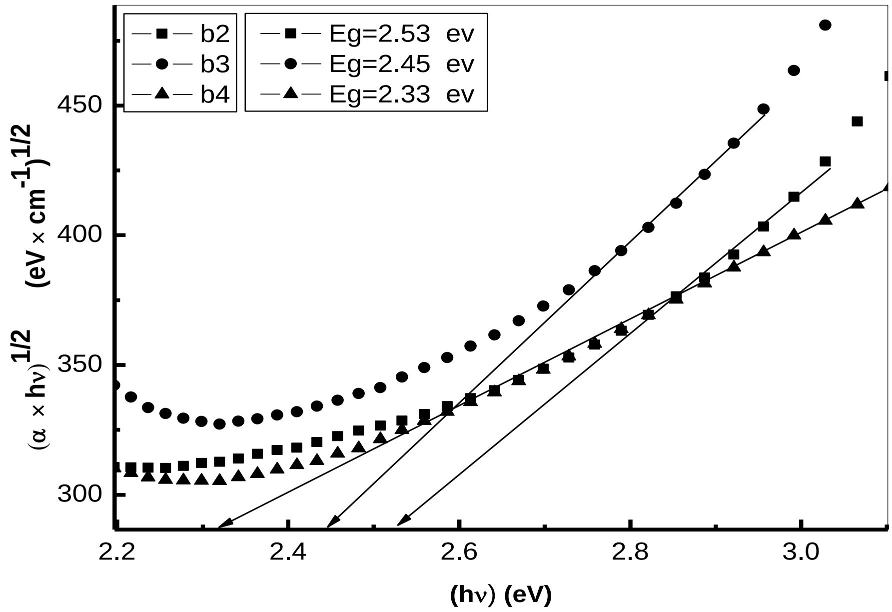

Fig. (5): $(\alpha h\nu)^{1/2}$ on the photon energy of $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO glass.

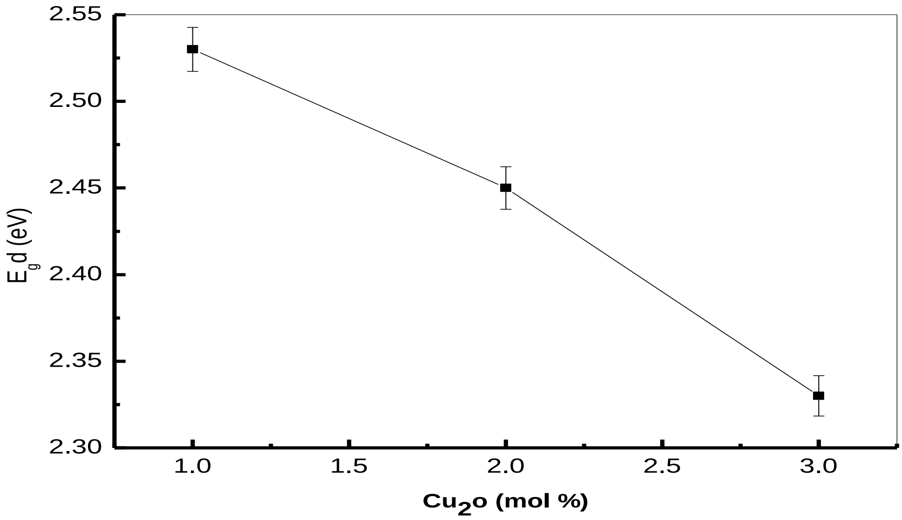

Fig. (6): The optical energy gap E_g versus Cu_2O (mol%) samples of $42P_2O_5$-40ZnO-(16-x)K_2O-$2Bi_2O_3$-xCuO glass.

In the present investigation, the decrease of E_g to lower energies with increases in Cu_2O content is probably related to the progressive increase in the concentration of non-bridging oxygen (NBO) [17].

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