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Structural and spectroscopic analyses of copper doped P_2O_5-ZnO-K_2O-Bi_2O_3 glasses

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Abstract

Homogeneous glass samples with different compositions 42 (P_2O_5)·40 (ZnO)·(16 –x)(K_2O)·2 (Bi_2O_3)·x(Cu_2O) (where x = 1, 2 and 3 mol%) were prepared by conventional melt-quenched technique under controlled conditions. The structure of the prepared glass samples was investigated by X-ray diffraction. Optical properties (transmittance and reflectance) of the glasses were measured in the wavelength range 200–900 nm. The optical band gap energy of the investigated glasses with 1, 2 and 3 mol% Cu_2O was estimated from absorption data using the Mott and Davis relation and found to be 2.33, 2.45 and 2.53 eV, respectively. The mechanism of optical absorption was found to be direct. The band tail width was also estimated and found to lay in the acceptable range. Refractive index, absorption coefficient, extinction coefficient and real/imaginary parts of dielectric constants were calculated. Further to this, some theoretical investigation of the spectral problems was carried out. The investigation was based on finite difference method.

Keywords: *copper doped P_2O_5-ZnO-K_2O-Bi_2O_3, UV optical glasses, optical properties*

I. 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 promising materials for their applications in the fields of optical communications (optical fibres), laser hosts, optical filters, γ-ray absorbers, photonic devices etc. [1–11].

The variations 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 larger refractive indices than conventional borosilicate glasses [12–19]. The metal oxides like ZnO, TeO_2, PbO and Bi_2O_3 are well known conditional glass modifiers. The glasses containing these metal oxides give rise to good non-linear optical properties [4]. The metal oxides like PbO and ZnO behave as glass network formers (GNF) and also as glass network modifiers (GNM). The glasses with good optical properties have found important technological applications. Thus, systematic studies of the optical properties of glasses, including borate glasses, are available in the literature. The present work is concerned with the study of the structure and optical properties of glass with a composition 42 (P_2O_5)·40 (ZnO)·(16 –x)(K_2O)·2 (Bi_2O_3)·x(Cu_2O) (where x = 1, 2 and 3 mol%).

II. Experimental

The glass samples with composition 42 (P_2O_5)·40 (ZnO)·(16 –x)(K_2O)·2 (Bi_2O_3)·x(Cu_2O) (where x = 1, 2 and 3 mol%) were prepared by the melt-quenching technique. The notation symbols b2, b3, and b4 were used to notify the different glasses with x = 1, 2 and 3 mol% Cu_2O, respectively. Precursor powders (ZnO, $(NH_4)H_2PO_4$, K_2CO_3, Bi_2O_3 and Cu_2O) were weighted by using electric balance, mixed well using an agate mortar and transferred to porcelain crucibles. The samples were melted using an electric muffle furnace that was heated at temperature of 1200 °C for four hours. The melts were shaken from time to time to get complete mixing and homogeneity. Finally, the melts were poured on stainless steel plate inside furnace with temperature equal to 300 °C for 30 min. The furnace was then turned off and the glass samples were left in it for next 24 h.

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The amorphous nature of the sample was proved by X-ray diffraction (Bruker AXS D8 Advance Diffractometer) and all XRD measurements were carried out at room temperature. The optical properties of the glass samples, the transmittance (T) and reflectance R), were measured over a wide wavelength range, from 200 to 900 nm, using a computerized double beam spectrophotometer (Shimadzu UV-2101 PC). Some other important optical properties were calculated from the obtained data.

III. Theoretical background

3.1. Absorption coefficient

The absorption coefficient (α) can be calculated from the relation [20,21]:

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

where T is transmittance, R reflectance, d thickness and α absorption coefficient [20,21]:

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

3.2. Refractive index

In addition to absorption, there is another important optical property, such as refractive index $n(\lambda)$, which can be calculated by [20,21]:

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

where k is extinction coefficient.

3.3. Extinction coefficient

When the absorption coefficient (α) is known, the extinction coefficient (k) can be found from the relation [20,21]:

$$k = \frac{\alpha\lambda}{4\pi} \tag{4}$$

The real and imaginary parts of dielectric constants ε_1 and ε_2 can also be calculated if the refractive index (n) is known using the following relation:

$$\varepsilon_1 = (n^2 - k^2) \text{ and } \varepsilon_2 = 2nk \tag{5}$$

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 lower than the band gap. The increase in absorption coefficient follows an exponential decay of density of the localized states into the band gap and the absorption edge is known as the 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 ($1\,\text{cm}^{-1} < \alpha < 10^4\,\text{cm}^{-1}$), the extent of the exponential tail of the absorption edge characterized by the Urbach energy is given by:

$$\alpha(\nu) = B \exp\left(\frac{h\nu}{E_{tail}}\right) \tag{6}$$

where $\alpha(\nu)$ is the absorption coefficient, B constant and $h\nu$ the photon energy. E_{tail} is an energy interpreted as the width of the tails of the localized states in the normally forbidden band gap and which is also known as the Urbach energy of a material. The origin of the exponential part in Eq. 6 arises from electronic transitions between localized states where the density of these states exponentially depends on energy. Davis and Mott [22] suggested that $\alpha(\nu)$, for direct transition, where the wave vector of the electron is conserved, can be given by:

$$\alpha(\nu) = \frac{C(h\nu - E_{opt})^2}{h\nu} \tag{7}$$

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

IV. Results and discussion

4.1. X-ray diffraction

The amorphous nature of the prepared glass samples was firstly examined by X-ray diffraction (XRD)

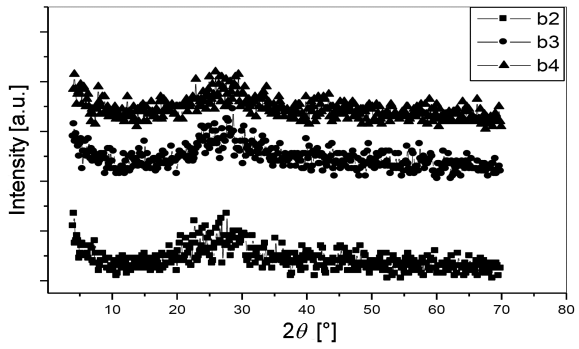

Figure 1. X-ray diffraction of glass samples

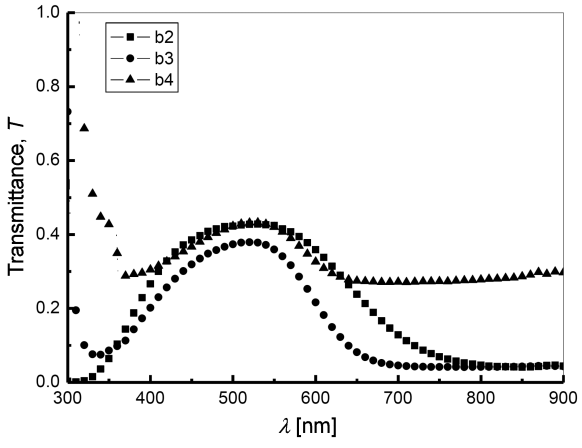

Figure 2. Transmission spectra of glass samples b2, b3 and b4 with 1, 2 and 3 mol% Cu_2O, respectively

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

CuO_2 content [mol%]	T	R	$\alpha \times 10^4$	$\ln(\alpha)$	k	n	ε_1	ε_2	E_{till} [eV]	E_g [eV]
1	0.42	0.03	4.21	10.64	0.179	1.43	2.01	0.51	0.42	2.53
2	0.38	0.04	4.62	10.74	0.197	1.50	2.22	0.59	0.34	2.45
3	0.43	0.05	4.10	10.60	0.171	1.53	2.30	0.52	1.60	2.33

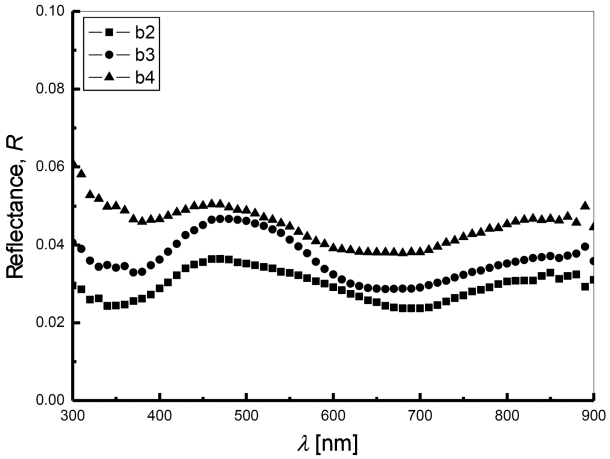

Figure 3. Reflectance spectra of glass samples b2, b3 and b4 with 1, 2 and 3 mol% Cu_2O, respectively

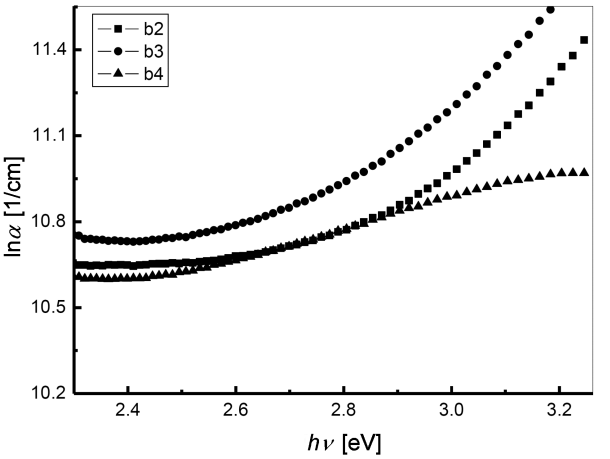

Figure 4. Dependence of the absorption coefficient on the photon energy of glass samples b2, b3 and b4 with 1, 2 and 3 mol% Cu_2O, respectively

at room temperature. Figure 1 shows XRD pattern of the prepared glasses with different Cu_2O concentration. It is obvious that there are no sharp peaks indicating the non-crystalline nature of the prepared glasses [21–23].

Transmittance (T) and reflectance (R) in the wavelength range from 200 to 900 nm of the prepared glasses are given in Figs. 2 and 3, respectively. It is quite clear that the decrease in transmittance can be observed at larger wavelengths (λ > 535 nm), indicating on the region with high absorption.

In accordance with the measured transmittance and reflectance at λ = 535 nm, the following values were calculated: refractive index (n), extinction coefficient (k), absorption coefficient (α), real and imaginary parts of dielectric constants (ε_1 and ε_2) that are listed in Table 1.

Figure 4 corresponds to the plots of ($\ln \alpha$) as a function of incident photon energy $h\nu$ for the different compositions of the prepared glasses. The values of Urbach (E_{till}) were calculated by fitting the linear region of the curves presented in Fig. 4 by the method of least squares to the straight-line (Eq. 6). The obtained values are listed in Table 1. The probable error for E_{till} was also estimated. For the prepared glasses E_{till} increases with the increase of Cu_2O contents. It has been suggested that the value of E_{till} is associated with structural disordering in many amorphous solid. Thus, the trend of E_{till} is consistent with the increase in structural disordering caused by substitution of K_2O with Cu_2O in the obtained glasses.

The relation between $(\alpha h\nu)^{1/2}$ and the photon energy $h\nu$ was obtained and presented in Fig. 5. The extrapolation of the straight line to the zero absorption (the cut of the energy x-axis) in the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot gives the optical energy gap (E_g). The obtained E_g values are given in Table 1. It is clear from Table 1 and Fig. 6 that E_g values of the glass samples decreased with the increase in Cu_2O content.

In the present investigation, the change of E_g towards lower energies with increases in Cu_2O content is probably related to the progressive increase in the concentration of non-bridging oxygen [25]. For the glass containing Cu_2O, E_g was also found to decrease from 2.53 to 2.33 eV with the increase of Cu_2O content from 1 to 3 mol%, respectively. These values are comparable with that reported in literature [26,27].

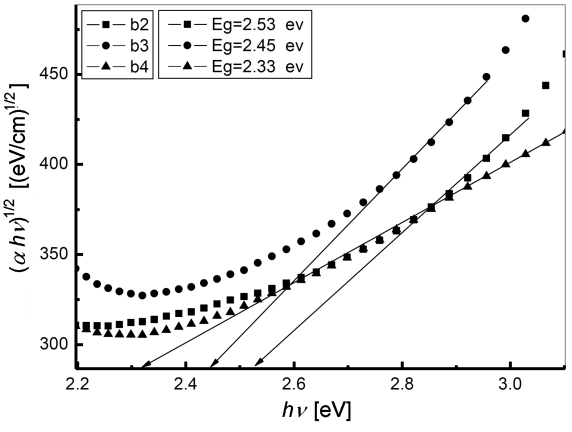

Figure 5. Dependence of $(\alpha h\nu)^{1/2}$ on the photon energy of glass samples b2, b3 and b4 with 1, 2 and 3 mol% Cu_2O, respectively

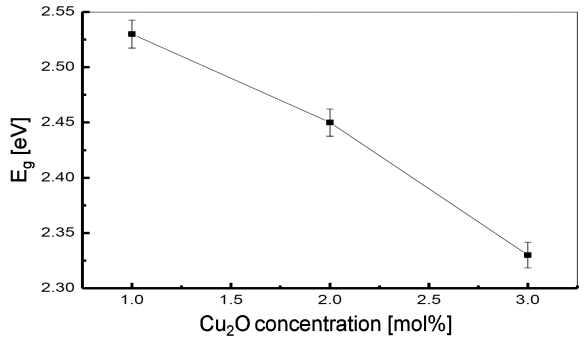

Figure 6. The optical energy gap E_g versus Cu_2O content in glass samples

V. Conclusions

The glass sample with composition corresponding to 42 (P_2O_5)·40 (ZnO)·$(16-x)(K_2O)$·2 (Bi_2O_3)·$x(Cu_2O)$ (where x = 1, 2 and 3 mol%) was prepared by the melt-quenching technique. Transmittance and reflectance of the prepared glasses were measured in the wavelength range 200–900 nm. The refractive index (n) increases was calculated and it rises with the increase of Cu_2O content. The optical band gap and Urbach energy were found to be dependent on Cu_2O content. Thus, the optical band gap (E_g) of the glasses containing 1, 2 and 3 mol% Cu_2O increases from 2.33 to 2.53 eV, whereas, for the same glasses the values of the Urbach energy (E_{till}) were in the range from 0.42 to 1.60 eV.

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