IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 4 Issue 7, July 2017
ISSN (Online) 2348 – 7968 | Impact Factor (2016) – 5.264
www.ijiset.com

Optical and Dielectric Properties OF $CuO-B_2O_3$ Glasses

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Abstract :

The optical adsorption and transmission spectra in (UV-VIS) have been recorded in the wavelength range 350-800 nm for different compositions of $CuO-B_2O_2$ glasses. The various optical properties such as absorption coefficient (α'), optical energy gap (E_{opt}), refractive index (n_o), optical dielectric constant (ε'_∞), measure of extent of band tailing (ΔE), constant (β) and ratio of carrier concentration to the effective mass (N/m*) for different glasses have been reported. The effects of composition of glasses on these parameters have been discussed. It has been indicated that a small modification of the glasses can lead to an important change in all the optical properties. These results are interesting showing non linear behaviour for all these parameters investigated. The optical parameters are found to be almost the same for different glasses in the same family. The values of dielectric constant at different temperature (313-573K) at a constant frequency of 1 KHz are reported. It is observed that the dielectric constant is independent of temperature upto certain temperature range, but after that the dielectric constant increases with temperature rapidly. The dielectric constant of all the samples studied is found to be composition dependent. In the glasses studied dipole relaxation phenomenon is observed.

Keywords : $CuO-B_2O_3$ glasses, Optical properties, non-linear behavior, Dielectric constant

1. Introduction :

In the recent years, the interest in the study of electrical, optical and structural properties of glassy semiconductors has increased [1] considerably. The variation of optical density of a few induced absorption bands in some sodium aluminium borate glasses has been studied by varying the radiation doses of gamma rays and cerium content by Hussein et al [2]. On the basis of the optical absorbance and transmittance measured at normal incidence of light in wavelength range 380-780 nm. some optical parameters of glassy Ge_{20} Te_{80-x} Se_x thin films were determined by Shokr et al [3]. Optical and electro-optical properties of $Ga_2O_3-PbO-Bi_2O_3$ glasses were studied by Janewioz et al [4]. Anomalous behaviour in the composition dependence of the photoacoustic properties of Si-As-Te glasses has been studied by Srinivasan et al [5]. The frequency dependent optical and dielectric properties of binary semiconducting glasses in the system $60V_2O_5$-(40-x)TeO_2-XPbO were measured as a function of lead content by Memon et al [6]. Studies on the optical properties and structure for $SiO_2-TiO_2-PbO_2$ system glass were reported by Zhu et al [7]. A structural model of the glass network was proposed. Optical absorption, Infrared, differential thermal analysis and density studies were conducted on the glass system (80-x) TeO_2-$XNiO_2$-$20B_2O_3$ by Khaled et al [8]. The divalent state of Ni has been confirmed by IR spectra. The optical properties of the $CaO-Al_2O_3-B_2O_3$ glasses are reported by Kudesia et al [9]. Linear and non-linear optical properties of chalcogenide glass were investigated by Hajita et al [10]. Very little work appears to have been done on the optical properties of oxide glasses. Therefore it has been decided to study the optical parameters of $CuO-B_2O_3$ glasses. The intention to study the optical properties of these glasses by UV-VIS spectra it to investigate the existence of localized states near band edge. Mandal et al [13] have reported the dielectric behaviour of glass system $BaO-PbO-TiO_2-B_2O_3-SiO_2$. The electric relaxation study of $V_2O_5-B_2O_3$ glasses has been done by singh et al [14].

2. Experimental Details :

2.1 Preparation of glass samples - The glass samples under investigation were prepared in a fireclay crucible. The muffle furnace used was of Heatreat co. Ltd. (India) operating on 230 volts AC reaching upto a maximum temperature of 1500 + 10°C. Glasses were prepared from AR grade chemicals. Homogeneous mixture of an appropriate amounts of CuO and B_2O_3 (mol%) in powder form was prepared. Then, it was transferred to fire-clay crucible, which was subjected to melting temperature (1300°C). The duration of melting was generally two hours. The homogenized molten glass was cast in steel disc of diameter 2 cm and thickness 0.7 cm. Samples were quenched at 200°C and obtained in glass state by sudden quenching method. All the samples were annealed at 350°C for two hours. The X-ray diffractograms of all the glass samples are determined at regional sophisticated instrumentation center, Nagpur. The absence of peak in the X-ray spectra confirmed the amorphous nature of the glass samples.

2.2 Dielectric Constant :

The dielectric constant of the glass samples was measured by measuring the capacitance of the samples at constant frequency 1 KHz in the temperature range 313 to 573 K. Digital LCR meter 925, systronics made (India), was used for the measurement of capacitance. The accuracy in the capacitance measurement was ±0.1 pF

3. Theory :

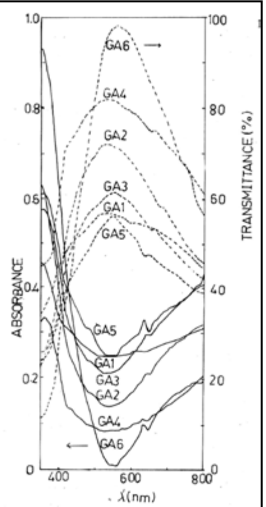

Fig.1 : Spectral dependence of both absorbance and transmittance for six different samples GA_1, GA_2, GA_3, GA_4, GA_5, GA_6.

The absorption 'A' and transmittance 't' of the glass samples were measured by means of CARY –2390 varaian make double beam automatic scanning spectrophotometer (at Regional sophisticated Instrumentation Centre, Madras) in the spectral range 350-800 nm at normal incidence. The glass powder pellet thickness used was approximately 0.05 mm at room temperature. The resolution of the instrument used was 0.1 nm. The optical absorption coefficient α' of the glass samples was calculated from the relation A = α' x d' where d' is the thickness of pellet. The spectral dependence of both A and t on composition of the glasses is shown in figure (1)

The optical absorption coefficient α'(ν) at the given frequency (ν) is given by

$$\alpha'(\nu) = \frac{4\pi\sigma_{min}}{Cn_0\,\Delta E} \cdot \frac{(h\nu - E_{opt})^{\gamma}}{h\nu} \quad \ldots\ldots\ldots\ldots (1)$$

Where σ_{min} is the extrapolated dc-conductivity at $T = \infty$, n_0 is the refractive index, C is the velocity of light, ΔE is the measure of the extent of band tailing, hν is the photon energy, E_{opt} is the optical gap, γ = 2 is a number which characterises the transition process, and

$$\beta = \frac{4\pi\sigma_{min}}{C.n_0\Delta E} \quad \text{is constant}$$

The reflectance R was calculated using the equation

$$t = (1 - R)^2 \exp(-A) \quad \ldots\ldots\ldots\ldots(2)$$

where R is the reflectance, 't' is the transmittance and 'A' is the absorbance.
The relation between optical dielectric constant, ε' and the square of the wavelength λ'^2, is given by

$$\varepsilon' = n^2 = \left[\frac{1+\sqrt{R}}{1-\sqrt{R}}\right] = \varepsilon'_{\infty} - \frac{e^2}{\pi C^2} \cdot \frac{N}{m^*} \cdot \lambda'^2 \quad \ldots\ldots\ldots\ldots (3)$$

where ε' is the dielectric constant, e is the electronic charge and N/m* is the ratio of carrier concentration to the effective mass. By knowing the values of absorbance A reflectance and transmittance and various optical properties were calculated.

4. Results and Discussion:

4.1 Optical Properties

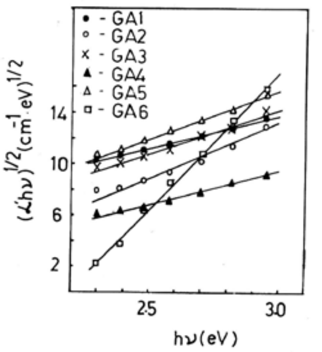

Fig. 2 : Plot of α'hν verses hν for samples GA_1, GA_2, GA_3, GA_4, GA_5, GA_6,

The results regarding the various optical properties such as optical energy gap (E_{opt}) constant β, measure of extent of band tailing (ΔE) mean refractive index n_0 infinitely high frequency dielectric const. ε'_∞ and ratio N/m* for different glasses is listed in table (1).

Figure (2) Shows the plots $(\alpha h\nu)^{1/2}$ versus hν for different compositions of glass samples. The most satisfactory representation is obtained by plotting the quantity $(\alpha h\nu)^{1/2}$as a function of hν. Similar behaviour was also observed by other workers [11]. The observed behaviour suggests forbidden indirect transition for some glassy and amorphous material. The values of optical energy gap E_{opt} obtained from the extrapolation of the linear region and constant β from the slopes of the derived curves.

Table 1 : Variation of optical energy gap (E_{opt}) dielectric constant at infinite freq. (ε'_∞), refractive index (n_o), constant (β), measure of the extent of band tailing (ΔE) and the ratio of carrier concentration to the effective mass (N/m*) with different glass compositions.

Glass No.	Glass composition (mol%)		Optical energy gap E_{opt}(eV)	Constant β ($cm^{-1}eV^{-1/2}$)	Measure of extent of band tailing ΔE(eV)	Mean refractive index n_o	Infinitely high frequency dielectric constant ε'_∞	Ratio of carrier concentrati-on to effective mass N/m* (cm^{-3}) x 10^{21}
	CuO	B_2O_3						
GA1	10	90	0.32	23.04	0.114	2.33	8.6	0.49
GA2	15	85	1.44	77.44	0.044	2.03	8.2	2.33
GA3	20	80	0.85	36.00	0.066	2.30	8.8	2.09
GA4	25	75	1.22	27.04	0.26	1.70	5.0	1.23
GA5	30	70	0.95	57.76	0.105	2.52	11.8	3.07
GA6	35	65	2.20	449.44	0.031	1.93	12.8	5.15

The extrapolated dc electrical conductivity, σ_{min} at t = ∞ is obtained from the plot of logσ versus 1/T (plot not shown). The values obtained for E_{opt} for the six different compositions of glass samples are found to be non-linear. Similar observation are reported in case of As-S, Ge-Se, As-Se and Ag-As systems investigated by Hajto *et al* [10].

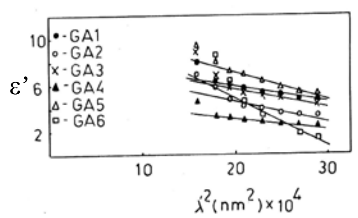

Fig. 3 : Plot of optical dielectric constant ε' verses λ'^2 for six samples GA_1, GA_2, GA_3, GA_4, GA_5, GA_6,

The dielectric constant ε' versus λ'^2 plots shown in Figure (3) are linear, verifying equation (3), Values of ε'_∞ and N/m* determined from the extrapolation of these plots at $\lambda'^2 = 0$ and the values of the ratio of carrier concentration to effective mass are listed in Table 1 as a function of glass composition. The dependence of refractive index and dielectric constant on composition of glasses is rather non-linear and is observed to be similar to other amorphous materials [10]. The values of refractive index n_o are calculated from optical dielectric constant ε' for all the wavelengths of λ'^2. These values are found to be more or less same throughout the wavelength range (350-800 nm). Therefore average values of n_o are reported in this wavelength region. The average value of refractive index n_o shows dependence on CuO composition.

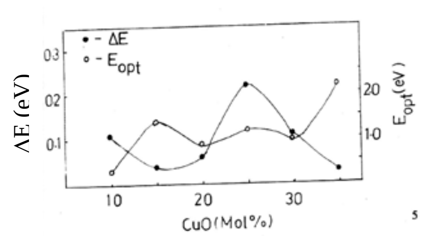

Fig.4 : Plot of optical energy gap E_{opt} and band tailing energy ΔE verses mol% of CuO composition of six different samples

The variation of ΔE, the width of the tail of localised states in the normally forbidden gap against CuO (mol %) is shown in Figure (4). The optical energy gap E_{opt} is found to be minimum for the glass sample having 10 (mol %) of CuO and ΔE for 35 (mol %) of CuO. The decreasing trend of the band tailing energy suggests the presence of sharp localised states in the ratio of carrier concentration to the effective mass. N/m* has been calculated from the slope of the plot ε' versus λ'^2 (Fig.3). The values of N/m* for different glass samples are tabulated in Table 1. It has been observed that the values are found to be of the order of 10^{21} which are in agreement with the values reported by other workers for oxide glasses [12] and calculated by other methods. The value of ΔE shows dip at 15 mol% and peak at 25 mol% of CuO. It is observed that the nature of plot of E_{opt} and ΔE verses composition is opposite to each other. The decreasing trend of the band tailing energy suggests the presence of sharp localized states in the band gap.

The ratio of carrier concentration to the effective mass, N/m* has been calculated from the slope of the plot ε' verses λ'^2

4.2 Dielectric Constant :

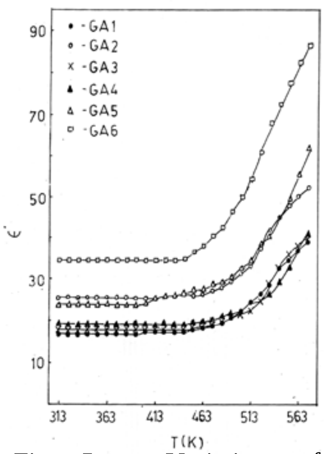

Fig 5 : Variation of dielectric constant with temperature at constant frequency of 1KHz for the

The variation of dielectric constant (∈') at different temperature (313-573K) at a constant frequency of 1 KHz for the glass samples is shown in Fig. 5. It is observed that the dielectric contant (∈')is independent of temperature upto certain temperature range, but after that the dielectric constant increases with temperature rapidly. A similar trend has been reported for different transition metal oxide glasses by Sayer et al [15], Mansingh et al [16]. This increase in dielectric constant is partly due to a change in electronic structure and partly due to thermal expansion. In glasses rise of temperature may increase the free carrier density to introduce conduction losses. The change in dielectric constant at high temperature is a characteristics of Debye type relaxation process where symmetrical distribution of relaxation time takes place. The rapid rise is likely to arise from the other sources of polarization possibly from enhanced electrode polarization as temperature rises. More sharp rise of (∈') at high temperature was also observed in other oxide glasses by Sunder et al [17] and Singh et al [14]

The dielectric constant of all the sample studied is found to be composition dependent. Variation of dielectric constant with composition at a constant temperature is shown in figure 6. A peak is observed at 15 mol% of CuO. In these glasses dipole relaxation phenomenon is observed.

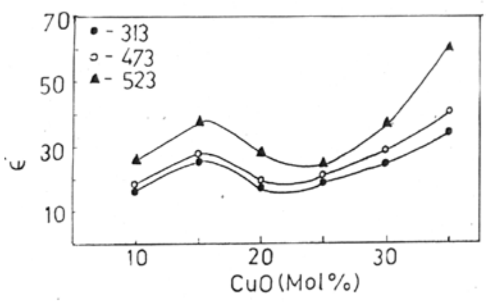

Fig 6 : Variation of dielectric constant with composition at a constant temperature for the glass samples

5. Conclusion :

The optical parameters such as absorption coefficient, optical dielectric constant, refractive index, optical energy gp, constant β, measure of extent of band tailing, infinitely high frequency dielectric constant and ratio of carrier concentration to the effective mass are found to be composition dependent. The linear behaviour is observed in $(\alpha' h\nu)^{1/2}$ with hν suggesting forbidden indirect transition. The value of optical energy gap (E_{opt})are found to be non-linear with composition. Non-linear behaviour is observed in measures of the extent of band tailing (ΔE) with composition (mol%). The ratio of carrier concentration to the effective mass (N/m*) is found to be to the order of 10^{21} cm^{-3}. The dielectric constant of the glass samples is found to be temperature and composition dependent. In the glasses dipole relaxation phenomenon is observed.

Acknowledgement :

Authors express their sincere thanks to the Head, Dept of Physics & Director of Govt Vidarbha Institute of Science and Humanities, Amravati for providing the necessary laboratory facilities during the progress of this work.

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