

Optical Properties of CuO-MnO₂-B₂O₃ Glasses

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Abstract: The optical absorption and transmission spectra in (UV-VIS) have been recorded in the wavelength range 350-800 nm for different compositions of CuO-MnO₂-B₂O₃ 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.

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 Ge₂₀Te_{80-x}Se_x thin films were determined by Shokr et al [3]. Optical and electro-optical properties of Ga₂O₃-PbO-Bi₂O₃ 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 60V₂O₅-(40-X)TeO₂-XPbO were measured as a function of lead content by Memon et al [6]. Studies on the optical properties and structure for SiO₂-TiO₂-PbO₂ 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) TeO₂-XNiO₂-20B₂O₃ by Khaled et al [8]. The divalent state of Ni has been confirmed by IR spectra. The optical properties of the CaO-Al₂O₃-B₂O₃ 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-MnO₂-B₂O₃ glasses. The intention to study the optical properties of these glasses by UV-VIS spectra is to investigate the existence of localized states near band edge.

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, MnO₂ & B₂O₃ (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.

3. Theory :

The absorption 'A' and transmittance 't' of the glass samples were measured by means of CARY -2390 variable wavelength 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 $A = \alpha \times d$ 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 $\alpha(\nu)$

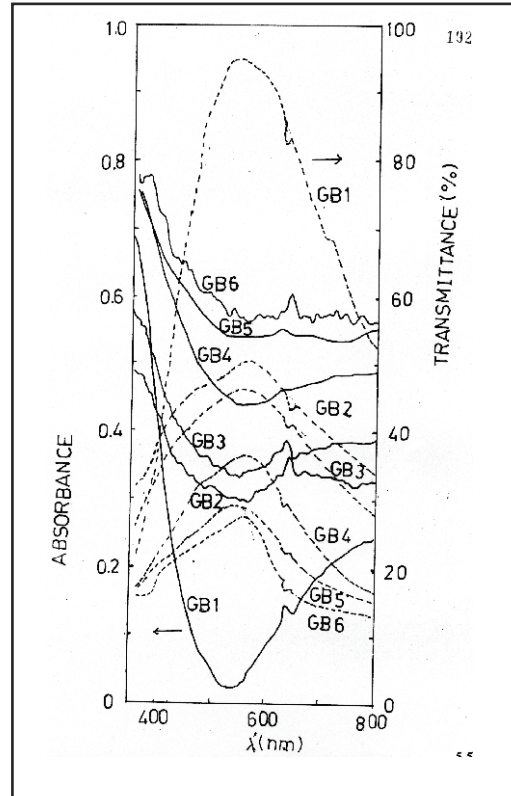


Fig.1 : Spectral dependence of both absorbance and transmittance for six different samples GB₁, GB₂, GB₃, GB₄, GB₅, GB₆

at the given frequency (ν) is given by

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

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, $h\nu$ is the photon energy, E_{opt} is the optical gap, $\gamma = 2$ is a number which characterises the transition process, and

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

The reflectance R was calculated using the equation

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

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

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

where ϵ' is the dielectric constant, e is the electronic charge and N/m³ 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:

The results regarding the various optical properties such as optical energy gap (E_{opt}), constant, measure of extent of band tailing (E), mean refractive index n_0 , infinitely high frequency dielectric constant ϵ'_∞ and ratio N/m³ for different glasses are listed in table (1). Figure (2) Shows the plots $(\alpha h\nu)^{1/2}$ versus h 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 h. 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 from the slopes of the derived curves

The extrapolated dc electrical

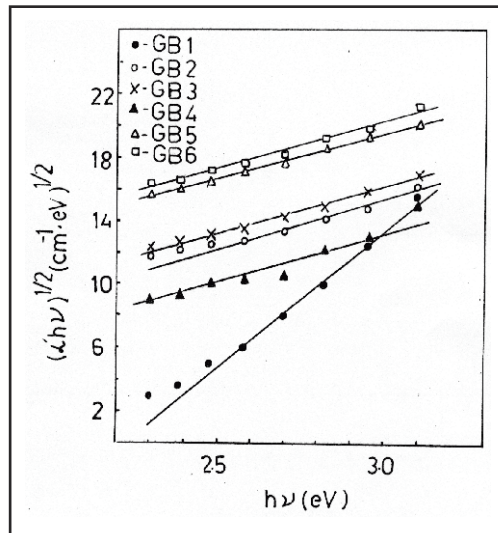


Fig. 2 : Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for samples GB₁, GB₂, GB₃, GB₄, GB₅, GB₆

conductivity, σ_{\min} at $t = \infty$ is obtained from the plot of $\log \sigma$ 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.4 : Plot of optical energy gap E_{opt} and band tailing energy E versus mol% of MnO₂ composition of six samples

The dielectric constant ϵ' versus λ^2 plots shown in Figure (3) are linear, verifying equation (3), Values of ϵ'_∞ and N/m³ 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_0 are calculated from optical dielectric constant.

ϵ' for all the wavelengths of λ^2 . These values are found to be more or less same

Table 1 : The values of optical energy gap (E_{opt}) dielectric constant at infinite frequency (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^*) for 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 concentration to effective mass $N/m^* (cm^{-3}) \times 10^{21}$
	CuO	MnO	B ₂ O ₃						
GB1	20	5	75	2.24	282.24	0.088	1.66	9.6	3.80
GB2	20	10	70	0.56	36.00	0.185	2.58	10.2	1.84
GB3	20	15	65	0.32	36.00	0.150	2.72	10.8	1.72
GB4	20	20	60	0.87	36.00	0.070	3.25	20.0	4.91
GB5	20	25	55	0.12	31.36	0.344	3.56	22.4	5.40
GB6	20	30	50	0.10	36.00	33.21	3.72	22.8	4.66

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 MnO₂ composition.

The variation of E , the width of the tail of localised states in the normally forbidden gap against MnO₂ (mol %) is shown in Figure (4). The optical energy gap E_{opt} is found to be minimum for the glass sample having 30 (mol %) of MnO₂ and E for 20 (mol %) of MnO₂. 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 ϵ'^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

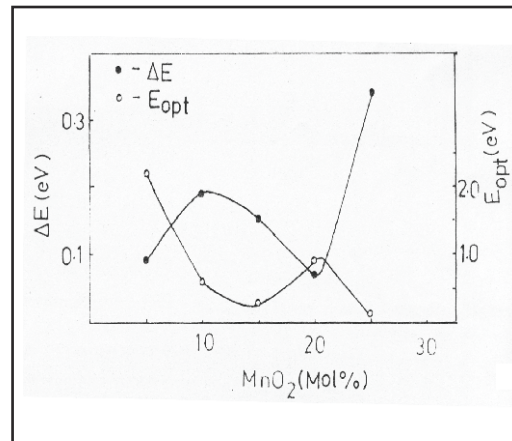


Fig.4 : Plot of optical energy gap E_{opt} and band tailing energy E versus mol% of MnO₂ composition of six samples

with the values reported by other workers for oxide glasses [12] and calculated by other methods. The value of E shows dip at 20 mol% and peak at 10 mol% of MnO_2 . It is observed that the nature of plot of E_{opt} and E 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 ' verses l^2

5. Conclusion :

The optical parameters such as absorption coefficient, optical dielectric constant, refractive index, optical energy gap, constant, 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 $(h\nu)^{1/2}$ with $h\nu$ 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 (E) 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} .

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