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Optical and Electrical Properties of CuO-MnO_2-B_2O_3 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-MnO_2-B_2O_3 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. Due to the technological importance of CuO-MnO_2-B_2O_3 glasses, dc-conductivity measurement with increasing concentration of MnO_2 (in the range of 5-30 mol%) have been reported in the temperature range of 313-573 K in the present study. A plot of $-\log \sigma$ versus 1/T shows two different regions of conduction suggesting two types of conduction mechanisms switching from one type to another occurring at knee temperature. The DC conductivity increases with increase in temperature of the sample and also with increase of mol% of MnO_2. Activation energy calculated from both regions (LTR and HTR) is below 1 eV. Thus electrical conduction is electronic. Activation energy in LTR and HTR are temperature independent but composition dependent.*

Keywords— *CuO-MnO_2-B_2O_3 glasses, Optical properties, non-linear behavior, DC-conductivity.*

I. 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-MnO_2-B_2O_3 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. Ghosh et al. [13] discussed the results of dc-conductivity of semiconducting vanadium bismuth oxide, containing 80-95 mol% vanadium pentaoxide in the 300-500 K temperature range on the basis of polaronic hopping model similarly they observed adiabatic hopping conduction. The electrical properties of V_2O_5-B_2O_3 glasses are discussed on the basis of small polaron hopping model by Culea et al. [14]. The charge transfer mechanism plays a dominant role in semiconducting glasses. Dc-conducting and hopping mechanism in Bi_2O_3-B_2O_3 glasses has been studied by Yawale et al. [15]

II. EXPERIMENTAL DETAILS

A. 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, MnO_2 & 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.

B. Electrical Measurement

The dc resistance of the glass samples was measured by using D.C. microvoltmeter, Systronics 412 India; having an accuracy of ±1 μV and input impedence 10 MΩ, by voltage

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drop method given by Kher et al. [16]. Before electrical measurements all the samples were polished to smooth surfaces using fine quality emery paper. After application of conducting silver paint at either sides, the samples were used for electrical measurements. The silver paint acts like electrodes for all the samples.

III. THEORY

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)

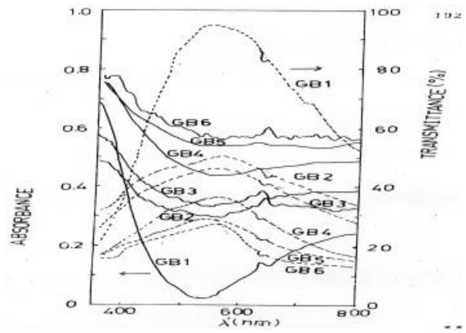

Fig. 1. Spectral dependence of both absorbance and transmittance for six different samples GB_1, GB_2, GB_3, GB_4, GB_5, GB_6.

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

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

Where σ_{min} is the extrapolated dc-conductivity at T = ∞, 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

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

The reflectance R was calculated using the equation

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

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

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

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.

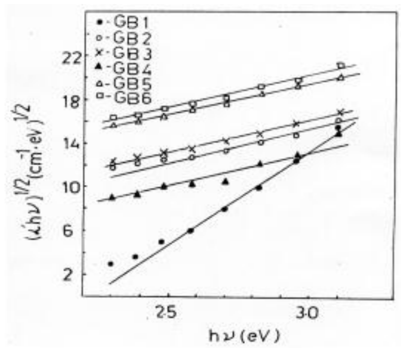

Fig. 2 . Plot of α'hν verses hν for samples GB_1, GB_2, GB_3, GB_4, GB_5, GB_6.

IV. RESULTS AND DISCUSSION

A. Optical Properties

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 constant ε'_∞ and ratio N/m* for different glasses are listed in table (I). 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 I. 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}) x 10^{21}
	CuO	MnO	B_2O_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

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].

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 I 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.

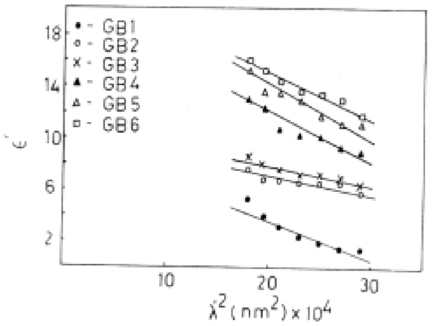

Fig. 3. Plot of optical dielectric constant ε' verses λ'^2 for six samples GB_1, GB_2, GB_3, GB_4, GB_5, GB_6.

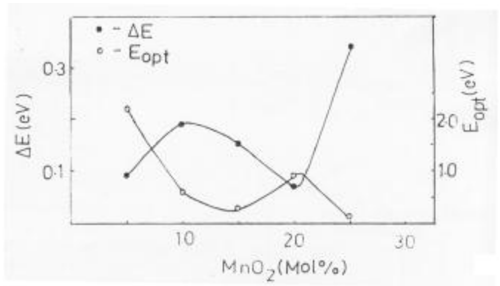

Fig. 4. Plot of optical energy gap E_{opt} and band tailing energy ΔE verses mol% of MnO_2 composition of six samples.

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 MnO_2 composition.

The variation of ΔE, the width of the tail of localised states in the normally forbiden gap against

MnO_2 (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 MnO_2 and ΔE for 20 (mol %) of MnO_2. 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 I. 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 20 mol% and peak at 10 mol% of MnO_2. 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

B. Dc-electrical Conductivity

D.C. electrical conductivity of the glass samples is measured in the temperature range 313 to 573 K. The value of d.c. conductivity is found to be of the order of 10^{-10} to 10^{-11} ohm^{-1} cm^{-1} at 313 K. Fig 5 shows the plot of -log σ versus 1/T. It is observed that, the conductivity of all the glass samples studied increases with increasing temperature.

This plot is found to consists of two distinct straight linear regions called as low temperature regions (LTR) (313 to 413 K) and high temperature region (HTR) (523 to 573 K). In LTR conductivity increases linearly with increasing temperature at very slow rate where as in HTR conductivity increases linearly with increasing temperature at a faster rate. Obviously two activation energies and two conduction mechanisms are associated with electronic conduction in all the glasses studied. The same type of dc conductivity behaviour is reported in literature [15, 17, 18]. The activation energies are obtained from slope of the plot of log σ versus 1/T in both the regions and reported in table II. It is observed that the activation energy is temperature independent but depends on composition.

TABLE II. Activation energies, Kink Temperature and Pre- exponential factor σ_o of $CuO-MnO_2-B_2O_3$ glasses.

Glass No.	Composition (mol%) $CuO-MnO_2-B_2O_3$	Activation energy W (eV)		Kink Tempera-ture θ_c (K)	Activation energy at θ_c W (eV)	Pre-exponential factor σ_o (ohm x cm) $^{-1}$ 10^{-9}
		LTR (W_L)	HTR (W_h)			
G B1	20-5-75	0.0035	0.250	476	0.0754	15.8
G B2	20-10-70	0.0052	0.181	471	0.0603	6.60
G B3	20-15-65	0.0060	0.258	456	0.0517	5.62
G B4	20-20-60	0.0069	0.310	450	0.0431	3.16
G B5	20-25-55	0.0086	0.422	440	0.0388	14.7
G B6	20-30-50	0.0090	0.474	378	0.0345	1700

The activation energies obtained are found to be of order of borate vanadate and other semiconducting glasses reported in literature [12], [19-22]. Activation energy calculated for both regions (LTR and HTR) is found to be less than 1 eV, thus the electrical conduction is electronic.[23] The kink temperature θ_c is the temperature at which the Arrhenius plot is divided in to two linear regions of different slopes. The kink temperature (θ_c) is determined from the plot of $-\log \sigma$ versus 1/T and is reported in table II. The kink temperature θ_c for the series of glasses studied decreases with increasing mol% of MnO_2. The activation energy is also calculated at kink temperature and the values are reported in table II. The inetecept on $-\log \sigma$ axis of $-\log \sigma$ versus 1/T plot gives the values of pre-exponential factor ($-\log \sigma_0$)

Table II reports the values of activation energy, kink temperature, pre-exponential factor of $CuO\text{-}MnO_2\text{-}B_2O_3$ glasses. The values of different parameters reported in the table agreed with the values reported for semiconducting glasses in the literature [12, 15, 19-22]. Fig. 6 shows the variation of activation energy (w) with MnO_2 mol% in LTR and HTR for the glass samples. Fig. 7 shows variation of pre-exponential factor ($-\log\sigma_0$) versus Composition for the glasses studied.

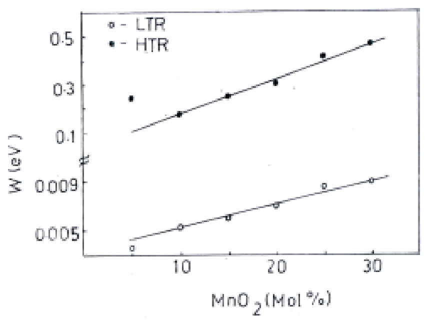

Fig. 6. Variation of activation energy (w) with MnO_2 mol% in LTR and HTR for the glass samples.

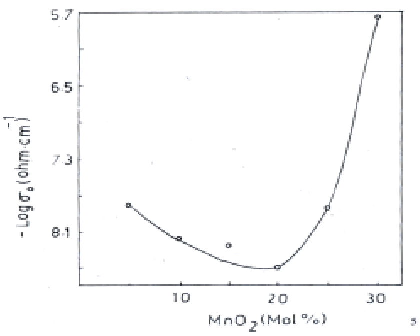

Fig. 7. Variation of pre-exponential factor ($-\log\sigma_0$) versus Composition for the glass samples.

V. CONCLUSION

The optical parameters such as absorption coefficient, optical dielectric constant, refractive index, optical energy gap, 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 $h\nu$ 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 (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}. D.C. conductivity of $CuO\text{-}MnO_2\text{-}B_2O_3$ glass system is studied in the temperature range 313-573K. The activation energy are found to be in the range of semiconducting glasses. The electrical conduction is electronic.

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