OPTICAL AND ELECTRICAL 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 ($\alpha'$), optical energy gap ($E_{\text{opt}}$), refractive index (n₀), optical dielectric constant ($\varepsilon_{\infty}'$), measure of extent of band tailing ($\Delta E$), constant ($\beta$) 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-MnO₂-B₂O₃ glasses, dc-conductivity measurement with increasing concentration of CuO (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 CuO. 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-MnO₂-B₂O₃ glasses, Optical properties, non-linear behavior, DC-conductivity

1. Introduction:
In the recent years, the interest in the study of electrical, optical and structural properties of glassy semiconductors has increased 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 Ge₂₀ Të₈₀-x Së thin films were determined by Shokr et al [3]. Optical and electro-optical properties of Ga₂O₃-PhBO-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-PbO 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 Khaleed 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. Ghosh et al [13] discussed the results of dc-conductivity of semiconducting chalcogenide glass, 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 V₂O₅-B₂O₃ 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 Bi₂O₃-B₂O₃ glasses has been studied by Yawale et al [15].

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 fireclay 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 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 impedance 10 MΩ. The values of optical energy gap (Eₒpt) dielectric constant (ε), refractive index (nₒ), constant (β) and measure of the extent of band carrier concentration to the effective mass (N/m*) for different glasses were obtained by various electrical measurements. The silver paint acts like electrodes for all the samples. The silver paint acts like electrodes for all the samples.

3. Theory :
The absorption ‘A’ and transmittance ‘t’ of the glass samples were determined from absorbance and transmittance for five different samples GC₁, GC₂, GC₃, GC₅, GC₆. The resolution of the instrument 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’ × 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).

4. Results and Discussion:

4.1 Optical Properties

The results regarding the various optical properties such as optical energy gap ($E_{\text{opt}}$), constant $\beta$, measure of extent of band tailing ($\Delta E$), mean refractive index ($n_0$), infinitely high frequency dielectric constant ($\varepsilon'_\infty$), and the ratio of carrier concentration to the effective mass ($N/m^*$) for different glass compositions are listed in Table 1.

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Glass composition (mol%)</th>
<th>Optical energy gap $E_{\text{opt}}$(eV)</th>
<th>Constant $\beta$ (cm$^{-1}$eV$^{-1/2}$)</th>
<th>Measure of extent of band tailing $\Delta E$(eV)</th>
<th>Mean refractive index $n_0$</th>
<th>Infinitely high frequency dielectric constant $\varepsilon'_\infty$</th>
<th>Ratio of carrier concentration to effective mass $N/m^*$(cm$^{-3}$) $\times$ 10$^{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC1</td>
<td>CuO 5 MnO$_2$ 20 B$_2$O$_3$ 75</td>
<td>0.42</td>
<td>57.76</td>
<td>0.167</td>
<td>3.38</td>
<td>18.4</td>
<td>3.80</td>
</tr>
<tr>
<td>GC2</td>
<td>CuO 10 MnO$_2$ 20 B$_2$O$_3$ 70</td>
<td>1.04</td>
<td>92.16</td>
<td>0.076</td>
<td>3.09</td>
<td>14.8</td>
<td>2.94</td>
</tr>
<tr>
<td>GC3</td>
<td>CuO 15 MnO$_2$ 20 B$_2$O$_3$ 65</td>
<td>1.58</td>
<td>108.16</td>
<td>0.060</td>
<td>2.12</td>
<td>8.2</td>
<td>2.21</td>
</tr>
<tr>
<td>GC5</td>
<td>CuO 25 MnO$_2$ 20 B$_2$O$_3$ 55</td>
<td>1.14</td>
<td>36.00</td>
<td>1.703</td>
<td>1.95</td>
<td>6.4</td>
<td>1.47</td>
</tr>
<tr>
<td>GC6</td>
<td>CuO 30 MnO$_2$ 20 B$_2$O$_3$ 50</td>
<td>0.78</td>
<td>36.00</td>
<td>0.373</td>
<td>2.12</td>
<td>7.8</td>
<td>1.83</td>
</tr>
</tbody>
</table>

The extrapolated dc electrical conductivity, $\sigma_{\text{min}}$ at $t = \infty$ is obtained from the plot of log$\sigma$ versus $1/T$ (plot not shown). The values obtained for $E_{\text{opt}}$ for the five 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 $\varepsilon'$ versus $\lambda^2$ plots shown in Figure (3) are linear, verifying equation (3). Values of $\varepsilon'_\infty$ 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.
The values of refractive index $n_0$ are calculated from optical dielectric constant $\varepsilon'$ for all the wavelengths of $\lambda^2$. These values are found to be more or less same throughout the wavelength range (350-800 nm). Therefore average values of $n_0$ are reported in this wavelength region. The average value of refractive index $n_0$ shows dependence on CuO composition. The variation of $\Delta E$, 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 $E_{\text{opt}}$ is found to be minimum for the glass sample having 5 (mol %) of CuO and $\Delta E$ for 15 (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 $\varepsilon'$ versus $\lambda^2$ (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 $\Delta E$ shows dip at 15 mol% and peak at 30 mol% of CuO. It is observed that the nature of plot of $E_{\text{opt}}$ and $\Delta E$ 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 $\varepsilon'$ versus $\lambda^2$ shows the plot of -log $\sigma$ 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 $\sigma$ versus 1/T in both the

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Composition (mol%): CuO-MnO₂-B₂O₃</th>
<th>Activation energy $W$ (eV)</th>
<th>Kink temperature $\theta_c$ (K)</th>
<th>Activation energy at $\theta_c$ $W$ (eV)</th>
<th>Pre-exponential factor $\sigma_0$ (ohm x cm)$^{-1}$ $10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC1</td>
<td>5-20-75</td>
<td>0.0086</td>
<td>0.345</td>
<td>485</td>
<td>0.1245</td>
</tr>
<tr>
<td>GC2</td>
<td>10-20-70</td>
<td>0.0051</td>
<td>0.198</td>
<td>478</td>
<td>0.0862</td>
</tr>
<tr>
<td>GC3</td>
<td>15-20-65</td>
<td>0.0069</td>
<td>0.181</td>
<td>476</td>
<td>0.0739</td>
</tr>
<tr>
<td>GC5</td>
<td>25-20-55</td>
<td>0.0051</td>
<td>0.276</td>
<td>469</td>
<td>0.0862</td>
</tr>
<tr>
<td>GC6</td>
<td>30-20-50</td>
<td>0.0051</td>
<td>0.163</td>
<td>471</td>
<td>0.0984</td>
</tr>
</tbody>
</table>
regions and reported in table 2. It is observed that the activation energy is temperature independent but depends on composition. 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 temperature at which the Arrhenius plot is divided into two linear regions of different slopes. The kink temperature ($\theta_c$) is determined from the plot of $-\log \sigma$ versus $1/T$ and is reported in table 1. The kink temperature $\theta_c$ for the series of glasses studied decreases with increasing mol% of CuO. The activation energy is also calculated at kink temperature and the values are reported in table 2. The intercept on $-\log \sigma$ axis of $-\log \sigma$ versus $1/T$ plot gives the values of pre-exponential factor ($-\log \sigma_0$).

Table 2 reports the values of activation energy, kink temperature pre-exponential factor of CuO-MnO$_2$-B$_2$O$_3$ 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 CuO 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.

5. Conclusion:

The optical parameters such as absorption coefficient, optical dielectric constant, refractive index, optical energy gap, constant $\beta$, 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 ($E_{\text{opt}}$) are found to be non-linear with composition. Non-linear behaviour is observed in measures of the extent of band tailing ($\Delta E$) 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$^{-3}$. D.C. conductivity of CuO-MnO$_2$-B$_2$O$_3$ 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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References: