5. OPTICAL PROPERTIES OF GLASSES

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References
5. Optical Properties of Glasses

5.1 Introduction

The glasses can be used as semiconductors, photoconductors, magnets, transducers, optical switches, memory materials and superior insulators and dielectrics (Memon et al 1993). Application point of view, optical properties of glasses are very important. The different optical parameters are absorption coefficient, optical energy gap, refractive index and optical dielectric constant etc. The refractive index is an important parameter for the design of optical components such as prism, windows and optical fibers.

The phototropic and photochromic behaviour of the halide glasses gives birth to the photosun glasses or specs. It has been observed that the structural changes would occur in the halide glasses when they are irradiated by UV-VIS light. The bond breaking and making phenomenon proved to be a new way to ophthalmicians for exploiting the photosun glasses.

In order to interpret conduction, some band structure models have been proposed (Mott 1979). The model accepted for conduction in amorphous materials involves a narrow band of localized states near the centre of the band gap (Davis 1970).

The optical processes that occur for photons having energies comparable to that of the band gap. For most of amorphous semiconductors, the band gap often lie in the range 1–3 eV and for insulators the energies are considerably larger (10 eV for SiO₂).

5.2 Review of Literature

Hussein et al (1981) have studied the variation of optical density of a few induced absorption bands in some sodium aluminum borate glasses by varying the radiation doses of gamma ray and cerium content. The intensity of the induced absorption bands in the visible spectrum increases with the gradual increase of cerium.
Rashed et al (1984) have measured optical absorption coefficient of a series of glass specimens prepared from mixture of ZnO and $P_2O_5$, as a function of photon energy in the range 3.18 – 6.53 eV. Values of the optical energy gap are calculated and found to decrease linearly with the ZnO concentration in these glasses. The results are interpreted in terms of mechanism of optical absorption arising from electronic transitions as described by the theory of the Davis and Mott.

Optical behaviour of sputter deposited vanadium pentoxide was reported by Carolyn et al (1986). Optical transmission and reflection characteristics were measured by double-beam spectrophotometry in 390 to 700 nm wavelength regions. The absorption coefficient ($\alpha$) was determined as a function of the incident photon energy ($hv$).

The transition behaviour of manganese containing alkali-lime-silica glasses have been investigated with and without CeO$_2$ and As$_2$O$_3$ as dopants by Muqtader et al (1990). The changes taking place owing to irradiation with solar and ultra-violet rays are reported and the roles of arsenic and ceria in causing the observed changes are discussed by them.

The refractive index measurement of the tellurium halide (Te$_x$) (where x is the halide elements) based glasses as a function of temperature and wavelength has been studied by Ma et al (1993), showing that a small modification of glass composition can lead to an important change of the refractive index.

Hajto et al (1993) have studied linear and nonlinear optical properties of chalcogenide glasses. The compositional dependence of the nonlinear refractive index for As-S, Ge-Se, As-Se and Ag-As-S system is investigated by them.

Ezz-Eldin et al (1993) have studied the change in optical absorption of some gamma irradiated alkali-borate glasses containing Ti, V, Mn, Fe, Ni, or Cu. The effect of irradiation dose and the role of transition metal oxides have been investigated and the changes in optical spectra of base glass and other derived glasses after irradiation with gamma rays...
are compared. Upon increasing the irradiation dose, different rates of the colour center formation have been observed.

The electrical and optical study of Cr\(^{3+}\) doped chlorophosphate and phosphate glasses have been discussed by Bishnoi et al (1993). The observed absorption bands in the region 350-800 nm have been assigned to different transitions assuming an octahedral symmetry.

Guo et al (1993) have investigated optical properties and chemical durability of lead indium aluminium phosphate glass prepared by a wet-chemical process. The results are compared with recent data for other phosphate glasses and indicate that lead-indium aluminum phosphate glass has a promising combination of good optical properties and chemical durability.

Canioni et al (1994) have reported experimental and theoretical investigation of highly non-linear optical properties of the Na\(_2\)O-TiO\(_2\)-P\(_2\)O\(_5\) glass system with a high sensitivity absolute interferometric technique.

The optical properties of the CaO-Al\(_2\)O\(_3\)-B\(_2\)O\(_3\) glasses are reported by Kudesia et al (1994). Inflections in physical property curves are discussed in terms of formation of non-bridging oxygen. Infrared spectroscopy indicated the presence of the boroxyl group up to 40 mol% of CaO. The tetraborate groups gradually diminish on increasing the CaO concentration higher than 25 mol%.

Kobayashi et al (1994) have studied optical polarizable and MOS properties of crystallizable ZnO and PbO based glasses. The purpose of experiment was to prepare low temperature reflow glasses for the use in ultra large scale integrated circuits since they require the formation of shallow junction.

Terashima et al (1995) have measured non-linear optical properties of M\(_2\)O-B\(_2\)O\(_3\) (M equal Li, Na, K, Rb, Cs and Ag) binary borate glasses by the third harmonic generator (THG) method.
The nature of the optical energy gap of rare earth doped glasses was studied and the effect of composition on the position of the absorption edge and the value of optical energy gap was investigated by Sharma et al (1995). The studies were done on Pr$^{3+}$ doped $\text{B}_2\text{O}_3$-$\text{P}_2\text{O}_5$-$\text{BaO}$ glasses. The results suggest the potential of rare earth oxide doped glasses for LASER applications.

The optical properties of PbO glass containing a small amount of silica have been studied by Dayanand et al (1995). The optical band gap (2.56 eV) of PbO glass was determined. The results confirm the thermal vibrations constitute the physical origin of the tail of the optical absorption edge.

The thermal and optical properties of PbO–KF glasses have been studied by Nachimuthu et al (1995). They found that the refractive indices and optical band gap of these glasses lie in the range of 1.410-1.653 and 3.13-3.74 eV respectively. The PbO content markedly influences the optical properties due to the formation of strong -Pb-O-Pb-covalent linkages.

Burghate et al (1995) have recorded the optical transmission and absorption spectra (UV-VIS) in the wavelength range 350 –800 nm for different compositions of lead-bimuth-titanate glasses. The optical properties such as absorption coefficient, optical energy gap, refractive index, optical dielectric constant and width of the tail localized states in the normal forbidden gap have been reported. The effect of composition of glasses on these parameters have been discussed. The non-linear behaviour for all the parameters have been investigated.

Takebe et al (1996) have studied compositional dependence of optical parameters of Na$^{3+}$ for potassium tantalum and lead bismuth gallate glasses. The variations of Judd-Ofelt parameters with composition are discussed in terms of glass structure.

Sidebottom et al (1997) have studied structure and optical properties of rare earth doped zinc oxyhalide tellurite glasses. They found that zinc-tellurite glasses

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appears to be excellent candidates for hosting rare earth ions since they provide a low phonon energy environment to minimize non-radiative losses as well as possessing good chemical durability and optical properties.

Optical properties of rare-earth ions in lead germanate glasses were investigated by Wachtler et al (1998). From absorption and emission spectra in ultraviolet visible and near infrared region, the intensity parameter, spontaneous emission probabilities, branching ratios, radiative lifetime are reported.

Burghate et al (1999) have recorded the optical transmission and absorption spectra in (UV-VIS) in the wavelength range 350-800 nm for different composition of lead-bismuth glasses. The various optical properties such as absorption coefficient, optical energy gap, refractive index, optical dielectric constant at infinite high frequency, measure of extent of band tailing, constant $\beta$ and ratio of carrier concentration to the effective mass have been evaluated. The effect of composition of glasses on these parameters have been discussed. It has been indicated that a small modification of glass composition can lead to a important changes in all the optical properties. These results are interesting, showing nonlinear behaviour for all the parameters being evaluated. The optical parameters are found to almost same for different glasses in the same family.

Senthil et al (1999) have examined structural, dielectric and optical properties of lithium borate- bismuth tungstate glass ceramic. The optical transmission properties of these glass- ceramics were found to be composition dependent.

Wakkad et al (2000) have performed optical properties and calorimetric studies of Ge-Sb-Se glasses in the visible and near-infrared spectral region.

5.3 Theory of Optical Properties

Mott and Davis (1979) have outlined the general theory of optical absorption of amorphous semiconductors. Mott (1967) have shown that there are some
similarities between the energy band structure of crystalline and glassy nonmetallic materials. The crystalline materials show well-defined energy bands with sharp conduction and valence band edges. The glassy materials show band-tailing into the normally forbidden gap (Rashed 1984).

The form of the energy dependence of the optical absorption typically observed is shown in fig (5.1) (Elliot 1984).

![Graph showing optical absorption in amorphous semiconductor](image)

**Fig. 5.1 Optical absorption in amorphous semiconductor showing the interband region (I) and the urbach edge region (II).**

The section is divided into two parts, with optical transitions at energies above and below the mobility gap. The difference between the energies of the mobility edges in valence and conduction bands is called 'mobility gap' (fig 5.2) (Mott 1979).
The absorption at slightly higher energies (associated with absorption coefficient $\alpha > 10^4$) may provide information on the combined density state at the valence band and conduction-band-edges. Basically there are two types of optical transitions that can occur at the edge of crystalline semiconductors, direct or indirect (Davis and Mott 1970). Both involves the interaction of an electromagnetic wave with an electron in the valence band, which is raised across the fundamental gap to the conduction band. However, indirect transitions also involve simultaneous interaction with lattice vibrations. Thus the wave vector of an electron can change in the optical transition, the momentum change being taken or given up by photon. (The radiation imparts negligible momentum to the electron). In amorphous materials, account is essentially taken for the localized electronic states in the mobility gap.

The matrix element $D(E)$ for optical transitions between state in different bands have the same value whether or not the initial and final states are localized. Also, the densities of states at the band edges are assumed to be linear functions of the energy. Moreover,
transitions are improbable whenever both initial and final states are localized (Davis and Mott 1970).

The general theory of the optical absorption of amorphous semiconductors has been reported by Mott and Davis (1979).

The optical absorption coefficient, \( \alpha(v) \) at a given frequency \( (v) \) is given by

\[
\alpha(v) = \frac{4\pi \sigma_{\text{min}}}{Cn_\circ \Delta E} \left( \frac{hv - E_{\text{opt}}}{hv} \right)^\gamma
\]

(5.1)

Where,

\( \sigma_{\text{min}} \) is the extrapolated dc-conductivity at \( T = \infty \),
\( n_\circ \) is the refractive index,
\( C \) is the velocity of light,
\( \Delta E \) is a measure of the extent of band tailing,
\( hv \) is the photon energy,
\( E_{\text{opt}} \) is the optical energy gap,
\( \gamma = 2 \) is a number which characterizes the transition process and
\( \beta = \left( \frac{4\pi \sigma_{\text{min}}}{Cn_\circ \Delta E} \right) \) is the constant

The reflectance can be calculated using the equation (Moss 1959) given by

\[
T = (1-R)^2 \exp(-A)
\]

(5.2)

Where,

\( R \) is the reflectance,
\( T \) is the transmittance and
\( A \) is the absorbance,

The relation between optical dielectric constant (\( \varepsilon \)) and square of wavelength (\( \lambda^2 \)) is given by (Bottcher 1952, Spitzer et al 1957)
\[ e = n^2 = \left[ \frac{(1 + \sqrt{R})}{(1 - \sqrt{R})} \right]^2 \]  \hspace{1cm} (5.3)

\[ e = \varepsilon_\infty - \left( \frac{e^2}{\pi C^2} \right) \left( \frac{N}{m^*} \right) \lambda^2 \]  \hspace{1cm} (5.4)

Where,

- \( \varepsilon_\infty \) is infinitely high frequency dielectric constant
- \( e \) is the electronic charge,
- \( N/m^* \) is the ratio of carrier concentration to the effective mass,
- \( C \) is the velocity of light and
- \( \lambda \) is the wavelength of the light.

5.4 Experimental

The absorbance 'A' and transmittance 'T' of glass samples were measured by means of Chemito (USA) UV-2600 double beam spectrophotometer in the spectral range 220-260 nm. By knowing the values of absorbance 'A', reflectance 'R' and transmittance 'T' various optical properties were calculated.

5.5 Results and Discussion

The spectral measurements were made in the wavelength range of 220 to 260 nm in UV region on Chemito (USA) UV – 2600 double beam spectrophotometer. The absorbance 'A' and transmittance 'T' of glass samples were measured at room temperature. The absorbance 'A' and transmittance 'T' spectra of different lead borate glasses are shown in figures (5.3) and (5.4) respectively.

The plots of \((\alpha h\nu)^{1/2}\) against \(h\nu\) for different compositions of PbO are shown in fig (5.5). The linear behaviour of the plots is observed which suggests the forbidden indirect transition for glassy and amorphous materials (Mott et al 1979). The observed
Fig 5.3 Absorbance spectra of lead-borate glasses.

Fig 5.4 Transmittance spectra of lead-borate glasses.
plots shows the validity of the relation given by the equ. (5.1) (Dayanand et al 1994). This equation gives forbidden indirect transition for amorphous material. The value of optical energy gap $E_{\text{opt}}$ and the constant $\beta$ are obtained from extrapolation of the linear region and slopes of straight-line plot shown in fig. (5.5).

The values obtained for various glass composition of lead oxide are tabulated in table 5.1. The optical energy gap values are found to be of the order of the oxide glasses (Burghate et al 1995). The compositional dependence of $E_{\text{opt}}$ is shown in figure 5.6. This plot shows somewhat linear behaviour. The $E_{\text{opt}}$ values decreases with increasing concentration of PbO. The optical band gap is closely related to the forbidden energy gap between valence band and conduction band (Davis et al 1970) because the optical transition takes place between this gap.

![Graph](image.png)

Fig 5.5 Variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$).

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Table 5.1 Optical energy ($E_{opt}$), constant ($\beta$), measure of extent of band tailing ($\Delta E$), mean refractive index ($n_o$), infinitely high frequency dielectric constant ($\varepsilon_\infty$) and ratio of carrier concentration to the effective mass ($N/m^*$) for the different glass sample.

<table>
<thead>
<tr>
<th>Glass No</th>
<th>Chemical Composition mol %</th>
<th>Optical energy ($E_{opt}$)(eV)</th>
<th>Constant ($\beta$) (cm$^{-1}$ eV$^{-1/2}$)</th>
<th>Measure of extent of band tailing ($\Delta E$)(eV)</th>
<th>Infinitely high frequency dielectric constant ($\varepsilon_\infty$)</th>
<th>Mean refractive index ($n_o$)</th>
<th>Ratio of carrier concentration to the effective mass ($N/m^*$)$x10^{22}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB1</td>
<td>20 PbO, 80 B$_2$O$_3$</td>
<td>4.55</td>
<td>23.72</td>
<td>0.123</td>
<td>19.70</td>
<td>1.86</td>
<td>4.30</td>
</tr>
<tr>
<td>LB2</td>
<td>30 PbO, 70 B$_2$O$_3$</td>
<td>4.54</td>
<td>26.20</td>
<td>0.109</td>
<td>19.00</td>
<td>1.95</td>
<td>4.20</td>
</tr>
<tr>
<td>LB3</td>
<td>40 PbO, 60 B$_2$O$_3$</td>
<td>4.54</td>
<td>26.56</td>
<td>0.100</td>
<td>21.40</td>
<td>2.05</td>
<td>4.21</td>
</tr>
<tr>
<td>LB4</td>
<td>50 PbO, 50 B$_2$O$_3$</td>
<td>4.52</td>
<td>26.34</td>
<td>0.071</td>
<td>22.00</td>
<td>2.00</td>
<td>3.94</td>
</tr>
<tr>
<td>LB5</td>
<td>60 PbO, 40 B$_2$O$_3$</td>
<td>4.51</td>
<td>25.00</td>
<td>0.358</td>
<td>22.10</td>
<td>2.07</td>
<td>4.24</td>
</tr>
<tr>
<td>LB6</td>
<td>70 PbO, 30 B$_2$O$_3$</td>
<td>4.51</td>
<td>27.27</td>
<td>0.316</td>
<td>22.70</td>
<td>2.00</td>
<td>3.55</td>
</tr>
<tr>
<td>LB7</td>
<td>80 PbO, 20 B$_2$O$_3$</td>
<td>4.48</td>
<td>26.09</td>
<td>0.535</td>
<td>22.90</td>
<td>1.83</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Fig 5.6 Variation of optical energy gap, $E_{opt}$ with PbO content.
It is known that the S and P orbitals of Pb$^{2+}$ and P orbital of oxygen interacts with each other to form bonding and antibonding states which contributes to valence band and conduction band respectively. In these glasses, -Pb–O–Pb– covalent linkage is formed which is very strong (Rao et al 1984). This reduces the forbidden energy band gap between the valence band and conduction band of the material and thus the optical band gap. Similar type of behaviour has been observed by Machimuthu et al (1995) in lead fluoride glasses. The decrease of $E_{\text{opt}}$ with increase in lead oxide content is probably related to the progressive increase in the number of non-bridging oxygen (NBO). This increase in NBO is attributed to the structural changes, which are the results of the differing site occupation of Pb$^{2+}$ ions. In lead borate glasses, the covalent linkage -Pb-O-Pb- and Pb$^{2+}$ ions plays the important role in the formation of glass structure. Specially in lead borate glasses the PbO plays the important role of network modifier. The increase in content of PbO leads to the modification of network of borate glass. This may cause the decrease in the optical energy gap with rich concentration of PbO in these glasses.

The measure of extent of band tailing $\Delta E$ is calculated from the slope of the plot of $(\alpha h\nu)^{1/2}$ verses $h\nu$ (fig. 5.5). The $\Delta E$ values are reported in table 5.1 and are found to be of the order of borate glasses (Gawande et al 1997). It is observed that the $\Delta E$ values are found to be increasing with lead oxide content. The width of the tails of localized states for different materials have the same physical origin and is attributed to phonon assisted indirect electronic transition (Chopra et al 1972).

It is known in case of the single crystal that the absorption tail $\Delta E$ is temperature dependent (Sunandana et al 1978). However in a glassy material, where the short range order is limited, the edge and hence $\Delta E$ are independent of temperature. The random fluctuation in the microscopic densities of the glass, which cause local inhomogeneities, besides the localized modes are considered as the origin for the Urbach energy.

Without a detailed knowledge of the fluctuation potential it is impossible to
calculate the degree of tailing of band edges. The larger the fluctuations the larger is the tailing of the band edges. Thus the effective band gap becomes narrow in the disorder lattice. Tailing may extend deep in the forbidden zone and may even results in the overlapping of the conduction and valence band. The localization of states discussed on the basis of speculative criterion suggested that the localized and non localized states are separated by critical electron energy at which the electron mean free path and the electron wavelength are comparable.

The high frequency dielectric constant called optical dielectric constant is determined from reflectance R (eq 5.3) at different wavelengths λ. The optical dielectric constant ε versus square of the wavelength (λ^2) at which the dielectric constant is determined, plots are shown in fig (5.7).

![Graph showing variation of high frequency dielectric constant (ε) with square of wavelength (λ^2).]
The validity of eq (5.3) is checked by observing the linear behaviour of graph. The values of infinitely high frequency dielectric constant (\(\varepsilon_\infty\)) are determined from the extrapolation of these plots to \(\lambda^2 = 0\). Similarly the values of ratio of carrier concentration to the effective mass are also determined from the slope of the plots. These values are reported in table (5.1) for different compositions of PbO. The refractive index \(n\) is determined from the eq (5.3) by knowing the optical dielectric constant. The average values of refractive indices \(n_a\) are reported in table (5.1). The compositional dependence of refractive index and infinitely high frequency dielectric constant \(\varepsilon\) is observed. The observed values are found to be of the order of other oxide glasses (Hajto et al 1993). The infinitely high frequency dielectric constant increases with the increase in PbO content. The change in the value of dielectric constant with the change in PbO content is found to be small.

The value of ratio of carrier concentration to effective mass \(N/m^*\) calculated from the slope of plot \(\varepsilon\) and \(\lambda^2\), are reported in table (5.1). These values are found to be of the order of \(10^{22}\) cm\(^{-3}\) which are in agreement with the values reported for oxide glasses (Ghosh et al 1986) and calculated by other methods.

5.6 Conclusions

It is concluded that the evaluated optical parameters such as absorption coefficient, optical energy gap, optical dielectric constant, refractive index, constant \(\beta\), measure of extent of band tailing are found to be composition dependent. The linear behaviour of \((\alpha h\nu)^{1/2}\) versus \(\hbar\nu\) plot suggests the forbidden indirect transition. The optical parameters are found to be of the order of other oxide glasses. The decrease in the \(E_{\text{opt}}\) with increase in PbO concentration is closely related to the presence of strong \(-\text{Pb-O-Pb-}\) covalent linkage and Pb\(^{2+}\) ions. Hence, the structure of the glass. The increase in the width of tails of localized states \(\Delta E\) with PbO concentration is attributed to the phonon assisted indirect transitions.
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