Research Article

Optical Characterization of Zinc Modified Bismuth Silicate Glasses

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The optical characterization of glass samples in the system $40\text{SiO}_2 \cdot x\text{ZnO} \cdot (60 - x)\text{Bi}_2\text{O}_3$ with $x = 0, 5, 10, 15, 20, 25, 30, 35,$ and $40$ prepared by conventional melt-quench technique has been carried out in the light of Hydrogenic Excitonic Model (HEM). The absorption coefficient spectra show good agreement with theoretical HEM for the present glass system and the values of different parameters like $E_g, R, \Gamma_1, \Gamma_c,$ and $C_o$ have been estimated from fitting of this model. The values of energy band gap estimated from fitting of HEM with experimental data are in good agreement with those obtained from Tauc’s plot for direct transitions. The band gap energy is found to increase with increase of ZnO content. The decrease in values of Urbach energy with increase in ZnO content indicates a decrease in defect concentration in the glass matrix on addition of ZnO content. Optical constants $n$ and $k$ obey $k-k$ consistency and the dielectric response of the studied glass system is similar to that obtained for Classical Electron Theory of Dielectric Materials. The calculated values of the metallization criterion ($M$) show that the synthesized glasses may be good candidates for new nonlinear optical materials.

1. Introduction

Heavy metal oxides (HMO) based glasses have attracted the attention of researcher community for their excellent IR transmission as compared to conventional glasses [1, 2]. Among HMO, bismuth based oxide glasses exhibit extraordinary optical properties, due to which they have wide range of applications such as for optical switches, photonic and electronic devices, and reflecting windows [3, 4]. Bi$_2$O$_3$ is not a classical glass former, but it can form glass in the presence of other conventional glass formers like SiO$_2$, PbO, and B$_2$O$_3$. Bi$_2$O$_3$ plays the role of modifier with BiO$_6$ octahedral units and of glass former with BiO$_3$ pyramidal units. SiO$_2$ belongs to glass network former group that possesses strong Si-O bond. SiO$_2$ in its various amorphous forms has an extremely wide spectrum of industrial applications [5]. Bismuth-silicate glasses have special applications as low loss optical fibres, infrared-transmitting materials, or active medium of Raman-active fibre optical amplifiers and oscillators [6]. These glasses have high density, high refractive index, transmission in mid-IR region, high dielectric constant, third-order nonlinear susceptibility, and so forth [7–10]. These glasses have important applications in the field of glass ceramics, reflecting windows, layers for optical and electronic devices, plasma panel displays, thick film conductors, sealing glasses for metals, and so forth [10–14]. The structural and optical properties of Fe$_2$O$_3$, TiO$_2$, and MnO$_2$ modified bismuth silicate glasses have been extensively studied recently [15–18]. ZnO modified bismuth silicate glasses may be good candidates for many technological applications being ZnO a wide band gap ($E_g$) semiconductor having large exciton binding energy. ZnO works as intermediate group or network modifier group in the glass network system. Zinc oxide can be made versatile with broad applications through a proper doping process such as varistors, transparent dielectric, barrier ribs in plasma display panels, transparent-conducting electrodes, and piezoelectric as well as ferroelectric layers [19, 20].
The optical band gap of transparent glasses is generally estimated using Mott-Davis model, but in present study the optical band gap and other optical parameters have been studied in the light of Hydrogenic Excitonic Model (HEM).

2. Experimental Details

The glass samples in the system $40\text{SiO}_2 \cdot x\text{ZnO} \cdot (60-x)\text{Bi}_2\text{O}_3$, with $x = 0, 5, 10, 15, 20, 25, 30, 35, \text{and} 40$, were prepared by conventional melt-quench method using analar grade SiO$_2$, Bi$_2$O$_3$, and ZnO chemicals procured from Himedia having purity 99.5, 99.5, and 99 percent, respectively. The detail of preparation of samples has been reported elsewhere [21]. Glass samples were ground and polished so as to acquire the rectangular shape with thickness around 1 mm. Optical properties were studied using 3100 MC Shimadzu spectrophotometer in transmission mode as well as in reflection mode, at room temperature, in the spectral range 200–1400 nm. Reflectance, $R(\lambda)$, spectra of the prepared glass samples were recorded with the incident beam making an angle of 5.0° with the normal to the glass samples. Theoretical fitting of Elliott-Washington expression, that is, HEM to the experimental data, has been made by linear and nonlinear curve fitting modules of Origin Pro 8.6 software.

3. Results and Discussion

The spectral behaviour in transmittance ($T$) and reflectance ($R$) modes for all compositions of $40\text{SiO}_2 \cdot x\text{ZnO} \cdot (60-x)\text{Bi}_2\text{O}_3$, where $x = 0, 5, 10, 15, 20, 25, 30, 35, \text{and} 40$, have been recorded and are shown in Figures 1(a) and 1(b). The values of cut-off wavelength, $\lambda_{\text{cutoff}}$, of different glasses are estimated by extrapolation of linear region of the transmission curves to meet $\lambda$ axis and are listed in Table 1. The values of $\lambda_{\text{cutoff}}$ decrease with the increase in ZnO content. The values of absorption coefficient ($\alpha$) of the glass samples have been estimated using Beer-Lambert law [22]:

$$
\alpha = \frac{1}{L} \ln \left[ \frac{1}{2} \left( \frac{(1-R)^2}{T} + \sqrt{R^2 + \frac{(1-R)^4}{4T^2}} \right) \right],
$$

where $L$ is the sample thickness. The variations of absorption coefficient ($\alpha$) against wavelength ($\lambda$) for the different glass samples are shown in Figure 2(a). The band gap energy, $E_g$, is determined using Tauc’s relation [23]:

$$
\alpha \hbar \nu = B \left( \hbar \nu - E_g \right)^r,
$$

where $\nu$ is frequency, $h$ is Planck’s constant, and $r$ has different values, that is, 1/2, 2, 1/3, and 3 corresponding to direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions, respectively, in amorphous materials. The band gap energy can be estimated from $(\alpha \hbar \nu)^{1/r}$ versus $\hbar \nu$ plots by extrapolation of linear region of the curves to meet $\nu$ axis, that is, where $(\alpha \hbar \nu)^{1/r} = 0$. For the present glass system $r = 1/2$ is found to give best fit and it is shown in Figure 2(b). Thus, the present glass system shows direct allowed transitions and the values are listed in Table 1. The values of the band gap energy are found to increase with increase in ZnO content. This may be attributed to increase of bridging oxygen in the present glass system. The values of $\lambda_{\text{cutoff}}$ presented in Table 1 also agree with the trend followed by the band gap energy.

The shape of absorption spectrum of the present glass system is like that for the hydrogenic excitons formation.
Table 1: Cut-off wavelength ($\lambda_{\text{cutoff}}$), energy bandgap ($E_g$), and Urbach energy ($\Delta E$) of glasses of $40\text{SiO}_2 \cdot x\text{ZnO} \cdot (60-x)\text{Bi}_2\text{O}_3$ for different values of $x$.

| Parameter          | $x = 0$ | $x = 5$ | $x = 10$ | $x = 15$ | $x = 20$ | $x = 25$ | $x = 30$ | $x = 35$ |
|--------------------|---------|---------|----------|----------|----------|----------|----------|----------|
| $\lambda_{\text{cutoff}}$ (nm) | 434     | 432     | 430      | 430      | 430      | 427      | 427      | 415      |
| $E_g$ (eV)          | 2.79    | 2.88    | 2.91     | 2.92     | 2.94     | 2.95     | 2.96     | 3.00     |
| $\Delta E$ (eV)    | 0.22    | 0.19    | 0.24     | 0.19     | 0.24     | 0.21     | 0.22     | 0.20     |

Elliott [24] and Washington et al. [25] provided an explicit expression for the optical absorption due to bound and continuum excitons. An exciton is the bound state between an electron in the conduction band and a hole in the valence band. The excited states of an exciton can be considered as in hydrogen-atom-like model. Intrinsic parameters such as band gap and excitonic binding energy can be determined by fitting the absorption spectrum with an appropriate analytical model. The absorption coefficient ($\alpha$) introduced by Elliott-Washington model for hydrogenic excitons [HEM] is given as [24–29]

$$\alpha(E) = \frac{C_0 R^{1/2}}{E} \left\{ \sum_{m=1}^{\infty} \frac{2R}{m^3} \frac{\Gamma_m}{(E-E_m)^2+\Gamma_m^2} \right\} + \frac{1}{2} \left[ \frac{\pi}{2} + \arctan \left( \frac{\hbar \omega - E_g}{\Gamma} \right) \right] + \sum_{m=1}^{\infty} \frac{R}{m^3} \left\{ \frac{\Gamma_m}{(E-E_m)^2+\Gamma_m^2} + \frac{\pi}{2} \frac{\sinh (2u^+)}{\cosh (2u^+) - \cos (2u^-)} \right\},$$

where $C_0$ is the absorption strength parameter, $E_g$ is optical band gap, $E$ is the incident photon energy, $R$ is the excitonic binding energy, and $\Gamma_1$ and $\Gamma_c$ are the linewidths of the $m = 1$ state and of the continuum, respectively. Near the band edge, the first term gives rise to a single peak centred at energy $E_m = 1$ and approximately of width $\Gamma_1$. The rest of the terms represent the excitonic continuum and yield a step like absorption edge of width $\Gamma_c$ above the band gap.

$$u^\pm = \frac{\pi R^{1/2}}{2} \left[ \frac{(E-E_g)^2 + \Gamma_c^2}{(E-E_g)^2 + \Gamma_c^2} \right]^{1/2} \pm \left( E-E_g \right),$$

with $E_m = E_g - \frac{R}{m^2}$, $\Gamma_m = \Gamma_c - \frac{(\Gamma_c - \Gamma_1)}{m^2}$, $m = 1, 2, 3$,
Table 2: Values of band gap ($E_g$), excitonic binding energy ($R$), linewidths for $m = 1$ state ($\Gamma_1$), linewidth of continuum ($\Gamma_c$), and absorption strength ($C_o$) obtained from best fit to absorption spectrum using hydrogenic excitonic expression for $40\text{SiO}_2 \cdot x\text{ZnO} \cdot (60 - x)\text{Bi}_2\text{O}_3$ glass system.

| Compositions ($x$) | $E_g$ (eV) | $R$ (meV) | $\Gamma_1$ (meV) | $\Gamma_c$ (meV) | $C_o$ (eV$^{1/2}$/cm) |
|-------------------|------------|-----------|------------------|------------------|----------------------|
| 0                 | 2.81       | 3.00      | 25               | 137              | 450                  |
| 5                 | 2.88       | 3.01      | 25               | 55               | 942                  |
| 10                | 2.90       | 3.00      | 25               | 125              | 931                  |
| 15                | 2.91       | 3.15      | 25               | 54               | 877                  |
| 20                | 2.93       | 3.06      | 25               | 77               | 981                  |
| 25                | 2.94       | 3.07      | 25               | 54               | 858                  |
| 30                | 2.96       | 4.78      | 25               | 72               | 600                  |
| 35                | 3.00       | 3.40      | 25               | 56               | 822                  |

Figure 3: Fitting of absorption spectra using Hydrogenic Excitonic Model of $40\text{SiO}_2 \cdot x\text{ZnO} \cdot (60 - x)\text{Bi}_2\text{O}_3$ glass system (a) for $x = 0$, (b) for $x = 30$.

The values of parameters $E_g$, $R$, $\Gamma_1$, $\Gamma_c$, and $C_o$ have been estimated from the fitting of experimental data with the Hydrogenic Excitonic Model. The values of these fitting parameters obtained for all samples are listed in Table 2.

The best fit parameter $R^2$ is between 0.99 and 0.79, indicating thereby the good agreement between experimental data and theoretical model. The best fit of (3) to $\alpha(E)$ is shown in Figures 3(a) and 3(b) for compositions $x = 0$ and $x = 30$, respectively. So the optical transitions in the presently studied glasses are of hydrogenic excitonic excitations type. The values of energy band gap estimated from fitting of HEM with experimental data presented in Table 2 are in good agreement with those obtained from Tauc’s plot for direct transitions. Therefore, it may be concluded that the direct transition is most probable transition in the present glass system. The small values of exciton binding energy ($R$), listed in Table 2, lead to increase in the spatial separation between the electron and hole reducing the coulomb interaction between them [26, 29].

The Urbach energy ($\Delta E$) is used to characterize the degree of disorder in amorphous materials. The width of the band tails associated with valance and conduction bands was believed to be originated from electron transition between localized states, where the density of these localized states is exponentially dependent on energy [31]. The relation between $\Delta E$ and $\alpha(\nu)$ is given by empirical Urbach rule:

$$\alpha(\nu) = \text{constant} \times \exp\left(\frac{h\nu}{\Delta E}\right).$$

(5)

The relation can be rewritten as

$$\ln [\alpha(\nu)] = \frac{h\nu}{\Delta E} + \text{constant}. $$

(6)
\( \Delta E \) tells us about defect concentration as materials with large Urbach energy would have a greater tendency to convert weak bonds into defects. Its values were determined from the slope of the linear region of the curves between \( \ln \alpha(\nu) \) and \( h\nu \) as shown in Figure 4. The values of \( \Delta E \) are also listed in Table 1 and these values are in the range of 0.046 to 0.66 eV, which correspond to amorphous semiconductors as reported by Davis and Mott [32]. For the present glass system, the less value of Urbach energy indicates the possibility of decrease in the number of glass defects [33].

The refractive index (\( n \)) and extinction coefficient (\( k \)) have been calculated at different wavelengths as follows [34]:

\[
n = \frac{1 + R}{1 - R} + \sqrt{\frac{4R}{(1 - R)^2} - k^2},
\]

\[
k = \frac{\alpha\lambda}{4\pi}.
\]

The complex refractive index (\( n^* \)) can be written:

\[
n^* = n + ik,
\]

where \( n \) which is real part of complex refractive index is generally called refractive index and \( k \) which is imaginary part of complex refractive index is known as extinction coefficient or damping constant. The extinction coefficient is related to absorption of electromagnetic radiation in the medium and a nonzero extinction coefficient leads to an exponential decay of wave in the medium. Perusal of the data presented in Figure 5 shows that for the bump in \( k \) there is a wiggle in \( n \), which is an indication of \( k \)-\( k \) consistency in the optical constants [35].

The real (\( \varepsilon' \)) and imaginary (\( \varepsilon'' \)) parts of complex dielectric constant can be determined by the following relations [34]:

\[
\varepsilon' = n^2 - k^2,
\]

\[
\varepsilon'' = 2nk.
\]

The real part of complex dielectric is a measure of dielectric polarization and is proportional to it, whereas \( \varepsilon'' \) is often called the absorption product or absorption. The values of \( \varepsilon' \) and \( \varepsilon'' \) have been calculated by putting values of \( n \) and \( k \) in (9). The variations of \( \varepsilon' \) and \( \varepsilon'' \) with the energy of incident photon are shown in Figure 6. Perusal of the data presented in Figure 6 shows that the dielectric response of the studied glass system is similar to that obtained for Classical Electron Theory of Dielectric Materials (Bound Electrons) [36].

The metallization criterion was determined to characterize the nonlinear optical properties of the prepared glasses. The metallization criterion (\( M \)) of an oxide was determined on the basis of energy band gap (\( E_g \)) as follows [37]:

\[
M = 1 - \frac{R_m}{V_m},
\]

The values of \( 1 - R_m/V_m \) were determined from the relation suggested by Duffy [38] given in the following:

\[
E_g = 20 \left( 1 - \frac{R_m}{V_m} \right)^2,
\]

where \( R_m \) is molar refraction and \( V_m \) is molar volume of the prepared glass system. The oxide glasses with good optical nonlinearity possess a metallization criterion of approximately 0.30–0.45 [39]. The prepared glasses have metallization criterion in the range 0.38–0.39, which is the good basis for new nonlinear optical materials [26].

4. Conclusions

The absorption coefficient spectra show good agreement with theoretical Hydrogenic Exciton Model for the present glass system and the values of different parameters like \( E_g \), \( R \), \( \Gamma_1 \), \( \Gamma_o \), and \( C_o \) have been estimated from fitting of this model. The values of energy band gap estimated from fitting of HEM with experimental data are in good agreement with those obtained from Tauc’s plot for direct transitions. It has been found that the band gap energy increases with increase of ZnO content which may be attributed to formation of bridging oxygen in the prepared glass matrix. The values of Urbach energy show the decrease in defect concentration in the glass matrix with the addition of ZnO content. Optical constants \( n \) and \( k \) obey \( k \)-\( k \) consistency. Furthermore, the dielectric response of the studied glass system is similar to that obtained for Classical Electron Theory of Dielectric Materials. The calculated values of the metallization criterion (\( M \)) show that the synthesized glasses can be used as new nonlinear optical materials.
Figure 5: Variation of real ($n$) and imaginary ($k$) parts of refractive index with wavelength of 40SiO$_2$ $\cdot$ $x$ZnO $\cdot$ (60 $-$ $x$)Bi$_2$O$_3$ glass system for $x$ = 0, 5, 10, 15, 20, 25, 30, and 35 in (a), (b), (c), (d), (e), (f), (g), and (h), respectively.
Figure 6: Variation of real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of complex dielectric constants of $40\text{SiO}_2 \cdot x\text{ZnO} \cdot (60 - x)\text{Bi}_2\text{O}_3$ glass system for $x = 0, 5, 10, 15, 20, 25, 30,$ and $35$ in (a), (b), (c), (d), (e), (f), (g), and (h), respectively.
Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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