Investigation of optical and physical properties of zinc sodium bismuth borate glass system

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Abstract. A glass system with composition \( x\text{ZnO}-(15-x)\text{Na}_2\text{O}-15\text{Bi}_2\text{O}_3-70\text{B}_2\text{O}_3 \) (where \( x=0, 6, 8, 10, 12 \) mol %) have been prepared by conventional melt quenching technique in order to investigate the some physical and optical properties with impact of ZnO in the sodium bismuth borate glasses. The optical analysis of glass system is carried out by UV-Vis spectroscopic measurement technique. The optical study reveal that cut off wavelength and Urbach energy decreases while optical band gap increases with the addition of ZnO content. Further, the compositional dependence of different physical and optical parameters such as ion concentration, polaron radi, inter nuclear distance, molar refraction, molar polarizability, reflection loss, metallization criterion, refractive index and dielectric constant have also been evaluated.

Keywords. Optical Properties, Borate glass, UV-Vis. Spectroscopy, Band gap.

1. Introduction

Due to the valuable optical and physical properties, transition metal oxide glasses have become important in recent years. In glass networks zinc oxide has great relevance as it creates a wider band gap among semiconducting materials. For near ultraviolet and visible applications, it is considered as a reliable material [1, 2]. ZnO makes these glasses promising materials for photonic and optoelectronic applications. Depending upon the nature of bonding between metal and oxygen atom, ZnO can play the role of a modifier or a glass former. The study of adding ZnO to oxide glasses is also important due to their non-toxicity, non-hygroscopic nature, lower cost of production, higher polarizability and lower melting point [3]. Due to its high phonon energies, Boric oxide is a powerful glass former and flux material, higher bond strength and small cation size [4]. Keeping the temperature lower B\(_2\)O\(_3\) forms glass with good translucency, thermal stability and large chemical strength [5, 6]. In oxide glasses nonlinear optical applications are possible due to small field strength and large polarizability of Bi\(^{3+}\) ions [7-9] therefore the sodium bismuth borate glass doped with transition element can play an important role in photonic applications. Network formation and modification is a result of adding alkali and transition metal oxides to the bismuth-borate glass system [10]. The electronic polarization of oxide produces the optical nonlinearity when exposed to intense light beams which can be interrelated with several properties of materials such as electro-optical effect, conductivity and refractive index [11].

In the present studies, spectroscopic characterization of the \((15-x)\text{Na}_2\text{O}-15\text{Bi}_2\text{O}_3-70\text{B}_2\text{O}_3\) glass system doped with \( x = 0, 6, 8, 10 \) and 12 mol% of ZnO have been reported. The study includes the measurement...
of absorption spectra, band gap and urbach energy. Further, the different physical and optical parameters have also been evaluated.

2. Experimental details

2.1. Sample preparation

Glass samples were prepared by melt quenching technique. The framework of Zinc sodium bismuth borate was taken as $x\text{ZnO-(15-x) Na}_2\text{O-15Bi}_2\text{O}_3-70\text{B}_2\text{O}_3$ glass with ($x = 0, 6, 8, 10, 12$ mol%). The raw materials of ZnO, Na$_2$O, Bi$_2$O$_3$ and B$_2$O$_3$ were of analytic reagent (AR) grade. All the raw materials were weighed using electronic balance with precision of 1 mg and mixed together in pestle mortar with pestle and later put in alumina crucible. The alumina crucible was then placed in Muffle furnace at temperature with range 900-1000°C and kept for 1 hour till a bubble free liquid was formed. The sample was poured in a preheated graphite mould and immediately transferred to annealing furnace kept at 400°C for a period of 2 hours to remove internal stress. The glass sample formed after the annealing process was polished with sand papers of 1500, 1200 and 1000 grade and cerium oxide in order to acquire maximum flatness and smooth surface. The nomenclature and detailed composition of the glass system is tabulated in Table 1.

| Glass Code | ZnO | Na$_2$O | Bi$_2$O$_3$ | B$_2$O$_3$ |
|------------|-----|---------|-------------|------------|
| ZNBB1      | 0   | 15      | 15          | 70         |
| ZNBB2      | 6   | 9       | 15          | 70         |
| ZNBB3      | 8   | 7       | 15          | 70         |
| ZNBB4      | 10  | 5       | 15          | 70         |
| ZNBB5      | 12  | 3       | 15          | 70         |

2.2 Characterization and parameter calculations

2.2.1 UV Visible spectroscopy.

A double beam Shimadzu-2600 spectrometer in the wavelength region 300-800 nm was used to record the absorption spectra of the synthesized glass samples at room temperature. The optical absorption helps significantly in the analysis of electronic band structure and optically induced transitions of crystalline and amorphous materials. In amorphous system the band gap is nearly related to the gap of energy between valence and conduction bands. The conduction band is influenced by the glass forming anions while the role played by cations is different and important [12, 13].
The optical absorption coefficient of each curve was analysed by the given relation [14]:

$$\alpha(\omega) = \frac{2.303 A}{t}$$  \hspace{1cm} (1)

Where ‘t’ is the sample thickness and ‘A’ is absorbance. The proposed relation between absorption coefficient, $\alpha(\omega)$ and photon energy, $h\nu$ of the incident radiation [15-17] is written as follows:

$$\alpha(\omega) = \frac{B(h\nu - E_{opt})^n}{h\nu}$$ \hspace{1cm} (2)

Where $E_{opt}$ is the optical energy gap, $h\nu$ is the photon energy and ‘B’ is a constant called band tailing parameter and $n = 1/2$ and 2 for indirect allowed and direct allowed transitions [18].

The values of $(\alpha h\nu)$ as a function of $h\nu$ were plotted against one another. Using relation (2), $E_{opt}$ values were determined from the linear regions of the plots. The plots were extrapolated to intersect the energy axis at $(\alpha h\nu)^{1/n} = 0$ for indirect allowed and direct allowed band gap energies.

Urbach energy of prepared glasses were evaluated by the relation [19]:

$$\ln \alpha = C \exp\left(\frac{h\nu}{\Delta E}\right)$$ \hspace{1cm} (3)

2.2.2 Refractive index (n) and dielectric constant (\varepsilon), Reflection loss (R), molar refraction (Rm), molar polarizability (\alpha_m) and metallization (M).

Refractive index is one of the important feature of the glass and the factors affecting it are coordination number of the ion and the polarizability of the neighbouring ions correlated with anion. The refractive index of the glasses has been calculated from optical band gap energy given by the relation [20]:

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \frac{\sqrt{E_{opt}}}{20}$$ \hspace{1cm} (4)

The dielectric constant of the glass system was evaluated by the following relation [21]:

$$\varepsilon = n^2$$ \hspace{1cm} (5)

Reflection losses in the glass samples were calculated from refractive index using Fresnel’s relation [22]:

$$R = \left(\frac{n - 1}{n + 1}\right)^2$$ \hspace{1cm} (6)

Molar refraction, molar polarizability and metallization criterion is related to the glass structure and can be determined by Lorentz- Lorenz relation [14, 23-27]:

...
2.2.3. Ion concentration

The ion concentration of glass system was evaluated by following relation [29]:

\[
N = \frac{\text{Mol}\% \text{ of dopant} \times \text{density of glass} \times \text{Avogadro number} \times \text{ions}}{\text{Average molecular weight of glass}} \left( \text{cm}^{-3} \right) \tag{10}
\]

The density and molar volume of each sample were calculated by Archimede’s principle using benzene as an immersion liquid [28].

Some more parameters can be evaluated using ion concentration values.

Polaron radius

\[
r_p^o (\text{Å}) = \frac{1}{2} \left( \frac{\pi}{6N} \right) \tag{11}
\]

Inter-nuclear distance

\[
r_i^o (\text{Å}) = \frac{1}{2} \left( \frac{1}{N} \right) \tag{12}
\]

Field strength

\[
F = \frac{Z}{(r_p^o)^2} \tag{13}
\]

3. Results and discussion

The X-Ray studies have already been undertaken in our previous work which indicate the amorphous nature as well as long range structural disorder of the studied glass samples [28]. The variation of optical absorption of sample ZNBB2 with respect to wavelength of UV- Vis is shown in Fig.1. The cutoff wavelength values of the prepared glass samples are shown in Table 2. With change in ZnO concentration, the absorption edge and cutoff wavelength shifted towards lower wavelength. This can be attributed to the number of bridging oxygen enhancement (BO). The BO’s bind an excited electron tightly than a non bridging oxygen (NBO), thereby making structure more stable which increases the value of $E_{opt}$ and therefore shift towards lower cutoff wavelength is observed. Fig. 2 and 3 shows the evaluation of indirect band gap for the sample ZNBB2 and the data of all the glass samples is depicted in Table 2. It is noted that
the band gap energy increases with the rise of ZnO concentration. The band gap of prepared glass samples was evaluated by the same manner. The variation of band gap energy shows that there is slight increase in band gap energy on addition of ZnO concentration. On addition of ZnO, no major structural changes take place in spite of slight increase in intensity of these structural units. These results confirm that ZnO involves in the present glass system in the form of network former and not as network modifier [30]. It is well established that fairly large band gap energy is found in borate glasses having no modifiers and blocking of formation of non bridging oxygen takes place.

Table 2: Physical and optical properties of ZNBB glasses

| Parameters                          | ZNBB1 | ZNBB2 | ZNBB3 | ZNBB4 | ZNBB5 |
|-------------------------------------|-------|-------|-------|-------|-------|
| Density (gm/cm³)                    | 3.75  | 3.97  | 3.99  | 4.08  | 3.99  |
| Molar Volume(cm³/mol)               | 34.04 | 32.50 | 32.37 | 31.81 | 31.38 |
| \(N\times10^{24}\)ions/cm³          | -     | 0.11  | 0.14  | 0.18  | 0.21  |
| \(r_p\times10^{-8}\) Å              | -     | 0.83  | 0.76  | 0.70  | 0.67  |
| \(r_i\times10^{-8}\) Å              | -     | 2.07  | 1.89  | 1.74  | 1.66  |
| \(F\times10^{16}\) cm²              | -     | 2.90  | 3.46  | 4.08  | 4.46  |
| Refractive index (n)                | 2.40  | 2.39  | 2.34  | 2.32  | 2.30  |
| Dielectric constant (\(\varepsilon\)) | 5.76  | 5.71  | 5.47  | 5.38  | 5.32  |
| Reflection loss (R)                 | 0.168 | 0.168 | 0.16  | 0.157 | 0.154 |
| Metallization (M)                   | 0.30  | 0.29  | 0.30  | 0.31  | 0.31  |
| Molar refractivity \(R_m\)(cm⁻³)     | 23.82 | 22.81 | 22.37 | 21.84 | 21.76 |
| Molar polarizability \(a_m\)(Å³)    | 0.944 | 0.904 | 0.887 | 0.866 | 0.902 |
| Cut-off wavelength (nm)             | 351   | 348   | 346   | 341   | 339   |
| Indirect band gap (eV)              | 2.93  | 3.01  | 3.12  | 3.25  | 3.30  |
| Direct band gap (eV)                | 3.10  | 3.29  | 3.11  | 3.41  | 3.47  |
| Urbach energy (eV)                  | 0.37  | 0.29  | 0.30  | 0.16  | 0.14  |

The continuous reduction in the concentration of non bridging oxygen (NBO) is related to increase in ZnO and this aspect give rise to a possible increase in bridging oxygen. Instead of NBOs; bridging oxygen are more excited, therefore with the increase of ZnO concentration; there is slight increase in the value of \(E_{\text{opt}}\).
Urbach energy characterizes the strength of disorder in amorphous and crystalline solids. The greater tendency of converting weak bonds into defects is given by the materials which have large value of $\Delta E$.

Figure 1. Optical absorption spectra of ZNBB2 glass system
Figure 2. Indirect band gap of ZNBB2 glass system
Figure 3. Direct band gap of ZNBB2 glass system
Figure 4. Urbach energy of ZNBB2 glass system

The electron transitions occurred between the different localized states introduce the band tail width ($\Delta E$) related with the valence and conduction bands; where the density of localized states is exponentially based on energy [31]. It has been reported that distinct structures have identical physical origin as per the observations of experimental tail in various materials; which is ascribed to the photon assisted indirect electron transitions [32, 33]. The reciprocal of slope of $\ln \alpha$ versus energy curve gives the value of Urbach energy as displayed in Fig 4. The measured values of $\Delta E$ for the ZNBB glass system are depicted in Table 2. The value of refractive index lies between 2.40 to 2.30. It can be seen from the Fig. 5 that the refractive index reduces with increase of $E_{opt}$. 
From Herzfeld theory of metallization, metallization criterion decides whether ZNBB glass system is metallic or insulator. If \( R_m/V_m > 1 \), the material shows metallic nature, and if \( R_m/V_m < 1 \), the material exhibits insulating nature [34]. The metallization parameter values of present glasses are listed in Table 2. The given set of values suggests that the present glass system act as non-metals.

For further clarification on structural changes produced by ZnO in sodium bismuth borate glasses. It is seen from Table 2 that increase in ion concentration decreases the polaron radius and internuclear distance with the enhancement of ZnO contentand there is a decrease in distance between Zn and O atoms in the glass system which leads to increase the Zn–O bond strength. As a consequence of increased bond strength there is stronger field strength around Zn\(^{2+}\) ions and hence the stronger field strength supports the density results of previous work done by other authors [35, 36].

**Conclusion**

The study of optical and physical properties of zinc sodium bismuth borate glass system was undertaken. The samples were made by standard melt quenching technique. Physical parameters such as ion concentration, polaron radius, inter-nuclear distance and field strength have been evaluated. The band gap increases and urbach energy decreases with the inclusion of ZnO content. Different optical parameters such as refractive index, dielectric constant, molar refraction, molar polarizability, reflection loss and metallization criterion were also calculated. It is observed that with increase in the ZnO content there is variation in the different calculated parameters.
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