Synthesis and Characterization of Cadmium Containing Sodium Borate Glasses

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ABSTRACT

Glass system (80% B₂O₃ – (20 – y)% Na₂CO₃ – y% CdO, where y = 3, 6, 9, 12 and 15 mol%) prepared by meltquenching technique and checked by XRD technique reveals the amorphous nature of these glasses. Increases in density from 2.18 to 2.82 (g/cm³) were observed with an increase in CdO content. Ultraviolet-Visible (UV-VIS) absorption spectra of polished parallel surfaces glass samples showed a decrease in the optical band gap from 3.72 to 3.59 eV with increasing CdO content. The results suggest that CdO content in glass samples plays a role as a network modifier. In addition, a correlation between the results from density, UV-VIS and FTIR measurements indicates that change in the atomic structure is due to the formation of BO₄ units.

Keywords: Sodium Borate Glasses; Optical Band Gap; Molar Volume; UV-VIS and FTIR Spectroscopy and Bandgap Energy

1. Introduction

In recent years, the physical, electrical, optical mechanical and magnetic properties of pure and various transition and rare earth metal ions doped borate glasses are under investigation. Semiconducting glasses can be generally divided into two groups, chalcogenide glasses and oxide glasses, containing transition metal ions. Oxide glasses containing transition metals such as cadmium, copper, etc. exhibit semiconducting properties [1-8]. These glasses are potential candidates for electrical memory and optical switching devices [9-11], cathode materials for making solid devices and optical fiber [12-14]. Glasses containing high concentration of transition metal ions are electronic conductors [15-17]. This classifies them as a form of amorphous semiconductors.

The borate glasses are quite useful as they are relatively easy to obtain and moreover, there appears a large variety of structural units in their over a wide range of modifier concentration [18-19]. In borate glasses, B₂O₃ is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and valence 3 of B. In borate glasses, B⁴⁺ ions triangularly coordinated by oxygen form glasses easily. In B₂O₃ the units are triangles, which are corner bonded in a random configuration [20]. The addition of sodium carbonate helps in forming BO₄ groups and non bridging oxygen.

In the present work, an attempt has been made for the preparation and optical characterization of sodium borate glasses with the addition of cadmium oxide. To study the short range structure of glasses i.e. the immediate surroundings of the absorbing atoms, we use the UV-VIS absorption spectra of the samples. Also, the optical properties of solids depend on the nature and local arrangement of the constituent atoms or ions. We report the molar volume, IR spectra and UV-VIS spectra of the glass samples.

2. Experimental Techniques

2.1. Sample Preparation

The glass samples {80% B₂O₃ – (20 – y)% Na₂CO₃ – y% CdO, here y = 3, 6, 9, 12 and 15 mol%} were prepared by weighing the appropriate amounts of chemically reagent grade powders of CdO, here y = 3, 6, 9, 12 and 15 mol%} were prepared by weighing the appropriate amounts of chemically reagent grade powders of CdO, and B. The chemical composition of the prepared glasses is listed in Table 1.

Table 1. Composition of Prepared Samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>CdO (%)</th>
<th>Na₂CO₃ (%)</th>
<th>B₂O₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>17</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>14</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>11</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>5</td>
<td>80</td>
</tr>
</tbody>
</table>

*Percentage by weight used.
Melting was performed in porcelain crucibles placed in an electric furnace for about 2 h at temperatures ranging from 973°C - 1100°C. The homogenized molten glass was cast in graphite blocks. After quenching the glass, all the samples were immediately transferred to annealing furnace. All the samples were annealed at 400°C.

In order to confirm the amorphous nature of the glass samples, X-ray diffraction (XRD) study was made on each glass sample using Rigaku Mini-flex Table Top spectrometer with Cu-Kα line of wavelength $\lambda = 1.5418$ Å at the scanning rate of 20/min and $2\theta$ was varied from 10° to 80°.

The density of glass samples at room temperature was measured by the standard principle of Archimedes using a sensitive microbalance with pure benzene as the immersion fluid. The density was calculated according to the known formula

$$d = \frac{W_a}{(W_a - W_b) \times D}$$

(1)

where $W_a$ is the weight of the sample in air, $W_b$ is the weight of the sample in benzene and $D$ is the density of buoyancy at room temperature. All the measurements were made using a digital balance (M/S Sartorius, model BP 221S, USA). The experiment was repeated five times to get an accurate value of density. The overall accuracy in the density measurements was ±0.5 kg·m⁻³ and hence, the percentage error in the measurements of density was ±0.006 g·cm⁻³.

The molar volume values were calculated by using the obtained densities and weight of one mole of the sample, with the help of the following equation:

$$V_m = \sum \frac{M_i}{d}$$

(2)

$M_i$ denotes the molar mass of the glass and $M_i = C_iA_i$. Here $C_i$ and $A_i$ are the molar concentrations and molecular weights of the $i$th component, respectively and $d$ is measured density.

3. Results and Discussion

3.1. XR Diffraction Analysis

The powder XR diffraction analysis of some of the prepared samples is shown in Figure 1. This figure exhibits no detectable peaks thus confirms the amorphous nature of the glass samples.

![Figure 1. XRD of the samples for different glass compositions.](image-url)
3.2. Density and Molar Volume

The density measurement is considered to be a very important tool to detect the structural changes in the glass-network. The density is supposed to change abruptly when the structure of the glass is slightly changed. On the other hand, the molar volume of glass can be preferably used to describe the network structure and the arrangement of the building units, since it deals directly with the spatial structure of the oxygen network. The density and calculated molar volume values are shown in Table 2.

The network formed by primary glass forming oxides such as B$_2$O$_3$ contains a large no. of interstices and with addition of network modifiers density increases. In the present study also, density is observed to increase with the increase of CdO content. This increase can be attributed to conversion of BO$_3$ into 4-fold coordinated boron atoms as BO$_4$. The increase in density may be because of replacement of low density sodium element (0.97 gm·cm$^{-3}$) by high density cadmium element (8.65 gm·cm$^{-3}$) [21]. Also non-bridging oxygen decreases in the glass network with increasing CdO content, which tends to consolidate their structure, maintaining homogeneity of the glasses and thus increasing density [22]. All these observations verify the role of CdO as network modifier. Molar volume indicates the spatial distribution of the oxygen in the glass network. The decrease in the molar volume can be attributed to closing up of structure of glasses. Increase in CdO content leads to substitution of longer ionic Na-O bond with shorter covalent bond i.e. the formation of B-O-B linkages with strong covalent B and Cd oxygen bond, leading to close structure [23].

3.3. FTIR Analysis

For structural analysis of oxide glasses the following information is required [24]:

1) Type of the bridging bonds of oxygen which link the coordination polyhedra of framework and the composition of chemical inhomogeneities in the structure of glass;
2) The coordination number of the compound with respect to oxygen, especially of network formers;
3) The change in oxygen bonds of the framework, induced by the cations modifiers which combine with those bonds.

Borate glasses provide an ideal case, in comparison to other glass forming systems, to demonstrate the effectiveness of infrared spectroscopy in glass science [25]. Boron has smallest mass as compared to the other network forming elements, and thus the main vibrational modes associated with the glass network appear well above 500 cm$^{-1}$ (in the mid-infrared region) [26]. These network modes are well separated from the metal ion site vibrational modes which are active in the far infrared region [27-29]. The ability of boron to change its coordination number with oxygen between three and four provides a range of anionic environment that can coordinate the modifying metal ions.

In the present glass system, predominantly 8 bands are observed (Figure 2). The band 540 - 580 cm$^{-1}$ is due to vibrations of sodium cations through the glass network. The band 640 - 675 cm$^{-1}$ can be attributed to bending vibrations of BO$_3$ triangles and stretching vibrations of BO$_3$ units with non bridging oxygens respectively. The band around 740 cm$^{-1}$ can be due to vibration of the linkage between tetrahedral and triangle borate groups. The band 850 - 885 cm$^{-1}$ can be attributed to stretching vibration of B-O bond of BO$_2$ units. The shoulder in the band 1076 cm$^{-1}$ appears to shift at higher energy on going to sample No. 6. This may be due to vibrations of diborate bridging to pentaborate groups, and to the asymmetric and stretching vibrations of BO$_3$ groups [25]. A prominent band appeared at 1187 cm$^{-1}$ which seems to be absent in sample with lowest cadmium oxide concentration indicates that there is formation of four co-ordinated boron units with the addition of cadmium oxide which is also in accord with the observed results for density.

The band 1450 - 1510 cm$^{-1}$ can be assigned to B-O stretching vibrations mainly due to the linkage between oxygen and different groups as well as B-O bridging between boroxol rings and trigonal BO$_3$ [2,20]. The bands around 1650 cm$^{-1}$ and 2333 cm$^{-1}$ are attributed to O-H bending that give rise to absorption in this region and the possibility of some adsorbed water.

![Figure 2. FTIR spectra of glass samples for different contents of CdO.](image)
3.4. Optical Band Gap

Analysis of optical spectra is one of the most beneficial tools to figure out the electronic structures of amorphous semiconductors [30]. Measurement of the optical absorption coefficient (α) near the fundamental absorption edge is particularly a standard method for the investigation of optically induced electronic transitions in many materials. Two types of optical transitions, i.e. direct and indirect, occur at the absorption edge [31]. The absorption coefficient, below and near the edge of each curve was determined at different wavelengths using relation:

$$\alpha(\nu) = \frac{1}{I} \ln \left( \frac{I_0}{I} \right)$$  \hspace{1cm} (3)

where $I_0$ and $I$ are intensities of the incident and transmitted beams, respectively and $t$ corresponds to thickness of each sample. Optical band gaps were calculated using absorption spectra for direct and indirect transitions for all prepared glass samples.

For direct transitions:

$$\alpha(\nu) = B(\nu - E_{\text{opt}})^n / \nu$$  \hspace{1cm} (4)

where $n = 1/2$ for allowed transition, $B$ is a constant and $E_{\text{opt}}$ is direct optical band gap.

Above relation is also used for indirect transitions. In this equation, $n = 2$ for allowed transition, $B$ is a constant and $E_{\text{opt}}$ is indirect optical band gap. Using above equations and by plotting $(\alpha \nu)^{1/2}$ and $(\alpha \nu)^2$ as a function of photon energy $\nu$, optical band gaps for indirect and direct transitions could be found, respectively. The respective values of $E_{\text{opt}}$ were obtained by extrapolating to $(\alpha \nu)^{1/2} = 0$ for indirect transitions and $(\alpha \nu)^2 = 0$ for direct transitions [32].

Urbach energy values ($\Delta E$) were calculated by taking the reciprocals of the slopes of linear portion in the lower photon energy region of these curves as stated with relation (5) [33].

$$\alpha(\nu) = \alpha_0 \exp(\nu / \Delta E)$$  \hspace{1cm} (5)

Figures 3-5 show the plots for indirect band gap, direct band gap and Urbach energies for the prepared samples and their values are listed in Table 3. It is noticed that $E_{\text{opt}}$ decreases with increasing CdO content. Decrease in bandgap is also reported to be due to formation of four coordinated boron units which is also implied by observed band at 1187 cm$^{-1}$ of FTIR spectra. There must be some change in bonds which is reflected by lowering of band gap values. The noticed change may also arise from the photon-lattice interaction. The decrease in bandgap is also due to decrease of NBO and also the formation of bridging oxygen that changes the absorption characteristics. This also is in accord with our results for density i.e. the formation of BO$_4$ units at the expense of BO$_3$ units.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO %</td>
<td>3</td>
<td>6</td>
<td>9</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Direct bandgap (eV)</td>
<td>4.69</td>
<td>4.52</td>
<td>4.48</td>
<td>4.42</td>
<td>4.39</td>
</tr>
<tr>
<td>Indirect bandgap (eV)</td>
<td>3.72</td>
<td>3.70</td>
<td>3.66</td>
<td>3.61</td>
<td>3.59</td>
</tr>
<tr>
<td>Urbach energy (eV)</td>
<td>0.73</td>
<td>1.12</td>
<td>0.47</td>
<td>0.91</td>
<td>0.75</td>
</tr>
</tbody>
</table>
4. Conclusion

The prepared samples were found to be in pure non crystalline phase. The density of the glass samples increases gradually on increase of CdO content. The molar volume appears to decrease due to closing up of structure of glasses. The groups like BO3 and BO4 act as network structural groups while sodium and cadmium appeared in interstitial positions. The optical energy gap ($E_{opt}$) for indirect allowed transitions showed a decrease with increasing the CdO content. The studied glass systems obey bandgap energy measurements are in agreement with results obtained from the density, FTIR spectroscopy and magnetic susceptibility studies of Vanadium Phosphate Glasses.

REFERENCES


