Physical and Structural Characterization of Manganese Ions Doped SrO-Li₂O-CaO-B₂O₃ (SLCB) Glasses

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Abstract: The physical and structural characterization of 0.1 mol% MnO doped x SrO+ (20-x) Li₂O+ (10-y) CaO+70B₂O₃+y, (5≤x≤15) mol% glass systems (SLCB) are synthesized and studied. Various physical parameters are evaluated for the glasses under study. The glassy nature of all the SLCB glasses is confirmed from X-ray diffractograms (XRD). The various assignments are given in the Fourier Transform Infrared spectra (FT-IR).

Keywords: XRD, FT-IR Spectra

1. Introduction

In comparison, among the other oxide glass forming systems, Borate glasses provide an ideal case to demonstrate the effectiveness of UV-visible, infrared spectroscopy in glass science. Borate is one of the most important glass forming oxides and has been incorporated into various kinds of glass systems to obtain required physical and chemical properties. Borate glasses (B₂O₃) are easily melted and are good hosts for transition metals ions. Hence when glasses are doped with transition metal ions, they will become suitable for many practical applications. The properties of glasses have been established in terms of the stereo chemical environment that they provide and the oxidation number that they favor for the transition metal ions [1]. These properties can change according to the alkali oxide or modifiers content [2]. With the earlier elements in the first transition series it is found that increasing the alkali oxide content, tends to favor upper oxidation state, for example chromium favors the +3 state in low alkali borate glasses and the +6 state in the high alkali content [3]. Even when there is no change in oxidation number, there can be a change in stereochemistry or coordination as in the case of cobalt (II) which transforms from octahedral to tetrahedral as the alkali oxide content is increased [4]. Another advantage of borate glasses is when compared with other network forming elements boron has the smallest mass and thus the main vibrational modes associated with the glass network appear well above 500 cm⁻¹ in the mid-infrared region [5]. These network modes are well separated from the metal ion site and vibrational modes active in the far-infrared region, i.e., below 600 cm⁻¹ [6–8]. Borates have the ability to change the boron coordination with oxygen between three and four to certain limit and this provides a range of anionic environments that can coordinate the modifying metal ions. Recently, the interest in borate glasses has been renewed in views of the fast conductive properties exhibited by some of these glasses containing transition metal ions [9, 10]. This glass system is important in laser and infrared detection applications [11]. Borate glasses containing transition metal oxides are very useful materials for the radiation dosimetry applications in view of the fact that their effective atomic number is very close to that of human tissue [12].

2. Experimental

2.1 Synthesis of xSrO+ (20-x) Li₂O+ (10-y) CaO+70B₂O₃+y MnO glasses

The starting materials SrCO₃, Li₂CO₃, CaO, H₂BO₃ and MnO, used in the preparation of the glasses are of analar grade (AR). The batch compositions of the glasses studied in the present work are listed in Table 1.

<table>
<thead>
<tr>
<th>Glass System</th>
<th>Glass Code</th>
<th>Glass chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLCB₀</td>
<td>M₀</td>
<td>10 SrO+10 Li₂O+10 CaO+70 B₂O₃+</td>
</tr>
<tr>
<td>SLCB₁</td>
<td>M₁</td>
<td>5 SrO+15 Li₂O+9.9 CaO+70 B₂O₃+0.1 MnO</td>
</tr>
<tr>
<td>SLCB₂</td>
<td>M₂</td>
<td>10 SrO+10 Li₂O+9.9 CaO+70 B₂O₃+0.1 MnO</td>
</tr>
<tr>
<td>SLCB₃</td>
<td>M₃</td>
<td>15 SrO+5 Li₂O+9.9 CaO+70 B₂O₃+0.1 MnO</td>
</tr>
</tbody>
</table>

The chemicals are weighed accurately, mixed thoroughly and ground to fine powder. The batches are melted in air in an electrical furnace at 950°C for 20 min. The melts are then poured onto the surface of a polished brass plate and pressed with another brass plate. The formed glasses are annealed at 400°C for about 1 h to make the glasses free from the structural stress and cooled to room temperature. Translucent glasses are obtained.

2.2 Measurements

Using the Archimedes principle with xylene (99.99% pure) as inert buoyant liquid, the density (ρ) of the prepared glass samples are determined with a precision of ±0.001g/cm³. For recording the x-ray diffractograms of glass samples prepared...
are taken in powder form and done using XRD-6100 (Shimadzu) diffractometer with Copper Kα radiation. The infrared spectra were recorded in the wave number range 400-2000 cm⁻¹ using IR Affinity-1s (Shimadzu) spectrometer using KBr pellet technique at room temperature.

3. Results and Discussion

3.1 Physical Parameters

Using conventional formulae [13], density (ρ) of the synthesized glass samples, total molecular weight M of glass samples, various physical parameters such as transition metal ion concentration (Manganese ion), mean separation (r₁), polaron radius (r_p), and Optical basicity (Λ_th) values are determined.

3.11 Optical Basicity

The optical basicity of an oxide glasses can be conveniently measured in terms of the ability of the glass to donate a negative charge to an acidic probe ion [14-17]. Duffer and Ingram [18] reported that the optical basicity can be predicted from the composition of the glass and the basicity moderating parameters of various cations present. The theoretical values of optical basicity (Λ_th) of the SLCB glasses can be estimated using the formula,

\[
(\Lambda_{\text{th}}) = \frac{\sum Z_i r_i}{2 \gamma_i}
\]

where ‘n’ is the total number of cations present. Z_i is the ‘i’ is the oxidation number of the i_th cation to the number of oxides present and ‘γ_i’ is the basicity moderating parameter of the i_th cation. The basicity moderating parameter ‘γ_i’ can be calculated from the following equation

\[
\gamma_i = 1.36(x_i - 0.26)
\]

where x_i is the Pauling electro negativity of the cation [19]. The theoretical optical basicity values computed for the glasses in the present study are given in Table 2.

### Table 2: Physical parameters of Manganese ions doped in SLCB glasses

<table>
<thead>
<tr>
<th>Physical Parameters (Units)</th>
<th>Glass System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SLCB₀</td>
</tr>
<tr>
<td>Average molecular weight(M)(g/mol)</td>
<td>67.69</td>
</tr>
<tr>
<td>Density (gr/cc)</td>
<td>2.65</td>
</tr>
<tr>
<td>Transition metal ion (N_i) Concentration (10^19 ions/cc) (±0.005)</td>
<td>.....</td>
</tr>
<tr>
<td>Inter ionic distance (r_i)(Å)(±0.005)</td>
<td>.....</td>
</tr>
<tr>
<td>Polaron radius (r_p)(Å)(±0.005)</td>
<td>.....</td>
</tr>
<tr>
<td>Optical basicity (Λ_th)</td>
<td>0.43</td>
</tr>
</tbody>
</table>

It is observed that for the Λ_th values gradually increases from SLCB₀ to SLCB₃.

3.2 X-ray Diffraction Study (XRD)

The X-ray diffraction spectra have not shown any sharp peaks, indicating that the samples prepared are amorphous in nature are shown in Figure 1.

### Figure 1: Powder X-ray diffraction patterns of undoped and Manganese ions doped SLCB glasses

3.6 FT-IR Studies

The FT-IR transmission spectrum is shown in Figure 2.

### Figure 2: FT-IR spectra of Manganese ions doped SLCB glasses

The assignments of various absorption bands are given in Table 3.

The IR spectra have been divided into three spectral regions. The first group of band is reported to occur from 1200-
1600 cm\(^{-1}\) which arise due to the asymmetric stretching vibrations triangular BO\(_3\) units. The second group of bands region is from 800-1200 cm\(^{-1}\) which was assigned to the stretching vibrations of tetrahedral BO\(_4\) units. The third group observed around 700 cm\(^{-1}\) and was attributed to bending of B-O-B linkages in the networks. The band at 900 cm\(^{-1}\) was a characteristic of glass with high boric acid content i.e. due to boroxil rings [20].

Table 3: Assignments of absorption bands in the FTIR spectra of Manganese ions doped in SLCB glasses

<table>
<thead>
<tr>
<th>M(_0)</th>
<th>M(_1)</th>
<th>M(_2)</th>
<th>M(_3)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>-</td>
<td>436</td>
<td>427</td>
<td>Ca-O stretching mode of BO(_3) units.</td>
</tr>
<tr>
<td>462</td>
<td>471</td>
<td>-</td>
<td>460</td>
<td>Ca-O(_2) stretching mode of BO(_3) units.</td>
</tr>
<tr>
<td>509</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Ca-O stretching mode of Borate units.</td>
</tr>
<tr>
<td>570</td>
<td>-</td>
<td>565</td>
<td>-</td>
<td>Ca-O stretching mode of Borate units.</td>
</tr>
<tr>
<td>687</td>
<td>692</td>
<td>689</td>
<td>692</td>
<td>B-O-B bending vibrations.</td>
</tr>
<tr>
<td>-</td>
<td>977</td>
<td>973</td>
<td>975</td>
<td>Boroxil ring vibrations.</td>
</tr>
<tr>
<td>1015</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>B-O-B stretching vibrations of BO(_2) units.</td>
</tr>
<tr>
<td>1109</td>
<td>1113</td>
<td>1087</td>
<td>1085</td>
<td>Pyro-borate units, meta borate units.</td>
</tr>
<tr>
<td>1263</td>
<td>1235</td>
<td>1237</td>
<td>1237</td>
<td>Stretching vibrations B-O' bonds in BO(_3) units from pyro-ortho borate group's</td>
</tr>
<tr>
<td>1385</td>
<td>1364</td>
<td>1366</td>
<td>1369</td>
<td>Stretching vibrations of B (III)-O-B (IV) units.</td>
</tr>
</tbody>
</table>

The FT-IR spectrum of the undoped glass system contains three major broad bands with some shoulders in the wavenumber range of 400 cm\(^{-1}\) - 460 cm\(^{-1}\), 500 cm\(^{-1}\) - 600 cm\(^{-1}\). These bands are the characteristics band vibrations of the calcium-oxygen. When Li\(_2\)O is incorporated in the glass, some of borons become tetrahedrally coordinated. The spectrum of fused B\(_2\)O\(_3\) consists of a completely continuous triangle like coordinated network and also contains some BO\(_3\) tetrahedral coordination. The band which lies in the region 800 cm\(^{-1}\) - 1200 cm\(^{-1}\) splits into two broad bands whose intensity increases with increase in mol% of SrO and decrease of mol% of Li\(_2\)O content. In the undoped glass with x=5 mol% SrO and 15 mol% Li\(_2\)O a shift in vibrational band at 1385 cm\(^{-1}\) is noticed with feeble increase in intensity. When x=10 mol% SrO and Li\(_2\)O, Li\(_2\)O causes a shift in the vibrational band from 1364 cm\(^{-1}\) to 1366 cm\(^{-1}\) with a noticeable increase in intensity of these peaks. Another band at 1235 cm\(^{-1}\) with x=10 mol% SrO and x=10 mol% Li\(_2\)O is assigned to stretching vibrations of B-O bonds in BO\(_3\) units from pyro-ortho borate groups. The bands 1109 cm\(^{-1}\), 1113 cm\(^{-1}\), 1087 cm\(^{-1}\) and 1085 cm\(^{-1}\) are assigned B-O stretching vibrations of tetrahedral BO\(_4\) units in tri-borate, tetra borate and penta borate groups [21]. The bands at 977 cm\(^{-1}\), 973 cm\(^{-1}\), and 975 cm\(^{-1}\) are assigned to Boroxil ring vibrations. The bands 687 cm\(^{-1}\), 682 cm\(^{-1}\), 689 cm\(^{-1}\) and 692 cm\(^{-1}\) corresponds to B-O-B bending [22]. The bands 570 cm\(^{-1}\), 565 cm\(^{-1}\), 590 cm\(^{-1}\) are due to stretching vibrations of CaO stretching mode of Borate units [23]. The absorption bands 462 cm\(^{-1}\), 471 cm\(^{-1}\), 460 cm\(^{-1}\) and 420 cm\(^{-1}\), 436 cm\(^{-1}\), 427 cm\(^{-1}\) corresponds to Ca-O\(_3\) stretching mode of BO\(_2\) units [24]. It is observed that on increasing of SrO content, the frequency bands shifts from higher to lower wavenumber, which suggests the formation of non bridging oxygen (NBO’S) i.e. conversion of BO\(_3\) to BO\(_4\) structural units. The formation of NBO’S indicates that the addition of Lithium oxide (Li\(_2\)O) in SLCB glasses act as a modifier.

4. Conclusion

From the physical and optical characterization of 0.1 mol% of Manganese ions doped xSrO + (20x) Li\(_2\)O + (10-y) CaO + 70B\(_2\)O\(_3\) + y glasses with (5 ≤ x ≤ 15mol%) the following conclusions are drawn.

i. The density values are found to decrease with increase of SrO mol% or with decrease of Li\(_2\)O mol%. The density of undoped glass and the glass doped with Manganese oxide with 10 mol% of SrO and Li\(_2\)O are observed to be nearly equal.

ii. Powder XRD diffractograms confirm the glassy nature of the glasses under investigation.

iii. When x=5mol% of SrO and x=10 mol% Li\(_2\)O from the FT-IR spectra, the glass matrix is stable.

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References


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