List of Publications

1) Gamma ray induced changes on vibrational spectroscopic properties of strontium alumino-borosilicate glasses
   
   A. Rupesh Kumar, T.G.V.M. Rao, K. Neeraja, M. Rami Reddy, N. Veeraiah
   

2) The effect of manganese oxide on the properties and structure of strontium aluminium borosilicate glasses
   
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3) Optical and structural investigation of trivalent Dy\(^{3+}\)-Nd\(^{3+}\) co-doped in magnesium lead borosilicate glasses.
   

4) Spectroscopic properties of Sm\(^{3+}\) and V\(^{4+}\) ions in Na\(_2\)O-SiO\(_2\)-ZrO\(_2\) glasses
   

5) Optical and structural investigation of trivalent Eu\(^{3+}\)-Nd\(^{3+}\) co-doped in magnesium lead borosilicate glasses.
   

6) Optical and structural investigation of trivalent Samarium ions and Nd\(_2\)O\(_3\) co-doped in magnesium lead borosilicate glasses.
   
   T. G. V. M. Rao, A. Rupesh Kumar, N. Veeraiah, M. Rami Reddy
   
7) Spectroscopic studies of tungsten ions in PbO-PbF$_2$-SiO$_2$ glasses.
   T. G. V. M. Rao, A. Rupesh Kumar, M. Rami Reddy

8) Spectroscopical splitting of Cu ion energy levels in magnesium lead fluoro silicate glasses.
   T. G. V. M. Rao, A. Rupesh Kumar, Ch. Kalyan Chakravarthi,

9) Optical absorption, ESR, FT-IR spectral studies of iron ions in lead oxyfluoro silicate glasses.
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10) The Spectroscopic Properties of Mo$^{5+}$ in ZnO-ZnF$_2$-B$_2$O$_3$ Glass
    K. Neeraja, A. Rupesh Kumar, T. G. V. M. Rao, P. Vijayalakshmi
    M. Rami Reddy, Transactions of the Indian Ceramic Society,
List of Conferences/Workshops

1) “Spectroscopic properties of V$_2$O$_5$ ions in PbO-As$_2$O$_3$ glasses.”

2) “Luminescence emission of Chromium ions in PbO-Al$_2$O$_3$-P$_2$O$_5$ glass system”

3) “Spectroscopic Studies of Manganese ions in SrO-B$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ glasses”

4) “Spectroscopic characteristics of chromium ions in PbO-Al$_2$O$_3$-P$_2$O$_5$ glass system”

5) “The Spectroscopic Properties of Mo$^{5+}$ in ZnO-ZnF$_2$-B$_2$O$_3$ Glasses”

6) “Spectroscopic characteristics of Sm$^{3+}$ - doped Na$_2$O-ZrO$_2$-SiO$_2$-V$_2$O$_5$ Glasses”
7) “Quantitative study on effect of gamma radiation on some optical properties of strontium alumino boro silicate glasses”

Gamma ray induced changes on vibrational spectroscopic properties of strontium aluminoborosilicate glasses

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1. Introduction

Borosilicate glasses have wide range of applications in various domains of scientific technology and instrumentations due to their excellent optical, thermal, electrical, and mechanical properties. The addition of Al2O3 to borosilicate matrix improves the chemical durability, decreases thermal expansion coefficient and makes the glasses more thermal, electrical and even radiation resistant [1–6] and widens the range of scope of applications of these materials. B2O3 and SiO2 are both network-forming oxides, Al2O3 is an intermediate oxide. Since Si4+ and B3+ ions possess high field strength, there is a lack of oxygen ions in the structure of the Al2O3–B2O3–SiO2 system. Under these circumstances glass formation with the constituents of Al2O3–B2O3–SiO2 system is weak. Hence the introduction of alkaline earth oxide like SrO (which have low field strength) in the glass system improves the glass formation tendency markedly of the ternary systems like Al2O3–B2O3–SiO2. Further it was also reported that the alkali earth oxides like SrO effectively reduce the thermal expansion coefficient of binary/ternary glass systems.

When the glasses are exposed to strong ionization radiations like gamma rays, electron, proton and neutron radiations, several changes in chemical, structural, physical and electrical properties of the glasses are expected. Borosilicate glasses are important glass matrices for the immobilization of radioactive waste. The radiation resistive efficiency of the glasses is substantially determined by the coordination and structural positions of boron atoms in the glass network [7–9]. In recent years, the study of radiation induced effects on aluminoborosilicate glasses is being rigorously pursued with a view to evaluate the radiation resistance ability of these glasses. A considerable number of recent studies on the radiation induced effects of borate, silicate and borosilicate glasses mixed with various modifier oxides like ZnO, PbO, BaO and some transition metal ions are available in the literature [10–13]. However, most of them are restricted to understanding the variations of the valence states of the dopant ions due to the radiation and the influence of physical properties of the glasses. The studies as such on aluminoborosilicate glasses mixed with alkaline earth oxides like SrO and the investigations on the role of alumina on radiation resistance of borosilicate glasses by means of spectroscopy are very limited. Al3+ ion is very interesting ion that participate in the glass network with AlO4 and AlO6 structural units. The radiation resistance of borosilicate glass is much dependent upon the relative proportions of AlO4 and AlO6 structural units. The concentration of these structural units in the glass network is much reliant upon the gamma ray dose.

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and also on the concentration of Al$_2$O$_3$ in the glass matrix. Hence the studies on radiation effects of alumina borosilicate glasses by means of IR, Raman and UV–vis absorption spectra are expected to be much helpful in assessing the radiation resistance capability and for considering these materials for the possible use in radiation shielding.

In this study we have prepared a series of SrO–B$_2$O$_3$–SiO$_2$ glasses mixed with different concentrations of Al$_2$O$_3$ and explored their radiation resistance efficiency as function of Al$_2$O$_3$ concentration by investigating their IR, Raman and UV–vis absorption spectra before and after irradiation with different doses of gamma rays.

2. Experimental details

The SrO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glass samples are prepared by conventional melt quenching technique. The details of chemical compositions of the glasses used for the present study are furnished in Table 1. The raw materials used are AR grade reagents of SrCO$_3$, Al$_2$O$_3$, B$_2$O$_3$ and SiO$_2$ in appropriate amounts (in mol%).

The chemical compounds are thoroughly mixed in an agate mortar and were calcinated at 700 °C for 1 h. Then the calcinated powders were taken in silica crucibles and were melted in an automatic temperature controlled furnace in the temperature range ~1400–1430 °C for about 2 h. The bubble free molten form liquid was then poured in a pre-heated brass mould and subsequently annealed at a temperature of about 450 °C. The samples prepared were mechanically ground and optical polished to the dimensions of 0.1 cm × 0.1 cm × 0.2 cm.

Bulk density 'd' of the samples is measured using VIBRA HT density apparatus to an accuracy of ±0.0001 g/cm$^3$ by the standard principle of Archimedes' using o-xylene as the buoyant liquid. Refractive index was measured using Abbe Refractometer Model NAR4T to an accuracy of ±0.0002 with mono-bromonaphthalene as the contact layer. The molar volume ($V_m$) was calculated by using the relation $V_m = M/d$, where $M$ represents the average molecular weight.

For the confirmation of the amorphous nature of the prepared samples, we have recorded X-ray diffraction pattern on (XRDARLXTRA) diffractometer using Cu Kα radiation operated at 40 kV, 30 mA. The optical absorption spectra of the glass samples were recorded on a JASCO UV–VIS–NIR spectrophotometer (Model V-670) at room temperature in the range of 200–900 nm. The FT-IR spectra were recorded at room temperature on a Bruker IFS 66V-IR spectrophotometer with a resolution of 0.1 cm$^{-1}$ in the range of 400–1600 cm$^{-1}$ using potassium bromide pellets containing pulverized sample (1.5 mg). The Raman spectra were recorded on Fourier transform Raman spectrometer (Model Nicolet NXR 9650 FT-Raman spectrometer) with resolution of 4 cm$^{-1}$ in the range of 400–1600 cm$^{-1}$ with excitation wavelength of 1064 nm. All the samples are irradiated with gamma (γ) rays of doses 10 kGy and 30 kGy using $^{60}$Co radioisotope as radiation source and all the measurements were repeated.

3. Results and discussion

The glasses used in this study were colorless and when they are subjected to irradiation, the color of the glasses is slowly changed to dark brown with increase of the gamma ray dose. This observation indicates that the γ-rays have induced some structural defects including point defects like color centers and excitons in the glass sample.

3.1. X-ray diffraction

Fig. 1 indicates the XRD pattern of one of the glass samples viz. SA-3 before and after irradiation. In both the cases the spectra do not exhibited any sharp peaks indicating the samples prepared were amorphous in nature and even γ-rays irradiation does not induce any crystallinity in the samples.

3.2. Density and refractive index

3.2.1. Before irradiation

Density is one of the prominent parameters that helps in understanding the structural influence of various components in glass matrix. It can be proposed that each and every oxide in the glass matrix would have its contribution to the density. Before irradiation the density of the glasses is found to increase or the molar volume is found to decrease with increasing Al$_2$O$_3$ content (Table 2).

Among different constituents of the studied glass, B$_2$O$_3$ is a strong glass former, participates in the glass network with BO$_3$ and BO$_4$ structural units. SiO$_2$ participates in the glass network with tetrahedral [SiO$_{42}$]$^{4-}$ units and all the four oxygens in SiO$_4$ tetrahedra are shared. With the entry of modifiers like SrO into Si–O–Si network, the structure gets de-polymerized resulting in the formation of meta, pyro and ortho-silicates in the order: [SiO$_{42}$]$^{4-}$ (Q$^4$), [SiO$_{42}$O]$^{2-}$ (Q$^3$), [SiO$_{42}$O$_2$]$^{2-}$ (Q$^3$), [SiO$_{12}$O$_3$]$^{2-}$ and [SiO$_{42}$]$^{4-}$ (Q$^0$) [14].

Depending up on the composition of the glass, aluminum ions may participate in the glass network with AlO$_4$, AlO$_5$ and AlO$_6$ (modifiers) structural units. Earlier NMR studies on aluminum silicate glasses have indicated that aluminum ions occupy mainly tetrahedral (AlO$_4$) and octahedral (AlO$_6$) sites [15] as per the following chemical equilibria:

$$2\text{Al}_2\text{O}_3 \rightarrow [\text{Al}^{3+}]_0 + 3[\text{AlO}_4^{2-}]_0$$
Table 2
Physical parameters of SiO–Al₂O₃–B₂O₃–SiO₂ glasses before and after exposure of gamma rays.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (d) (g/cm³)</th>
<th>Molar volume (V_m) (cm³)</th>
<th>Refractive index (±0.0002)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before irradiation</td>
<td>After irradiation</td>
<td>Before irradiation</td>
</tr>
<tr>
<td></td>
<td>10 kGy</td>
<td>30 kGy</td>
<td>10 kGy</td>
</tr>
</tbody>
</table>

The AlO₄ tetrahedra enter the glass network and alternate with SiO₄ tetrahedra, whereas octahedral Al³⁺ ions and also the edge-sharing [AlO₄] tetrahedra or the oxygen triclusters induce bonding defects in the glass network. Coordination transformation of Al³⁺ from a network former to a network modifier in a melt with (Al³⁺ + Si⁴⁺)₂ O₅²⁻ stoichiometry with the presence of modifying cations like Sr²⁺ may be expressed with the formalized equation:

$$\text{SSi}_2\text{O}_5²⁻ + (\text{SrAl})_2\text{O}_3 = 10\left[(\text{SiO}_2)²⁻ / (\text{SiO}_2\text{O}_2)²⁻\right] + \text{Sr}²⁺ + 2\text{Al}³⁺$$

The presence of alumina tetrahedrons and octahedrons in the titled glass network is established from the IR and Raman spectra mentioned in the subsequent sections. The density of the studied glasses exhibited increasing tendency with increasing alumina content. The increases of structural compactness, the modification of the geometrical configuration of the glassy network, changes in the coordination of the glass forming ions and the fluctuations in the dimensions of the interstitial holes are some of the crucial factors responsible for such an increase. In this case the increase is possible if there is an increase in the concentration of AlO₄ tetrahedrons that enter the glass network and alternate with SiO₄ and BO₄ tetrahedrons.

The density and refractive index of glass are closely related with each other. The combined effect of alkaline earth metal (Sr²⁺) ion and tetrahedral aluminum ions gives higher density to the glass structure and thus higher refractive index is expected [16,17]. The refractive index values, in fact, increased with increasing the alumina content (Table 2).

3.2.2. After irradiation

After the exposure with gamma-rays, the density of the samples decreases with irradiation dose with respect to that of corresponding pre-irradiated samples (Table 2). This result is in good agreement with the results obtained by Arora et al. [18]. The decrease in the density due to the creation of dangling bonds, NBOs, formation of new bonds in the glass network and also allow the structure to relax and fill the moderately large interstices that exist in the interconnected network of boron and oxygen atoms. For the glass systems like alkaline earth oxy borosilicate glasses, Hanning et al. [19] suggested that some of the alkaline earth ions associate themselves with AlO₄ and BO₄ triangles. In either case, the irradiation creates displacements, electronic defects and weakens in the Si-O-Si and B-O-B bonds resulting decrease in the density of the samples. Further, we have also noticed that there is an increase in the concentration of octahedral Al³⁺ ions at the expense of AlO₄ tetrahedrons in the glass network with the increase of gamma irradiation dose as mentioned in the subsequent sections. The increasing presence of octahedral Al³⁺ ions weaken the glass network by breaking cross-linking borate, silicate chains similar to the role played by the conventional modifiers ions like Sr²⁺ as per the chemical equilibria discussed above. Recently, it was demonstrated by NMR studies that an oxygen triclusters oxygen ion bonded to two [AlO₄] and one [SiO₄] or one [AlO₄] and two [SiO₄] is another mechanism for inducing bonding defects in the glass containing Al₂O₃ and SiO₂. The edge-sharing AlO₄ tetrahedra are observed to be associated with such oxygen triclusters [20]. All such defects lead to increase the dimensions of the glass network and contribute to the decrease of density.

Borate groups also play a significant role in the density variations. When the concentration of modifiers is low there is a possibility for conversion of trigonal borate units to tetragonal borate units as per the following chemical equilibria:

$$2[\text{BO}_2\text{O}_3]²⁻ + \text{O}²⁻ → 2[\text{BO}_4\text{O}_4]²⁻$$

The tetrahedral [BO₄O₂]⁻ ion is not associated with an NBO, although the unit carries a negative charge. It only means that the negative charge is spread diffusely on the atoms of the BO₄ unit. For an optimal concentration of modifiers the concentration of BO₄ and BO₃ structural units will be equal (diborate groups). Beyond this optimal concentration of modifiers BO₄ units breakdown and form [B₁₂O₁₇]⁻ units:

$$2[\text{BO}_4\text{O}_4]²⁻ + \text{O}²⁻ → 2[\text{BO}_1\text{O}_2\text{O}_2]²⁻$$

Normally the oxygens of modifier oxide break the local symmetry as shown in the above equation while the cations occupy the interstitial positions. A similar role is also expected in the inter conversion of BO₄ → BO₃ structural units by the gamma rays. As a consequence, there is a network collapse and better volume utilization or increase of volume takes place with the increase of gamma ray dose.

Thus the inter conversion of BO₄ → BO₃ structural units and from ortho silicate units to pyro silicates due to gamma ray irradiation may play a crucial role in decreasing the compactness or decreasing the bulk density of the samples. The refractive index is also decreased with increasing the irradiation dose (Table 2); this is an expected result because the density of the samples is observed to decrease with γ-ray dose.

3.3. Optical absorption spectra

3.3.1. Before irradiation

Optical absorption (OA) spectra were recorded at room temperature in the wavelength region 200–900 nm. Fig. 2(a–c) represents the absorption spectra of all glass samples before and after irradiation. In all these figures, curve 1 indicates the OA spectrum of pre-irradiated glass samples. In the spectra of pre-irradiated samples no absorption band is detected in the wavelength region studied. However, the absorption edge is observed to shift spectrally toward slightly longer wavelength with increasing the alumina content [21,22].

3.3.2. After irradiation

The optical absorption spectra of SA-1, SA-2 and SA-3 samples irradiated with doses of 10 kGy (curve 2) and 30 kGy (curve 3) are presented in Fig. 2(a), (b) and (c), respectively. A broad absorption band in the wavelength region 600–750 nm with meta-center at about ~670 nm is observed in the spectra of all the irradiated samples. The position of the band remained unaltered due to the
variation in the Al₂O₃ content. However, with increase of irradiation dose, area under the absorption peak is observed to increase.

The action of gamma-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse in the glass network depending upon their energy and the composition of the glass and are finally trapped, thus forming color centers. The trapping sites may be the metal cations that constitute the glass structure, ions of admixtures to the main composition and the structural defects due to impurities in the glass. This process leads to the formation of (1) boron–electron centers, (2) non-bridging oxygen hole centers and (3) boron–oxygen hole centers [23,24]. Sometimes, if the irradiation is not sufficient to knock out the electrons completely, there may be possibility for the formation of excitons (bound electron–hole pairs) which may have strong coupling with the lattice. Unlike in crystalline materials it is difficult to say the exact nature of the color centers formed in amorphous materials like the titiated glass. However, some of the above factors may be responsible for the band observed in the irradiated samples. The growth of the band with the gamma ray dose obviously suggests the increase in the concentration of above mentioned point defects in the glass network.

3.4. FT-IR spectra

FT-IR spectroscopy is helpful to analyze the nature of environment of various cations in the glass network. The investigated glass samples are a combination of glass formers (SiO₂ and B₂O₃), intermediate oxide (Al₂O₃) and modifier (SrO). The addition of alkaline earth metal oxide (SrO) to the alumino-borosilicate glass provides additional oxygen atoms which are accommodated in the network, this means the alkali earth metal cations acquire an extra negative charge. This negative charge can transform the coordination of boron (BO₃ ↔ BO₂). SrO may transform Q⁴⁺ tetrahedra into Q³⁻ (viz., SiO₄ tetrahedra with three bridging oxygens and one terminal de-bonded oxygen) and Q²⁺ tetrahedra (viz., SiO₂ tetrahedra with two bridging oxygens and two terminal de-bonded oxygen) and Q¹⁻ as per the following chemical equilibria:

$[\text{SiO}_{4/2}^0 + \text{SrO}] \rightarrow [\text{SiO}_{3/2}^0] + \text{Sr}^{2+}$

$[\text{SiO}_{4/2}^0 + \text{SrO}] \rightarrow [\text{SiO}_{2/2}^0]^{2-} + \text{Sr}^{2+}$

$[\text{SiO}_{4/2}^0 + \text{SrO}] \rightarrow [\text{SiO}_{1/2}^0]^3- + \text{Sr}^{2+}$

Thus a SrO polyhedron is formed when it is surrounded by such Q¹⁻, Q²⁻ and Q⁴⁺ tetrahedrons. This structure behaves like a defect in the network of borosilicate glass.

3.4.1. Before irradiation

The FT-IR spectra of titiated glass samples mixed with 5.0%, 7.5% and 10.0% of Al₂O₃ are shown in the Figs. 3, 4 and 5, respectively. The curve (1) in each figure represents spectrum of the pre-irradiated glass samples. The spectra reveal main prominent and characteristic vibrational bands due to various borate and silicate structural units. The detailed positions and the corresponding assignments of various bands observed are furnished in the Table 3. The bands appeared in the region 900–1200 cm⁻¹ are attributed to combined stretching vibrations of borate and silicate structural units. In this region the band observed at about 1016 cm⁻¹ is identified as being due to the combined stretching vibrations modes of Si–O–Si and B–O–B of SiO₄ and BO₃ structural units [25,26]. Another significant band due to the vibrations of bridging oxygens between B–O–B in BO₃ triangles is also observed at 710 cm⁻¹ [27,28]. The band due to vibrations of AlO₄ structural units is located at 796 cm⁻¹ [29,30]. The spectra also exhibited prominent bands in the region 1200–1600 cm⁻¹ related to asymmetric stretching relaxation of B–O bond of trigonal BO₃ units with NBOs [31,32]. A band correlated to Si–O–Si and Si–O–B bending/rocking modes is also located at about 486 cm⁻¹. In this region the band due to vibrations of AlO₅ structural units is also expected [33]. The spectra also exhibited
Table 3
Summary of band positions of FTIR and Raman spectra of SA-2 glass sample after gamma ray irradiation with a dose of 30 kGy.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Band positions (cm⁻¹)</th>
<th>Band assignments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1512 (1515)</td>
<td>Asymmetric B—O stretching relaxations of [BO₃] structural units</td>
<td>[32]</td>
</tr>
<tr>
<td>2</td>
<td>1452 (1450)</td>
<td>Stretching vibrations of B—O units from different borate groups</td>
<td>[31,32]</td>
</tr>
<tr>
<td>3</td>
<td>1396 (1392)</td>
<td>Symmetric stretching relaxation of B—O band of triangle BO₃ units</td>
<td>[31]</td>
</tr>
<tr>
<td>4</td>
<td>1320 (1322)</td>
<td>Asymmetric stretching relaxation of B—O bond of trigonal BO₃ units with NBOs</td>
<td>[32,37]</td>
</tr>
<tr>
<td>5</td>
<td>1212 (1236)</td>
<td>Stretching vibrations of B—O of the BO₃ units</td>
<td>[33]</td>
</tr>
<tr>
<td>6</td>
<td>1142 (1142)</td>
<td>Characteristic vibrations of Q² species of Si—O units</td>
<td>[39]</td>
</tr>
<tr>
<td>7</td>
<td>1014 (1012)</td>
<td>Combined stretching vibrations modes of SiO₄ and BO₄ units</td>
<td>[25,26,36]</td>
</tr>
<tr>
<td>8</td>
<td>930 (930)</td>
<td>Characteristic vibrations of Q² species of Si—O units</td>
<td>[9,16,40]</td>
</tr>
<tr>
<td>9</td>
<td>830 (830)</td>
<td>Symmetric bending vibrations of di-tri- or dipenta-borate, meta borate rings</td>
<td>[9,42]</td>
</tr>
<tr>
<td>10</td>
<td>784 (796)</td>
<td>Bending vibrations of AlO₄ structural units</td>
<td>[29,30,36]</td>
</tr>
<tr>
<td>11</td>
<td>710 (710)</td>
<td>Vibrations of bridging oxygen between B—O—B in BO₃ triangles</td>
<td>[27,28,41]</td>
</tr>
<tr>
<td>12</td>
<td>629 (630)</td>
<td>Vibrations modes of Si—O—Si linkage</td>
<td>[26]</td>
</tr>
<tr>
<td>13</td>
<td>480 (480)</td>
<td>Si—O—Si rocking/AlO₄ units</td>
<td>[33,40]</td>
</tr>
<tr>
<td>14</td>
<td>447 (448)</td>
<td>O—B—O bending vibrations</td>
<td>[9]</td>
</tr>
</tbody>
</table>

The values in parenthesis represent the corresponding band positions of the pre-irradiated samples.

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increase in the concentration of Al₂O₃ there is a decrease in the intensity of the bands due to BO₃ structural units and Si—O—Si rocking vibrations, whereas that of BO₄/SiO₄ structural units exhibited increasing trend. Further, it is also clearly noticed that with increase in the concentration of Al₂O₃ from 5.0 to 10.0 mol%, there is a gradual increase in the intensity of the band due to AlO₄ structural units and exhibited the highest intensity at 10.0 mol%.

3.4.2. After irradiation
The FT-IR spectra of γ-ray irradiated samples with doses 10 kGy (curve 2) and 30 kGy (curve 3) are shown in Figs. 3–5. There was no significant change in the band positions of the irradiated glass samples when compared to the unirradiated ones. However, with the increase of γ-ray dose the intensity of vibrational band due to the combined stretching vibrational modes of SiO₄ and BO₄ at 1016 cm⁻¹ and also that of AlO₄ structural groups (observed at about 796 cm⁻¹) decrease, whereas the bands due to BO₃ and AlO₆ structural units are observed to grow at the expense of the bands due to SiO₄, BO₄ and AlO₄ units.

However, as can be seen from Figs. 3–5, the variation in the intensities of all the bands with respect to those of corresponding pre-irradiated samples is observed to be less significant in the spectra of the samples mixed with 10.0 mol% Al₂O₃. This can be clearly observed in Fig. 6 where the relative integral intensities of BO₃ and BO₄ structural units of all the three glasses were plotted with the gamma ray dose. The spectra of pre-irradiated samples,

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band at about 1515 cm⁻¹ ascribed to asymmetric B—O stretching relaxations of [BO₃] structural units, which are associated with the vibrational mode inside the various borate rings and the non-bridging B—O⁻ bonds [32].

The comparison of the IR spectra of pre-irradiated samples mixed with different concentration of Al₂O₃ indicated that with
as mentioned in the Section 3.4.1, indicated that Al$^{3+}$ ions predominantly participate with tetrahedral coordination in the glass network of the sample mixed with 10.0 mol% of Al$_2$O$_3$. From these two observations we can conclude that sample containing the highest concentration of AlO$_4$ structural units (SA-3) is more resistant to the gamma radiation.

3.5. Raman spectra

Raman spectra give more quantitative information over the structural aspects of the glass network when compared with those of IR spectra because some of the vibrations are more Raman active.

The characteristic Raman spectra of SiO$_2$ exhibits mainly four modes of vibrations viz., asymmetric ring breathing vibrations (430 cm$^{-1}$), symmetric stretching vibrations of Si–O–Si (800 cm$^{-1}$), stretching vibrations associated to SiO$_4$ composed of sites with three- and four-fold rings (1000–1200 cm$^{-1}$) and symmetric stretching vibrations (1200 cm$^{-1}$). On the other hand, pure B$_2$O$_3$ exhibits a strong band at 805 cm$^{-1}$ due to symmetric beating vibrations of boroxol ring oxygen, involving a very little boron motion. These boroxol ring structure splits into different ring structures (i.e. tri borate, tetra borate or penta borate, etc.) in the presence of suitable modifiers in the glass network [34,35].

3.5.1. Before irradiation

The Raman spectra of pre-irradiated SrO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glass samples are represented by curve 1 in Figs. 7–9. The summary of various band positions is given in the Table 3. The Raman spectra exhibited four vibrational bands at 487, 589, 629, 784 and 830 cm$^{-1}$ due to Si–O–Si rocking/Al$_6$O$_3$ units/bridging oxygen breathing mode in (Si and Al) three-membered rings, Al–O–Al vibrational modes of AlO$_4$ units, bending vibrations of B–O–B along with Si–O network, Si–O–Si symmetric/AlO$_4$ units and due to BO$_3$ vibrational modes, respectively. An intense band attributed to asymmetric stretching vibrations of Si–O–Si bonds is observed at 1012 cm$^{-1}$ [36]. In this region B–O stretching vibrations of BO$_4$ tetrahedral coordination is also possible. Weaker shoulders are also observed in these spectra at about 930 and 1142 cm$^{-1}$ due to the characteristic vibrations of Q$^2$ and Q$^4$ species of Si–O. Another band at 1444 cm$^{-1}$ presumably due to vibrations of BO$_3$O$^-$ triangles containing NBOs is also observed in the spectra [37–42].

The positions of all the bands remain unaltered with increasing the aluminum content in the glass matrix. However, the intensity of the bands due to Al–O–Al vibrational modes of AlO$_4$ units and due to vibrations of BO$_4$ structural units is observed to increase, whereas that of the bands due to vibrations of Si–O–Si rocking/Al$_6$O$_3$ units, BO$_3$ vibrational modes and BO$_3$O$^-$ triangles is observed to decrease gradually with increasing the concentration of Al$_2$O$_3$. This observation indicates a gradual decrease of de-polymerization of the titled glass network with increase in the concentration of Al$_2$O$_3$.

3.5.2. After irradiation

The curves 2 and 3 of Figs. 7–9 represent the Raman spectra of gamma ray irradiated glass samples. When the samples are exposed to γ-ray irradiation an increase in the intensity of all asymmetric bands is clearly visualized with shifting of the band positions toward slightly higher wave number. The other important inference from these spectra is that the hike in the intensity of various bands with respect to those of pre-irradiated samples of the glasses...
in the intensity of BO₃, asymmetrical silicate and AlO₅ structural units. Further a clear increase in the intensity of AlO₄ structural units is also visualized from these spectra with increase in the content of Al₂O₃ and the maximum intensity of this band is observed in the spectra of the glass SA-3 (glass mixed with 10.0 mol% of Al₂O₃). The pattern of various bands in the spectra of post-irradiated samples remained the same. However, with the increase of gamma ray irradiation dose intensity of BO₄ structural units is observed to decrease at the expense of BO₃ structural units. Such induced changes in these spectra of the sample SA-3, nevertheless, are observed to minimal.

From these observations it is concluded that the glasses mixed with 10.0 mol% of Al₂O₃ are relatively more resistant to the radiation when compared with the other studied samples.

**Acknowledgements**

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**References**


Fluorescence spectroscopic studies of Mn$^{2+}$ ions in SrO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glass system

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Mn$^{2+}$ ions
Spectroscopic properties

A B S T R A C T

The SrO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glasses doped with different concentrations of MnO were synthesized and their spectroscopic studies were carried out. The UV–vis absorption spectrum of these glasses exhibited a broad band centered at about 428 nm as being due to $^6$A$_1$(S) − $^4$T$_1$(G) tetrahedral transition of Mn$^{2+}$ ions. With the increase in the concentration of manganese oxide, a new band at about 525 nm corresponding to $^4$A$_2$(S) − $^4$T$_{1g}$(G) octahedral transition of Mn$^{2+}$ ions is developed. The photoluminescence spectra of these glasses excited at 420 nm exhibited two luminescence bands at about 540 (green emission) and 632 nm (red emission). As the concentration of MnO is increased up to 1.5 mol%, the red emission band is observed to grow at the expense of green band. The analysis of these results coupled with FT-IR and ESR spectral results has indicated that in the glass containing 1.5 mol% of MnO, the manganese ions predominantly occupy octahedral positions and are found to be responsible for rich red emission.

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1. Introduction

Strontium alumino borosilicate glasses are well-known due to their low thermal expansion coefficient, high chemical durability, superior biocompatibility and high electrical resistivity. In view of such characteristics these glasses are being widely used in various domains like low cost optical connectors, dielectrics, up-converting optical materials and as sealant materials for solid oxide fuel cells, etc. [1–3]. Cheng et al. [4] have recently investigated structural properties of aluminum borosilicate glasses and concluded that the ratio of B$_2$O$_3$/Al$_2$O$_3$ effectively influences the transition temperature of the glass. In general, the presence of Al$_2$O$_3$ in the glass matrix makes the glasses more resistant to attack by alkali metal ions like Li$^+$ and Na$^+$. This is obviously because of the entering of Al$_2$O$_3$ into the glass network with AlO$_4$ structural units that crosslink the neighboring borate and silicate chains [5].

Among various transition metal ions manganese ions exist in different valence states occupying tetrahedral or octahedral sites in glass network. For example, Mn$^{2+}$ ions in borate glasses exist only in octahedral coordination, whereas in silicate and germinate glasses as Mn$^{2+}$ in both tetrahedral and octahedral environment [6–8]. Both tetrahedral and octahedral Mn$^{2+}$ ions have been found to exhibit luminescence emission in the green and red regions, respectively, in several glasses [9–12]. The content of manganese in different coordinations in different valence states exist in the glass depends upon the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation, etc. Further, borosilicate glasses in view of their superior physical properties mentioned above are the most advantageous materials for hosting lasers ions like manganese to give laser emission of high intensity with minimum beam divergence [13].

In this investigation we have attempted to study the changes in the luminescence features of Mn$^{2+}$ ions in the scenario of varying environment of manganese ions in the strontium alumino borosilicate glass network. The obtained results were analyzed with the support of data from optical absorption, FT-IR and ESR spectral studies.

2. Experimental

MnO doped SrO–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glasses were prepared, using melt-quenching technique. The content of manganese in the glass composition is varied from 0.5 to 2.5 mol%. The details of chemical compositions chosen for the present study are listed in Table 1. The analytical grade reagents of raw materials (SrCO$_3$, H$_3$BO$_3$, Al$_2$O$_3$, SiO$_2$ and MnO) were fine powdered and thoroughly mixed in an agate mortar. The mixture was taken in a silica crucible placed in an automatic temperature controlled furnace at a temperature range 1430–1460 °C for 30 min. The bubble-free molten material was quenched on a pre-heated brass mold to the room temperature and subsequently annealed at 450 °C. The prepared samples
Table 1
Glass compositions.

<table>
<thead>
<tr>
<th>Glass code</th>
<th>SiO₂ (mol%)</th>
<th>B₂O₃ (mol%)</th>
<th>Al₂O₃ (mol%)</th>
<th>SiO₂ (mol%)</th>
<th>MnO (mol%)</th>
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<tr>
<td>M₁₅₀</td>
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<td>15</td>
<td>3.0</td>
<td>50</td>
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<tr>
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<td>50</td>
<td>0.5</td>
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<tr>
<td>M₁₃₀</td>
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<td>15</td>
<td>4.0</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>M₁₁₀</td>
<td>40</td>
<td>15</td>
<td>3.5</td>
<td>50</td>
<td>1.5</td>
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<tr>
<td>M₉₀</td>
<td>40</td>
<td>15</td>
<td>2.5</td>
<td>50</td>
<td>2.5</td>
</tr>
</tbody>
</table>

were optically polished. Final dimensions of the samples used for the present study are 1 cm × 1 cm × 0.2 cm.

The optical absorption spectra were recorded on a JASCO UV-VIS-NIR spectrophotometer (model V-670) at room temperature in the range 300–1000 nm. The ESR measurements of powder samples were carried out at room temperature using E112 Varian X-band (ν = 9.5 GHz) ESR spectrometer of 100 kHz field modulation. The photoluminescence spectra (PL) were recorded at room temperature on the fluorescence spectrometer (SPEX Fluorolog-3) using with a 450 W Xe-lamp as the excitation source. The FT-IR spectra were recorded for powder samples at room temperature on a Bruker IFS 66 V-IR spectrophotometer with a resolution of 1.0 cm⁻¹ in the range 400–1600 cm⁻¹ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). By using Archimedes’s principle, the density d of the glasses was determined to an accuracy of ±0.001 by means of o-xylene (99.9% pure) as the buoyant liquid. The refractive index of the glasses was measured using Abbe’s refractometer and mono bromo naphthalene as the contact layer.

3. Results

By means of conventional formulae [14] and practically measured density, various physical parameters such as manganese ion concentration (Nₘ), Mean separation (rₜ), Polaron radius (rₚ) and Field strength (F) of the glasses have been evaluated and presented in Table 2. The progressive introduction of MnO caused a slight increase in the density of the samples. The degree of structural compactness, the modification of the geometrical configuration of the glassy network, change in the coordination of the glass forming ions and the fluctuations in the dimensions of the interstitial holes might have influenced the density of the studied glass.

The UV–vis absorption spectra of manganese ions doped SrO–Al₂O₃–B₂O₃–SiO₂ glass recorded at room temperature are shown in the Fig. 1. The spectrum of glass M₁₅₀ exhibited an absorption band at about 428 nm identified as being to ⁴A₁(S) → ⁴T₂(G) tetrahedral transition of Mn²⁺ ions. With the increase in the concentration of manganese oxide, a new band at about 525 nm corresponding to ⁴A₁(S) → ⁴T₂(G) octahedral transition of Mn²⁺ ions [9–12] is developed. This band is observed to grow at the expense of the tetrahedral band with increase in the concentration of MnO up to 1.5 mol%. For further increase in MnO content a reversal trend in the intensity of these bands is observed.

From the observed absorption edges, optical band gap (E₉) of these glasses is evaluated by drawing Tauc plots between (xhν)² and hν as per the equation:

\[ x(\nu)h\nu = c(\nu^2 - E₉)^2 \]

From the extrapolation of the linear portion of the plots (Fig. 2) in the high energy side, the optical band gap energy were evaluated and are presented in Table 3; the value of E₉ is found to be minimal for the glass M₁₅₀.

Fig. 3 shows the ESR spectra of MnO doped SrO–Al₂O₃–B₂O₃–SiO₂ glass. No EPR signal was detected in the spectra of undoped glass specimen, indicating the samples are reasonably free from paramagnetic impurities in the starting materials used in the glass preparation. The spectrum of the glass M₁₅₀ exhibited standard hyperfine sextet (hfs) structure at about g = 2.0 which is a typical characteristic signal of Mn²⁺ ions. Additionally, the spectrum also exhibited two weak signals at g = 3.3, 4.3.

The intensity of the hfs signal is observed to increase gradually and is merged into a single broad line when the concentration of manganese ions is about 1.5 mol%. When the concentration of the dopant is raised beyond 1.5 mol%, a slight decay in the intensity of these signals is observed. This is due to both distribution of crystal field parameters and dipole–dipole interaction accompanied by the super exchange magnetic interaction. The pertinent data related to ESR spectra are furnished in Table 4.

Table 2
Physical parameters of MnO doped SrO–Al₂O₃–B₂O₃–SiO₂ glasses.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Glass code</th>
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<tbody>
<tr>
<td></td>
<td>M₁₅₀</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.516</td>
</tr>
<tr>
<td>Average molecular weight (M)</td>
<td>81.02</td>
</tr>
<tr>
<td>Transition metal ion concentration (×10¹⁶ ions/cm³)</td>
<td>–</td>
</tr>
<tr>
<td>Inter transition metal ion distance (Å)</td>
<td>–</td>
</tr>
<tr>
<td>Polaron radius (Å)</td>
<td>–</td>
</tr>
<tr>
<td>Field strength (×10¹⁴ cm⁻²)</td>
<td>–</td>
</tr>
<tr>
<td>Optical basicity (Aₒ)</td>
<td>–</td>
</tr>
<tr>
<td>Molar Volume Vmol (cm³/mole)</td>
<td>1.5267</td>
</tr>
</tbody>
</table>

Fig. 1. Optical absorption spectra of MnO doped SrO–Al₂O₃–B₂O₃–SiO₂ glasses.
The emission spectrum of manganese oxide doped SrO–Al2O3–B2O3–SiO2 glasses when excited at 420 nm, exhibited a bright green emission peak at about 540 nm corresponding to $^2$T2 (G) $\rightarrow$ $^4$A2(S) tetrahedral transition and a red emission peak corresponding to $^4$T1(G) $\rightarrow$ $^4$A2(S) octahedral transition of Mn2+ ions at about 632 nm (Fig. 4). A glass of Mn3, the relative area under green and red emission bands are found to be nearly in the ratio 1:0.9. As the concentration of the dopant is increased up to 1.5 mol%, the octahedral band is observed to grow at the expense of tetrahedral band and the above mentioned ratio is found to be nearly 1:3.51 for this glass indicating that there is a gradual transformation of manganese ions from tetrahedral coordination to octahedral coordination. When the concentration of manganese oxide is raised beyond 1.5 mol% in the glass matrix, a considerable decrement in the intensity of the octahedral band is visualized.

The Fourier transmission infrared spectra of SrO–Al2O3–B2O3–SiO2 glasses recorded at room temperature exhibited different bands due to the vibrations of borate, silicate and aluminium oxide structural units. In Fig. 5, the spectra of Mn0 and Mn05 glasses are presented. The bands observed are assigned to the following structural units based on the existing literature [3,4,15,16]:

1. The spectra exhibited a conventional band due to B–O stretching vibrations of BO3 structural units in the region 1428–1454 cm$^{-1}$.
2. Another band is identified at about 1060 cm$^{-1}$. This band consists of combined vibrational modes of asymmetric vibrations of Si–O–Si and BO4 structural units.

3. Additional band is observed due to symmetric vibrations of Si–O–Si units and due to the vibrations of AlO4 structural units at about 830 cm$^{-1}$.
4. A feeble band at about 465 cm$^{-1}$ attributed to the bending and rocking motions of Si–O–Si linkages is also observed.
5. As the concentration of MnO is increased up to 1.5 mol%, a significant increase in the intensity of asymmetrical vibrational bands is observed. The pertinent data related to spectral positions of various bands are furnished (Table 5).

### 4. Discussion

Among various constituents of SrO–Al2O3–B2O3–SiO2 glass composition, SiO2 is a well known glass former and expected to participate in the glass network with tetrahedral [SiO4]4− units and all the four oxygens in SiO4 tetrahedral are shared. On addition of modifiers like SrO, the Si–O–Si linkage is broken and form Si–O$^-$ termination. Thus, the structure is depolymerised and there will be a formation of meta, pyro and ortho-silicates viz., [SiO4]4−, [SiO4]4−, [Si2O7]6−, [Si2O3(O2)]5− and [SiO4]4− as per the following chemical equations:

$$2[SiO4]4− + SrO \rightarrow 2[Si2O3O]5− + Sr^{2+}$$

$$2[SiO2/2O2]^{2−} + SrO \rightarrow 2[SiO(O2)O]^{3−} + Sr^{2+}$$

B2O3 is also a strong glass former, when it is mixed in the silicate glasses, the tetrahedral boron entities dominate in the silicate-rich domain, whereas trigonal boron entities prevail in the borate-rich side and hence in the B–O–Si bridges. The highest stability for fully polymerized glasses and can be related to the energetics of the reaction B–O–B + Si–O–Si = 2(B–O–Si); this relation also suggests that the B–O–Si linkage is more stable relatively.

### Table 3

<table>
<thead>
<tr>
<th>Glass code</th>
<th>Cut off wavelength (nm)</th>
<th>Band position (nm)</th>
<th>Optical band gap (eV)</th>
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<tr>
<td>Mn0</td>
<td>530</td>
<td>425–525</td>
<td>3.58</td>
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<tr>
<td>Mn03</td>
<td>322</td>
<td>425</td>
<td>3.90</td>
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<td>Mn15</td>
<td>352</td>
<td>423</td>
<td>3.51</td>
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<td>Mn20</td>
<td>382</td>
<td>426</td>
<td>3.65</td>
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<td>Mn25</td>
<td>411</td>
<td>429</td>
<td>3.61</td>
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### Table 4

<table>
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<tr>
<th>Glass code</th>
<th>g (±0.001)</th>
<th>$\Delta g$</th>
<th>$A$ (10$^{-4}$/cm)</th>
</tr>
</thead>
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<tr>
<td>Mn0</td>
<td>2.0394</td>
<td>0.0371</td>
<td>82.5</td>
</tr>
<tr>
<td>Mn03</td>
<td>2.0401</td>
<td>0.0378</td>
<td>87.5</td>
</tr>
<tr>
<td>Mn15</td>
<td>2.0358</td>
<td>0.0335</td>
<td>89.6</td>
</tr>
<tr>
<td>Mn20</td>
<td>2.0186</td>
<td>0.0267</td>
<td>83.2</td>
</tr>
<tr>
<td>Mn25</td>
<td>2.0195</td>
<td>0.0373</td>
<td>82.5</td>
</tr>
</tbody>
</table>
than the mixture of B–O–B and Si–O–Si linkages. Earlier spectroscopic studies like NMR on Al₂O₃ mixed silicate glasses have indicated that aluminium ions occupy mainly tetrahedral (AlO₄) and octahedral (AlO₆) sites [17].

\[2\text{Al}_2\text{O}_3 \rightarrow [\text{Al}^{3+}]_6 + 3[\text{AlO}_4]_4\]

The transformation of Al²⁺ from a network former to a network modifier in a melt with (Al³⁺ + Si⁴⁺)₂ O₂⁻ stoichiometry can be expressed with the formalized equation as:

\[5\text{Si}_2\text{O}_5^2^- + (\text{SrAl})\text{O}_6^2^- = 10(\text{SiO}_3)^{2-} / (\text{SiO}_2/2\text{O}_2)^{2-} + 2\text{Sr}^{2+} + 2\text{Al}^{3+}\]

However, some previous studies on other silicate glasses containing Al₂O₃ have pointed out that Al(6) dominates the glass structure when Al₂O₃ is present in low concentrations and Al(4) structural units prevail when Al₂O₃ is present in higher concentrations [18]. Regardless of which participation is chosen, a coordination transformation of Al³⁺ in any of the compositions will cause a rapid increase in the relative intensities of IR/Raman bands of Si–O²⁻ stretch vibrations.

The experimental conditions (during melting and annealing of the glasses) may provide oxidizing atmosphere such that a fraction of Mn²⁺ ions get converted into Mn³⁺ ions as per the following reaction:

\[\text{Mn}^{2+} + 1/2 \text{O}_2 \leftrightarrow \text{Mn}^{3+} + \text{O}^2-\]

In such a case, there is a possibility for Mn³⁺ ions to occupy the positions of Al³⁺ ions because of their close ionic radii (R(Mn³⁺) = 0.58 Å and R(Al³⁺) = 0.53 Å) and same valance state. Such replacement causes to strengthen the glass network.

As mentioned earlier manganese ions are expected to exist in Mn⁴⁺ (with both tetrahedral and octahedral environments) and also in Mn³⁺ state. The octahedrally positioned manganese ions similar to strontium ions depolymerize the glass network by creating more bonding defects and non-bridging oxygens (NBOs). With the increase in concentration of Mn⁴⁺ (O₆) in the glass network, an increase in the formation of donor centers is expected and subsequently, the excited states of localized electrons originally trapped on Mn⁴⁺ sites begin to overlap with the empty 3d states on the neighboring Mn⁴⁺ sites, and as a result, the impurity or polaron band becomes more extended into the main band gap. This new polaronic development might have shifted the absorption edge to the lower energy, which leads up to a significant shrinkage in the band gap as the concentration of MnO is increased (Table 3). This may be the reason for the lowest optical band gap observed for the glass Mn₁₄.

The observed optical absorption bands in the optical absorption spectra are from the ground state 6A₁g to some quartet states and these are both spin and parity forbidden. Using Tanabe-Sugano diagram for d⁵ electron, the band observed at about 530 nm is identified as being due to 6A₁g(S) → 4T₂₂(G) octahedral transitions of Mn³⁺ ions. Further, the transition 6A₁g(S) → 4T₂₂(G) involve a change of configuration from (t₂g)⁵(e_g)⁰ to (t₂g)⁴(e_g)¹ and is therefore expected to be relatively broader [19,20]. Since all the excited states are spin quartet states, no spin allowed transitions would occur for Mn³⁺ ions. Hence, Mn³⁺ ions are characterized by weak bands, which arise due to the spin forbidden transitions. We have also observed the shifting of the octahedral bands towards slightly longer wavelengths as the concentration of MnO is increased up to 1.5 mol%. In other words, the optical activation energy associated with the octahedral bands of Mn²⁺ ions is decreased with the increase in the concentration of MnO (Table 3); this is clearly a characteristic signal of inter valence transfer or a polaronic type of absorption which is possible if local potential fluctuation is small as compared to the transfer integral, J. Thus we may assume that the optical absorption in the glass samples is dominated by polaronic transfer between the Mn²⁺ and Mn³⁺ species [21,22]. In earlier reports, an absorption band due to the octahedral transition of Mn⁴⁺ ions was reported at about 490 nm in different glass systems [8,23]. The observed shifting of the octahedral band of Mn⁴⁺ ions in

### Table 5

<table>
<thead>
<tr>
<th>Glass code</th>
<th>B–O stretching vibrations of (\text{B}_2\text{O}_3) (cm⁻¹)</th>
<th>Combined vibrational modes of asymmetric vibrations of (\text{Si}-\text{O}-\text{Si}) and (\text{BO}_4) structural units (cm⁻¹)</th>
<th>Symmetric vibrations of (\text{Si}-\text{O}-\text{Si}) and (\text{AlO}_4) structural units (cm⁻¹)</th>
<th>Bending and rocking motions of (\text{Si}-\text{O}-\text{Si}) (cm⁻¹)</th>
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<tbody>
<tr>
<td>Mn₀</td>
<td>1448</td>
<td>1047</td>
<td>829</td>
<td>463</td>
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<tr>
<td>Mn₁</td>
<td>1452</td>
<td>1018</td>
<td>831</td>
<td>467</td>
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<td>1443</td>
<td>1057</td>
<td>839</td>
<td>466</td>
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<td>Mn₃</td>
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<td>1069</td>
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<td>Mn₅</td>
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<td>1072</td>
<td>837</td>
<td>466</td>
</tr>
</tbody>
</table>
the spectra of the titled glasses towards slightly lower wavelength especially in the spectra of glasses Mn20 and Mn25 indicates there is a possibility of existence of a fraction of manganese ions in Mn20 state.

Concerning ESR spectra, two prominent signals one with the six-line hyperfine structure centered at g ~ 2.0 and another at g ~ 4.3 are observed. Out of these, the hyperfine structured signal is attributed to transitions between (the energy levels of the Mn2+ ions in an environment close to an octahedral symmetry) lower doublet (Kramers doublet, viz.) split by the Zeeman field. The low field signal at g ~ 4.3 is due to magnetically isolated Mn2+ ions in tetragonally (and or rhombically) distorted octahedral sites of $\frac{1}{2}^+$ symmetry subjected to strong crystal field effects and arises from transitions between the energy levels of the middle Kramers doublet $\frac{1}{2}^+$ [24–26]. The highest intensity of the signals observed in the spectrum of glass Mn25 clearly suggests that the concentration of octahedrally positioned Mn2+ ions is the highest in this glass. The resolved hyperfine spectrum at g ~ 2.0 and the magnitude of hfs (A) constant is 89.6 x 10^4 cm^(-1) in the glass matrix are strongly indicative of the Mn2+ ions being present in octahedral environment and sufficiently distant from each other. From ESR and optical absorption studies it is evident that the manganese ions are present largely in these glasses in +2 valence state and predominantly occupy octahedral positions. The considerable decrease in the intensity of the signal in the spectra of the glasses Mn20 and Mn25 suggests a slight decrease in the concentration of octahedral Mn2+ ions.

The room temperature fluorescence spectra of SrO–Al2O3–B2O3–SiO2: MnO exhibited two emission bands at about 632 nm and 540 nm assigned to 4G → 5S transitions. To be more specific, the 628 nm band is attributed to $^4T_2(G) → ^4A_2(S)$ transition of octahedrally positioned Mn2+ ions, whereas the green emission band is identified as being due to $^4T_2(G) → ^4A_2(S)$ transition of tetrahedrally positioned Mn2+ ions [27–29]. As the concentration of MnO is increased gradually up to 1.5 mol%, the intensity of the octahedral band is observed to increase and beyond this concentration of MnO, the tetrahedral band is observed to grow at expense of octahedral band. Thus the luminescence studies indicate that there is a maximum concentration of octahedrally positioned manganese ions in the glass Mn25 that exhibit red emission. This viewpoint is also supported by optical absorption, ESR and IR spectral studies.

5. Conclusions

SrO–Al2O3–B2O3–SiO2 glasses doped with different concentrations of MnO were synthesized, optical absorption, ESR, IR and photoluminescence were recorded at room temperature.

1. The optical absorption studies have revealed that Mn2+ ions gradually transform from tetrahedral occupancy to octahedral occupancy as the concentration of MnO is increased up to 1.5 mol% in the glass matrix.

2. The analysis of results of ESR spectral studies indicated that large proportions of Mn2+ ions occupy octahedral positions in the glass Mn25.

3. The IR spectral studies have pointed out that there is a larger degree of disorder in the glass network of Mn25.

This we have attributed to larger presence of Mn3+ ions that act as modifiers which create disorder in the glass network similar to conventional modifiers.

4. The photoluminescence spectra of Mn2+ ions in SrO–Al2O3–B2O3–SiO2 glasses exhibited rich red emission due to $^4T_2(G) → ^4A_2(S)$ octahedral transition of Mn2+ ions when excited at 420 nm. The intensity of this band is found to be the highest in the spectrum of glass Mn25; from this observation we have concluded that the Mn3+ ions predominantly occupy octahedral positions in this glass network.

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