Gamma ray induced changes on spectroscopic properties of strontium indium borosilicate glasses

5.1 Introduction

In earlier chapter, we have reported the effect of influence of aluminum, gallium ions on radiation damage of strontium borosilicate glasses studied by means of spectroscopic properties (viz., optical absorption (OA), emission, ESR, infrared and Raman spectra). These studies have yielded valuable information regarding the radiation resistant capability as a function of Al₂O₃, Ga₂O₃ concentration by studying the structural role of the aluminium, gallium ions in these glasses. In₂O₃ is yet another interesting oxide that participates in the glass network as network modifier and also as network former. The presence of In₂O₃ bring interesting changes in the properties of the glasses, for example, enhance the region of transparency [1-5], improve the physical properties of these glasses, to a substantial extent and is further expected to increase the radiation resistant capability and range of practical utility of these glasses.

With increase in the concentration of In₂O₃, the value of the glass transition temperature \( T_g \) and glass forming ability parameter \( K_{gl} \), have been observed to increase. The augmented cross-link density of various structural groups and closeness of packing are responsible for such an increase of these parameters. These results manifest that, with the growing presence of In₂O₃ in the glass network, indium ions mostly occupy network
forming positions, increase the cross-link density and enhance the mean bond strength. Many devoted studies on the role of In$_2$O$_3$ in various glass matrices are available in literature [6-12]. The desired properties of SrO-B$_2$O$_3$-SiO$_2$ glasses can be achieved by tailoring the concentration of these additive metal oxides (In$_2$O$_3$), to provide necessary structural units in the glass network. For example, earlier it was shown that the chemical durability of borosilicate glasses can be improved by minimizing the concentration of BO$_3$ structural units and maximizing BO$_4$ structural units with alumina and gamma ray irradiation.

The objective of this chapter is, to explore the structural influence of Ga$_2$O$_3$ on SrO-B$_2$O$_3$-SiO$_2$ glass system through a detailed investigation on spectroscopic (optical absorption (OA), emission, ESR infrared and Raman spectra) studies. The following three particular compositions of the SrO-B$_2$O$_3$-SiO$_2$: In$_2$O$_3$ glass system with different concentrations are chosen for the present study: The details of the composition are

SI-1: 40.0 SrO - 1.0 In$_2$O$_3$ - 19.0 B$_2$O$_3$ - 40.0 SiO$_2$

SI-2: 40.0 SrO - 2.0 In$_2$O$_3$ - 18.0 B$_2$O$_3$ - 40.0 SiO$_2$

SI-3: 40.0 SrO - 3.0 In$_2$O$_3$ - 17.0 B$_2$O$_3$ - 40.0 SiO$_2$

5.2 Brief review of the previous work

The studies as such on In$_2$O$_3$ glasses are very few and most of them available are on In$_2$O$_3$ films. Nevertheless, the following brief review gives information on some recent studies available on In$_2$O$_3$ glasses. Srinivasa
Reddy et al [13] investigated structural study and dielectric studies of CaO–Sb$_2$O$_3$–B$_2$O$_3$ glasses and reported that In$^{3+}$ ions occupy substitututional positions in the glass network and indium oxide behaves as a network modifier. Kityk et al [3] have reported that indium oxide is able to form very low dimensional nanoparticles, which have substantial polarizabilities influencing the surrounding structural clusters. Sahaya Baskaran et al [4] studied the properties of In$_2$O$_3$ doped PbO–P$_2$O$_5$–As$_2$O$_3$ glasses and reported that the results of differential thermal analysis suggests that there is a substantial improvement in the glass forming ability, with increase in the concentration of In$_2$O$_3$ in the glass matrix. The spectroscopic investigations pointed out that the indium ions mostly participates network forming positions with InO$_6$ structural units and increase the rigidity of the glass network. The studies of dielectric properties reveal that the presence of indium oxide in the glass network causes a considerable improvement in the insulating strength of the lead phosphate glasses. Qiu Jian Rong et al [14] have studied the infrared and Raman spectra of binary tellurite glasses containing boron and indium oxides and concluded that In$_2$O$_3$ behaves as a network modifier. Brian et al [15] have studied optical, structural, and chemical characteristics of lead-indium phosphate and lead-scandium phosphate glasses, and concluded that the glasses have a relatively high index of refraction in the visible region and exhibit moderate dispersion. They have shown that these glasses exhibit good chemical durability and
resistance to both weathering and intense gamma-radiation. Suzuya et al [2] have studied the structure of lead indium phosphate and lead scandium phosphate glasses. They have reported the short-range and intermediate-range order structures of these glasses. Tanaka et al [16] have studied the variation of optical properties with crystallization of InBO$_3$: Cr$^{3+}$ from sodium indium borosilicate glass. They have reported the origin for the high ligand field for In$^{3+}$ ions in the sodium indium borosilicate glass. Luis et al [17] have studied the frequency upconversion of orange light into blue light in Pr$^{3+}$ doped fluoroindate glasses and discussed the role of indium ions in the up conversion process. Bauer et al [18] have checked the suitability of indium–tin–oxide-coated glass as dichroic mirror for far-infrared electromagnetic radiation. They have proposed to utilize glass plates coated with indium tin oxide (ITO) as far-infrared dichroic mirrors.

Zhigang Zou et al [19] concluded that crystallinity is easily formed when In$_2$O$_3$ content added. Ravneet Kaur et al [20] have studied gamma radiation effect on borosilicate glasses and concluded that the decrease in the optical bandgap ($E_{opt}$) and increase in the refractive index from optical absorption analysis indicates the change in the glass network due to irradiation. C. Bootjomchai et al [21] have studied FTIR spectra and concluded that structural changes are occur due to irradiation. David L. Griscom et al [22] have reports that number of trapping carriers are increases with increasing the irradiation dose. Hanning. X., et.al [23] have
reported that the addition of SrO have influence of density and refractive index of these glass system. Y.P. Fu et al [24] have reported that the adding SrO can effectively reduce the thermal expansion coefficient of the studied glass ceramics.

In spite of the fact that considerable numbers of studies on In$_2$O$_3$ mixed glasses are available in literature, a thorough survey indicates that the detailed studies as such on borosilicate glasses mixed with these oxides are not available.

**5.3 Results**

**5.3.1 XRD**

Fig. 5.1 (a) and (b) shows X-ray diffraction pattern of SrO-B$_2$O$_3$-SiO$_2$: In$_2$O$_3$ glass samples before and after gamma ray irradiation. In the spectra, no sharp peaks are revealed which suggested that the atoms are randomly distributed by exhibiting amorphous nature.

![XRD pattern](image)

**Fig. 5.1** (a) XRD pattern of SI-3 glass sample before irradiation and (b) XRD pattern of SG-3 glass sample irradiated with 30 kGy dose
5.3.2 Physical properties

Table 5.1 represents the physical properties of the glass matrix. Here density and refractive index of the specified glasses exhibited decreasing tendency or molar volume exhibited increasing tendency with increasing In$_2$O$_3$ content. Likewise, after irradiation also we observed same trend in the glass matrix with increasing the intensity of the gamma irradiation.

5.3.3 Optical absorption spectra

The optical absorption spectra of pre irradiated SrO-B$_2$O$_3$-SiO$_2$:
In$_2$O$_3$ glasses are recorded in the wavelength region 300-900 nm at room temperature. Curve 1 of Figs. 5.2 (a), (b) and (c) represents the absorption spectra of all glass samples before irradiation. There is no absorption band is detected in the studied wavelength region of pre irradiated samples. The absorption edge is observed at 240 nm; and further increase of In$_2$O$_3$, the edge is shifted towards higher side. Whereas after impingement of gamma ray irradiation on glass samples a broad absorption band is observed in the wavelength region 500–650 nm with meta-center at about ~ 570 nm and shown in Figs. 5.2 (a), (b) and (c) (Curve 2, 3 and 4). The position of the band remains same for all the investigated glass samples with increasing the In$_2$O$_3$ content and gamma ray dose. Nevertheless, the absorption edge is shifted spectrally towards longer wavelength side with increase of gamma irradiation dose. From the observed absorption edges, we have evaluate the
<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (d) (g/cm³)</th>
<th>Molar Volume (Vₘ) (cm³)</th>
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<tbody>
<tr>
<td></td>
<td>Before irradiation</td>
<td>1 kGy</td>
</tr>
</tbody>
</table>

Table 5.1 Physical parameters of SrO–In₂O₃–B₂O₃–SiO₂ glasses before and after expose of gamma rays
Fig. 5.2 Optical absorption spectra of SrO–B₂O₃–SiO₂ glasses irradiated with different doses of gamma rays mixed with (a) 1.0 mol% (b) 2.0 mol% (c) 3.0 mol% of In₂O₃
Table 5.2  Data on optical absorption spectra of SrO–In$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glasses before and after exposure of gamma rays

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cutoff wavelength (nm)</th>
<th>Energy band gap ($E_o$) (eV)</th>
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<tbody>
<tr>
<td></td>
<td>Before irradiation</td>
<td>After irradiation</td>
</tr>
<tr>
<td></td>
<td>1 kGy</td>
<td>10kGy</td>
</tr>
<tr>
<td>SI-1</td>
<td>240</td>
<td>331</td>
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<tr>
<td>SI-2</td>
<td>249</td>
<td>336</td>
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<tr>
<td>SI-3</td>
<td>256</td>
<td>344</td>
</tr>
</tbody>
</table>
optical band gaps \((E_o)\) of these glasses by drawing Tauc’s and it is found to be the highest for the glasses SI-3.

### 5.3.4 Photoluminescence

Fig. 5.3 represents luminescence spectra of post irradiated SI-3 (3.0 mol\% In\(_2\)O\(_3\)) glass samples with varying gamma irradiation dose with excitation wavelength of 190 nm. The PL spectra pre-irradiated glass sample did not exhibit any peaks in the studied wavelength region. The PL spectra gamma irradiated glasses exhibits four emission peaks at ~265, ~462, ~520 and ~681 nm. The intensity of the peaks gradually is increased with increasing the irradiation dose [25, 26].

![Emission spectra of SI-3 glass sample irradiated with different gamma ray dose](image)

**Fig. 5.3** Emission spectra of SI-3 glass sample irradiated with different gamma ray dose
5.3.5 ESR Spectra

The pre-irradiated samples did not show any paramagnetic signals in ESR spectra. The room temperature ESR spectrum of the gamma irradiated SI-3 glass sample shown as Fig 5.4 (a). Fig. 5.4 (b) shows the SI-3 glass sample irradiated with different gamma ray dose in a smaller scale. Here an ESR signal is revealed at \( g \sim 2.0 \) and it is attributed to the paramagnetic defect centers generated due to gamma irradiation. The spectra are seemed to be same as we observe in aluminum and gallium ions incorporated strontium borosilicate glasses. It was seen that the nature of the paramagnetic defects formed on irradiation remained almost same.

![ESR Spectra](image)

**Fig. 5.4 (a)** ESR spectra of SI-3 glass sample irradiated with different gamma ray dose.
Fig. 5.4 (b) shows the SI-3 glass sample irradiated with different gamma ray dose in a smaller scale.

### 5.3.6 FTIR spectra

The FTIR spectra of SrO-B$_2$O$_3$-SiO$_2$: In$_2$O$_3$ glasses before and after irradiated are illustrated in Figs 5.5 (a) (b). Typically SiO$_2$ is expected to reveal four fundamental vibrations listed as follows; symmetric stretching vibrations ($v_1$) of Si–O–Si (~755–800 cm$^{-1}$), symmetrical bending vibrations ($v_2$) of Si–O–Si (~680 cm$^{-1}$), asymmetrical stretching vibrations ($v_3$) of Si–O–Si (~1020–1175 cm$^{-1}$) and asymmetrical bending vibrations ($v_4$) of Si–O–Si (~470 cm$^{-1}$). On the other hand the borate vibrations are active in mainly three infrared spectral regions with structural units like bending of B–O–B linkages in the borate networks (around 700 cm$^{-1}$), stretching
vibrations B–O bond of the BO$_4$ tetrahedral units (~800 –1200 cm$^{-1}$) and asymmetric stretching relaxation of B–O band of trigonal

![FTIR spectra of SrO–B$_2$O$_3$–SiO$_2$ glasses before irradiation with (i) 1.0 mol% (ii) 2.0 mol% (iii) 3.0 mol% of In$_2$O$_3$.](image)

**Fig. 5.5 (a)** FTIR spectra of SrO–B$_2$O$_3$–SiO$_2$ glasses before irradiation with (i) 1.0 mol% (ii) 2.0 mol% (iii) 3.0 mol% of In$_2$O$_3$

BO$_3$ units (~1200–1600 cm$^{-1}$). In the present investigation we observed ten FTIR band at about ~1584, ~1525, ~1352, ~1251, ~1052, ~752, ~551, ~485 and ~435 cm$^{-1}$ [27-33] and data is furnished in Table 5.3. From the literature survey, the bands are assigned to different structural vibrations as stretching modes of Si-OH /B-O tetrahedral of BO$_4$ units, BO$_3$ triangles with NBOs, asymmetric stretching relaxation of B-O bond of trigonal BO$_3$ units with NBOs, asymmetric stretching vibrations of Si-O-Si structural units/
vibration of BO$_4$ structural units, bending vibrations of B-O-B linkages, vibration modes of Si-O-Si linkage, Si-O-Si rocking units and O–B–O bending vibrations, respectively. On progressive increase of

![FTIR spectra](image)

**Fig. 5.5 (b)** FTIR spectra of SI-3 glass sample irradiated with different doses 1 kGy, 10 kGy, 30 kGy

In$_2$O$_3$ in the glass matrix, intensity of BO$_3$, SiO$_4$ structural vibrations are increased. Simultaneously, with increasing the gamma ray radiation dose, the intensity of the band due to combined stretching vibration modes of SiO$_4$ and BO$_4$ is observed sharpen at 1051 cm$^{-1}$. While the band observed at 778 cm$^{-1}$ became broader and shifter towards lower wavelength side.
Table 5.3 Summary of band positions of FTIR spectra of SrO–In$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glasses

<table>
<thead>
<tr>
<th>S.No</th>
<th>Glasses</th>
<th>Band assignments</th>
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<tr>
<td>1</td>
<td>1584</td>
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<td></td>
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<tr>
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<tr>
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<tr>
<td>4</td>
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</tbody>
</table>

5.3.7 Raman spectra

The Raman spectra illustrated in Fig. 5.6 (a) and (b) and the Raman data is furnished in the Table 5.4. The spectra consist seven bands in all specified glass samples, their band positions are ~1436, ~1237, ~1020, ~815, ~635, ~456 and ~206 cm$^{-1}$ [4, 34-37]. These bands are assigned as vibrations of BØ$_2$O$^-$ triangles containing NBOs, diborate groups consisting
**Fig. 5.6 (a)** Raman spectra of SrO–B\(_2\)O\(_3\)–SiO\(_2\) glasses before irradiation with (a) 1.0 mol\% (b) 2.0 mol\% (c) 3.0 mol\% of In\(_2\)O\(_3\)

**Fig. 5.6 (b)** Raman spectra of SI-3 glass sample irradiated with different doses 1 kGy, 10 kGy, 30 kGy
of six-membered rings containing two BO$_4$ teterahedra, asymmetrical Si-O-
Si structural units, symmetrical Si-O-Si structural units, symmetric breathing
vibrations of meta-borate rings, In–O vibrations of InO$_6$ structural units,
respectively. On progressive increasing gamma irradiation dose, there is no
significant change in the position of the observed bands but slightly change
in intensity as the intensity of the asymmetrical vibrational bands is
decreases whereas symmetrical vibrational bands intensity is increases with
increasing the gamma ray irradiation.

**Table 5.4** Summary of band positions of Raman spectra of SrO–In$_2$O$_3$–B$_2$O$_3$–SiO$_2$
glasses

<table>
<thead>
<tr>
<th>S.No</th>
<th>Glasses</th>
<th>Band assignments</th>
</tr>
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<tbody>
<tr>
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<td>SI-1</td>
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</tr>
<tr>
<td>1</td>
<td>1436</td>
<td>1436</td>
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<tr>
<td></td>
<td>vibrations of BØ$_2$O$^-$ triangles containing NBOs</td>
<td></td>
</tr>
<tr>
<td>2</td>
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</tr>
<tr>
<td></td>
<td>stretching vibrations of BO$_4$ teterahedral units</td>
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</tr>
<tr>
<td>3</td>
<td>1020</td>
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<tr>
<td>4</td>
<td>815</td>
<td>817</td>
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<td>Si-O-Si symmetrical vibrations</td>
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<td>6</td>
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</tr>
<tr>
<td>7</td>
<td>206</td>
<td>206</td>
</tr>
<tr>
<td></td>
<td>InO$_6$ structural units</td>
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</tr>
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</table>

**5.4 Discussion**

The titled SrO-B$_2$O$_3$-SiO$_2$: In$_2$O$_3$ glass system is with combination of
glass formers (SiO$_2$, B$_2$O$_3$) and with network modifier (SrO, In$_2$O$_3$). SiO$_2$
participates in the glass network with SiO$_4$ tetrahedra, whereas B$_2$O$_3$ participates with BO$_3$ and BO$_4$ structural units, all these units are shared with oxygens forming a fully polymerized network. Since the addition of Sr$^{2+}$ to the borosilicate glass, de-polymerizes Si–O–Si and B–O–B network, with the formation of Q$^4$ tetrahedra into Q$^3$ (viz., SiO$_4$ tetrahedra with three bridging oxygens and one terminal de-bonded oxygen) and Q$^2$ tetrahedra (viz., SiO$_4$ tetrahedra with two bridging oxygens and two terminal de-bonded oxygen) and Q$^1$. At the same time the mechanism involved in coordination transform of boron can be explained as per the following chemical equilibrium:

$$2 \text{[BO}_{4/2}\text{]} + \text{SrO} \rightarrow 2 \text{[BO}_{1/2}\text{O}_2\text{]} + \text{Sr}^{2+}$$

$$2\text{BO}_3 + \text{SrO} \rightarrow 2\text{BO}_3^- + \text{Sr}^{2+}$$

Before irradiation, with the gradual addition of In$_2$O$_3$, the intensity of the bands due to symmetric vibrations of the silicate and borate groups are observed to increase while that of the bands due to asymmetric vibrations of the silicate and borate groups is observed to decrease. Earlier spectroscopic studies on some binary glass systems containing In$_2$O$_3$ revealed that the indium ions behaves as a network modifier or network forming positions with InO$_6$ structural units in the glass network [2]. The concentration of In$_2$O$_3$ increases, indium ions taking network forming position and decreases the concentration of BO$_3$ structural units. Here the observations suggest that
indium ions act as network modifier even with increasing In$_2$O$_3$ content in the glass matrix and reduce the network connectivity.

On progressive gamma irradiation, here in the FTIR spectra stretching relaxation of B-O bond of BO$_3$ units with NBOs are gradually increased which suggests that BO$_4$ structural units transform to BO$_3$ because the gamma radiation reducing the constraints on the structural relaxation process, accompanied by decrease of the average bridging bond angle and bond strength. Therefore the network becomes de-polymerized. Thus, the analysis of the FT-IR and Raman spectral studies pointed out that there is an increasing degree of disorder in the glass network with increasing content of In$_2$O$_3$ as well as intensity of the gamma radiation.

The optical absorption spectra also support the earlier arguments, here optical band gap is decreased gradually and absorption edge shifts towards higher wavelength side [38]. This may be due to increase in the degree of localization of electrons with increase in the concentration of In$_2$O$_3$. As discussed in earlier chapters-III and IV, the action of gamma-ray irradiation on glasses to the formation of boron–electron centers, non–bridging oxygen hole centers and boron–oxygen hole centers [39-41]. However, these factors may be responsible for the band observed in the irradiated samples. The increase in the intensity of the band with the gamma irradiation dose clearly suggested that the increase in the concentration of
above mentioned defects in the glass network. The optical absorption edge is shifted further towards higher wavelength side with increasing the concentration of In$_2$O$_3$. Due to the formation of different types of color centers and other defects formed in the glass matrix, the absorption edge shift towards higher wavelength side, which indicates that the disorder in the glass network increases with increasing the irradiation dose. The presence of higher concentration of NBOs, color centers leads to an increase in the degree of localization of electrons there by increase the donor centers in the glass matrix. The increasing of donor centers in the glass matrix absorption edge shifts towards higher wavelength side and decreases the optical band gap especially for the post irradiated glass samples [42].

The post irradiated glass samples exhibit four emission peaks in PL spectra. The emission peak at ~ 665 nm was assigned to the non-bridging-oxygen-hole centers (NBOHC) and its structure is denoted by ≡Si–O’, here dot symbol on oxygen indicates an unpaired electron [43, 44]. The emission from electron trap (E’) centers such as ≡Si’ was observed at ~230 and ~465 nm [45]. The band at ~500 nm was attributed to the well-known oxygen deficiency centers (ODC) [46]. The generation of these defects is due to the bond cleavage occurring at regular Si-O sites due to the impinging gamma rays on the glass. It has been suppose that ionizing radiation causes the following radiolysis reaction:
\[ =\text{Si-O-Si} = \rightarrow =\text{Si-O}^\cdot + =\text{Si}^\cdot \]

In the ESR spectra, the intensity of the ESR signal at \(g \approx 2.0\) is increases with increase of the gamma irradiation dose which is suggested that the concentration of paramagnetic defect centers are increases with increase of dose. The action of gamma ray irradiation on these glasses produces the paramagnetic defect centers, such as boron - oxygen hole centers (BOHC) (\(=\text{B}^\cdot-\text{O}^\cdot\)) due to which arises from a hole trapped on one oxygen atom bonded to a boron atom [47, 48] or breaking the B-O-B bonds, silicon hole centers due to breaking the Si-O-Si bonds and electron trap centers.

5.5 Conclusions

The gamma radiation resistant capability of \(\text{SrO-In}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2\) glasses was evaluated as a function of \(\text{In}_2\text{O}_3\) concentration by studying their spectroscopic properties. XRD pattern reveals that the amorphous nature of studied glass samples does not change with the gamma irradiation. The analysis of optical, photoluminescence, ESR investigations clearly suggested that formation of defect centers with gamma irradiation. With the support of FTIR and Raman spectral data, suggested that the network connectivity is gradually decreased with content of \(\text{In}_2\text{O}_3\) whereas the network depolymerization is increases with gamma irradiation.
References


