Spectroscopic and radiative properties of Nd$^{3+}$ ions doped zinc bismuth borate glasses

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Glasses having composition 20ZnO·xBi$_2$O$_3$·(79-x)B$_2$O$_3$ (15 ≤ x ≤ 35, in mol%) doped with 1 mol% of Nd$^{3+}$ ions were prepared. The different physical and absorption spectral properties have been investigated to understand the variation of the hypersensitive absorption band intensities. From the absorption spectra, Judd-Ofelt intensity parameters, $\Omega_i$ ($i = 2, 4, 6$) have been calculated and these parameters were used to estimate the radiative properties. The values of Judd-Ofelt parameters increase with increase in the concentration of Bi$_2$O$_3$, which may be due to the increase in neodymium-oxygen (Nd-O) covalency. The glass having high bismuth content has displayed a significant increase in the intensity of the hypersensitive transition $^5G_{45/2}^+G_{7/2}^- \leftrightarrow ^7H_{9/2}$ of Nd$^{3+}$ ion which may be attributed to the asymmetry ligand field around the rare earth ion site. The shifting of the hypersensitive band shows that the covalency of the rare earth (RE-O) bond increases with Bi$_2$O$_3$ content in the glass due to increased interaction between the rare earth ion and the non-bridging oxygen. The large radiative transition probabilities in the present glasses suggest their suitability for various laser applications. The structure of the present glasses has been studied using FTIR spectroscopy.

Keywords: Glasses, Optical materials, Optical properties, FTIR spectra

1 Introduction

The first demonstration of laser action in a neodymium doped glass was done by Snitzer$^1$ in 1961 and since then considerable progress has been made in evaluating the effects of amorphous host materials on the lasing properties of various rare earth ions. A large variety of laser glasses doped with Nd$^{3+}$ ions has been investigated with the purpose of generating efficient broadband laser emission$^2$ around 1060 nm. It has been shown recently that the heavy metal oxide (HMO) glasses are very attractive hosts for rare earth ions because of the high refractive index (~ 2.4 at 633 nm), lower transition temperature than silicate and phosphate glasses$^3$, large spectral transmission window (~ 0.5-8.80 μm) and low phonon energy. HMO glasses doped with trivalent rare earth ions are also considered to be promising material for optical amplifiers$^4$. The glasses containing rare earth in various forms such as network formers, modifiers or luminescent ions are of great deal of interest for their unique optical, electrical and magnetic properties$^4$. Among the conventional glasses, borate glasses have been known to be excellent host matrices for the rare earth oxides because of their good glass forming nature compared to several other conventional systems like phosphate, germanate, vanadate and tellurite glass families$^5$. Waveguide lasers and amplifiers fabricated using rare-earth doped glasses provide optical amplification in the 1.3 and 1.5 μm windows and moreover these may offer an unusual method of realizing more compact and efficient laser devices that would be difficult to fabricate with rare-earth-doped fibers$^5$. In addition, inorganic glass containing heavy metal networks is of particular interest. For instance, it is known that for borate glasses the phonon energy can be as high as 1400 cm$^{-1}$, but the presence of heavy metal ion reduces the non-radiative transition probability substantially. A host glass doped with rare earth ion has higher luminescence quantum efficiency particularly for the longer wavelength transitions. However, heavy metal glasses possess relatively higher optical non-linearity$^6$, therefore, it would be fruitful to investigate the features of optical non-linearity in such materials, which happens to be highly luminescent. The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelt theory$^7,8$. This theory defines a set of three intensity parameters: $\Omega_i$ ($i = 2, 4, 6$), which are sensitive to the environment of the rare earth ion. From these parameters, important optical properties such as
radiative transition probability for spontaneous emission, radiative lifetime of the excited states and branching ratio (which predict the fluorescence intensity of laser transitions) can be estimated and used further to examine the dependence of the spectroscopic parameters on the glass composition. In order to examine the significance and importance of heavy metal oxide (HMO) based glasses, the optical and structural properties of rare earth doped glasses have been investigated\textsuperscript{9-12} wherein it is reported that B\textsubscript{2}O\textsubscript{3} functions as a good network-former and CdO working as a network-modifiers, B\textsubscript{2}O\textsubscript{3} as unconventional network former as well as modifiers.

2 Experimental Details

The Nd\textsuperscript{3+} ion doped glasses having composition 20ZnO·xBi\textsubscript{2}O\textsubscript{3}·(79-x)B\textsubscript{2}O\textsubscript{3}·1Nd\textsubscript{2}O\textsubscript{3}, (15 \leq x \leq 35 mol\%) were prepared using melt-quenching technique. The 15 g batches of analar grade chemicals were taken in appropriate proportion and melted in a crucible at 1150°C for 40 min. The melt was stirred frequently for homogeneous mixing of all the constituents. The glass samples were obtained by pouring and quenching the melt in between two stainless steel plates. Density ($D$) was measured by standard Archimedes’s principle using xylene as the immersing liquid. The refractive index ($n$) was measured by the Brewster angle method using He-Ne laser (632 nm). Differential scanning calorimeter (DSC) profiles were recorded on Q-10 (TA-Instrument) DSC in the temperature range 40-520°C at the rate of 10°C per min under nitrogen atmosphere. The optical absorption spectra (400-3200 nm) were recorded on Cary-Varian 5000 spectrophotometer at room temperature. IR transmission spectra of the glasses were recorded at room temperature using KBr pellet technique on a Shimadzu FTIR 8001PC spectrometer in the range 400-1400 cm\textsuperscript{-1}.

3 Results and Discussion

The X-Ray diffraction pattern of all the glasses is shown in Fig. 1 and it confirms the amorphous nature of the prepared glass samples. The values of density ($D$), molar volume ($V_M$), refractive index ($n$), number density of Nd\textsuperscript{3+} ions ($N_d$), dielectric constant ($\varepsilon$), optical basicity ($A_{30}$) etc. for the present glass samples are listed in Table 1. Since Bi is incorporated as B\textsubscript{2}O\textsubscript{3} and Zn as ZnO, the concentration of Bi in the resulting glass is about two or three times higher than that of Zn. This has important consequences on the overall glass structure and properties. It is observed from Table 1 that density as well as refractive index

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Mol% (x)</th>
<th>D (g/cm\textsuperscript{3})</th>
<th>$V_M$ (cm\textsuperscript{3}/mol)</th>
<th>n</th>
<th>$\varepsilon$ ($n^2$)</th>
<th>$R_L$ ((n-1)/(n+1))$^2$</th>
<th>$R_M$ (cm\textsuperscript{3})</th>
<th>$\Lambda_{30}$</th>
<th>$N_d$ (10\textsuperscript{22} ions/cm\textsuperscript{3})</th>
<th>$r_i$ (Å)</th>
<th>$r_o$ (Å)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBN1</td>
<td>15</td>
<td>4.13</td>
<td>32.47</td>
<td>1.85±0.01</td>
<td>3.42</td>
<td>8.89</td>
<td>14.51</td>
<td>0.260</td>
<td>3.71±0.02</td>
<td>1.54±0.02</td>
<td>2.60</td>
<td>486</td>
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<tr>
<td>ZBN2</td>
<td>20</td>
<td>4.49</td>
<td>34.28</td>
<td>1.91±0.01</td>
<td>3.65</td>
<td>9.77</td>
<td>16.02</td>
<td>0.274</td>
<td>3.51±0.03</td>
<td>1.52±0.02</td>
<td>2.65</td>
<td>480</td>
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<tr>
<td>ZBN3</td>
<td>25</td>
<td>4.74</td>
<td>36.65</td>
<td>1.98±0.01</td>
<td>3.92</td>
<td>10.81</td>
<td>18.08</td>
<td>0.289</td>
<td>3.28±0.01</td>
<td>1.48±0.02</td>
<td>2.71</td>
<td>476</td>
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<tr>
<td>ZBN4</td>
<td>30</td>
<td>5.06</td>
<td>38.25</td>
<td>2.04±0.01</td>
<td>4.16</td>
<td>11.70</td>
<td>19.63</td>
<td>0.304</td>
<td>3.15±0.03</td>
<td>1.46±0.03</td>
<td>2.75</td>
<td>473</td>
</tr>
<tr>
<td>ZBN5</td>
<td>35</td>
<td>5.21</td>
<td>40.95</td>
<td>2.11±0.01</td>
<td>4.45</td>
<td>12.73</td>
<td>21.91</td>
<td>0.318</td>
<td>2.94±0.01</td>
<td>1.43±0.01</td>
<td>2.81</td>
<td>459</td>
</tr>
</tbody>
</table>
increase with increase in the concentration of Bi$_2$O$_3$. Similar trend is observed for the molar refractivity ($R_{md}$) values. The molar refractivity is considered as the sum of the contributions of the cationic refraction and oxygen ion refraction and it is the measure of bonding condition in the glass. The optical basicity $(A_{ob})$ addresses the ability of oxide ions to contribute the negative charge into the glass matrix. In other words, it is the electron donating power of the oxygen in the oxide glasses. It is well known that the free oxygen has the ability to donate negative charge (–2) but when it is participating in the chemical bond with the surrounding cations in the matrix, its donating power to the metal ion reduces. Certain metal ions exhibit change in colour or oxidation state depending upon the degree of electronic charge they receive from the neighbouring oxygen ions. There are several approaches to estimate the optical basicity theoretically. In the present glasses, optical basicity increases with increasing Bi$_2$O$_3$ content (Table 1). This increase indicates that the polarisability of the oxide species in the glass network increases which further results in increase in the number of non-bridging oxygen ions. The refractive index of a glass usually depends on individual ions present in the glass and polarisability of cations. In general, the refractive index of glass increases for the highly polarizable cations. For all ZBN glasses, dopant ion concentration ($N_d$), ionic radius, their inter-ionic distance have been estimated using relevant equations and are also presented in Table 1.

The measured values of glass transition temperature ($T_g$) are listed in Table 1. It is observed that $T_g$ decreases with increase in Bi$_2$O$_3$ content which indicates more open structure formation of the glass.

The optical absorption spectra of ZBN1 and ZBN5 glasses in the range 430-980 nm are shown in Fig. 2. The following transitions are observed in this spectral region: $^4$F$_{5/2}$, $^4$F$_{7/2}$+$^2$H$_{15/2}$, $^4$S$_{9/2}$+$^2$F$_{5/2}$, $^4$F$_{9/2}$, $^2$H$_{11/2}$, $^4$G$_{5/2}$+$^2$G$_{7/2}$, $^4$G$_{7/2}$, $^4$G$_{9/2}$+$^4$I$_{9/2}$. These transitions have been assigned as proposed by Carnall et al. The experimental oscillator strength ($f_{\text{meas}}$) of the absorption transitions has been calculated using the following relation:

$$f_{\text{meas}} = 4.32 \times 10^{-9} \int \varepsilon(\nu) d\nu \quad \cdots (1)$$

Where $\varepsilon(\nu) = \frac{OD}{\kappa t}$ is the molar extinction coefficient, $OD$ being the optical density, $\kappa$ is the concentration of rare earth ion in moles/litre and $t$ is the optical length of the glass in cm and $\nu$ is the energy. According to Judd-Ofelt theory, the oscillator strength of a transition between an initial manifold $(S, L) J$ and a final manifold $(S', L') J'$ is given by:

$$f_{\text{cal}}(aJ, bJ') = \frac{8 \pi^2 m \nu}{3h(2J+1)} \left[ \frac{(n^2+1)^2 S_{el} + n S_{md}}{9n} \right] \cdots (2)$$

where $S_{el}$ is electric dipole line strength and $S_{md}$ is the magnetic dipole line strength, $n$ is the refractive index, $m$ is the mass of electron, $h$ is Planck’s constant and $(2J+1)$ is the degeneracy of the ground state of Nd$^{3+}$ ions. On substituting measured oscillator strength ($f_{\text{meas}}$) from absorption spectra, the values of calculated oscillator strength ($f_{\text{cal}}$), and intensity parameters; $\Omega_i$ ($i = 2, 4, 6$) have been calculated by least square method.

The values of $f_{\text{meas}}$, $f_{\text{cal}}$ and deviation parameter, $\delta_{\text{rms}}$ are given in Table 2 for all the glass samples. The variation of Judd-Ofelt intensity parameters with concentration of Bi$_2$O$_3$ is shown in Fig. 3. The values of $\Omega_2$, $\Omega_4$ and $\Omega_6$ increase with increasing Bi$_2$O$_3$ content (Fig. 3). $\Omega_2$ is the quantity that mainly
Table 2 — Oscillator strength of some transitions from the indicated level to the \(^{4}I_{9/2}\) and the root mean square \(\delta_{\text{RMS}}\), which indicates the fit quality of theoretical and experimental results of Nd\(^{3+}\) ions, doped zinc bismuth borate glasses.

<table>
<thead>
<tr>
<th>Transition from ground state</th>
<th>(\lambda) (nm)</th>
<th>(\delta_{\text{RMS}}(10^{-6}))</th>
<th>ZBN1</th>
<th>ZBN2</th>
<th>ZBN3</th>
<th>ZBN4</th>
<th>ZBN5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{4}F_{9/2}) \rightarrow (^{4}I_{9/2})</td>
<td>870</td>
<td>1.85</td>
<td>1.91</td>
<td>1.98</td>
<td>2.04</td>
<td>2.43</td>
<td>2.64</td>
</tr>
<tr>
<td>(^{4}F_{9/2},^{4}H_{9/2})</td>
<td>800</td>
<td>2.97</td>
<td>3.94</td>
<td>3.21</td>
<td>3.56</td>
<td>3.96</td>
<td>4.23</td>
</tr>
<tr>
<td>(^{4}S_{9/2},^{4}F_{9/2})</td>
<td>744</td>
<td>3.30</td>
<td>2.93</td>
<td>3.90</td>
<td>4.12</td>
<td>4.65</td>
<td>4.87</td>
</tr>
<tr>
<td>(^{4}F_{9/2})</td>
<td>678</td>
<td>1.87</td>
<td>2.74</td>
<td>2.54</td>
<td>2.67</td>
<td>2.99</td>
<td>3.22</td>
</tr>
<tr>
<td>(^{4}G_{9/2},^{4}G_{7/2})</td>
<td>582</td>
<td>3.05</td>
<td>3.24</td>
<td>3.69</td>
<td>4.01</td>
<td>4.22</td>
<td>4.63</td>
</tr>
<tr>
<td>(^{4}G_{7/2})</td>
<td>524</td>
<td>1.09</td>
<td>0.90</td>
<td>1.78</td>
<td>1.92</td>
<td>2.58</td>
<td>2.86</td>
</tr>
<tr>
<td>(^{4}G_{9/2})</td>
<td>512</td>
<td>2.67</td>
<td>1.08</td>
<td>2.98</td>
<td>3.19</td>
<td>3.42</td>
<td>3.67</td>
</tr>
</tbody>
</table>

Fig. 3 — Compositional dependence of Judd-Ofelt intensity parameters on Bi\(_2\)O\(_3\) content

depends on the crystal field parameters and the asymmetry of the rare-earth site. The presence of Bi-O as well as Zn-O bonds in the glass results in a more symmetric crystal field. These parameters do not vary with the variation in the concentration of Nd\(^{3+}\) ions for the same glass matrix. However, these parameters vary with the change in glass matrix. The position and shape of some of the electric dipole transitions of the rare earth (RE) are very sensitive to the environment. These transitions are called hypersensitive transitions and can be employed for finding out the covalency of the rare earth-oxygen (RE-O) bond. These transitions shift in wavelength with the variation in glass host because of the nephlauxetic effect\(^{30}\). This happens when the electronic orbitals within the \(4f\) configuration are deformed in the presence of the host ligand field. With the increase in overlap of the oxygen orbitals and the \(4f\) orbitals, the energy level structure of the Nd\(^{3+}\) ion contracts, leading to the wavelength shift. Henrie et al\(^{18}\) have reported that in halide complexes such as NdI\(_3\) (gas), NdBr\(_3\) (liq), NdI\(_3\) (sol), Nd[EDTA], the degree of covalency of the neodymium-oxygen (Nd-O) bond increases in the order Cl \(<\) Br \(<\) I, as indicated by the shift of the peak wavelength of the hypersensitive transition of Nd\(^{3+}\) to longer wavelength. In the present zinc bismuth borate glasses, the red shift in the peak wavelength of the hypersensitive transitions for Nd\(^{3+}\) ions with increase in Bi\(_2\)O\(_3\) content, indicates an increasing covalent nature for the RE-O bond.

The variation of spectral profiles of the transitions \(^{4}I_{9/2}\rightarrow^{4}G_{9/2},^{4}G_{7/2}\) (HST) and \(^{4}I_{9/2}\rightarrow^{4}S_{9/2},^{4}F_{9/2}\) of Nd\(^{3+}\) with glass composition has also been investigated. In these transitions, two peaks are distinguished by the Stark splitting and the relative intensity ratio between the peaks varies with glass composition. The peak intensity of the short wavelength and long wavelength components are designated as \(I_S\) and \(I_L\), respectively. Increase in intensity ratio \(I_L/I_S\) indicates a shift of the centre of gravity of the absorption spectra to longer wavelengths which further indicates an increase in the covalency of the Nd-O bond. As pointed out by Krupke\(^{20}\) the transition intensities of \(^{4}I_{9/2}\rightarrow^{4}G_{9/2},^{4}G_{7/2}\) and \(^{4}I_{9/2}\rightarrow^{4}S_{9/2},^{4}F_{9/2}\) are determined mainly by \(\Omega_2||\langle \mu_f \rangle^2\rangle^2\) and \(\Omega_6||\langle \mu_i \rangle^2\rangle^2\) terms, respectively. Therefore, from the relationship between the parameters and relative intensity ratio \(I_L/I_S\) (which varies with glass composition in these transitions), the effect of Nd-O bond on the intensity parameters can be obtained. In zinc bismuth borate glasses, the stark
splitting of the transition $^4I_{9/2} \rightarrow ^4G_{5/2}, \ ^2G_{7/2}$ of Nd$^{3+}$ is not well resolved. The dependence of $\Omega_2$ on the intensity ratio $I_4/I_6$ is, therefore, not clear. The spectral profile of the transition $^4I_{9/2} \rightarrow ^4S_{3/2}, \ ^2F_{7/2}$ of Nd$^{3+}$ for different Bi$_2$O$_3$ concentrations is shown in Fig. 4. The above discussion reveals that the dependence of intensity parameters $\Omega_2$ on the intensity ratio $I_4/I_6$ of the transition $^4I_{9/2} \rightarrow ^4G_{5/2}, \ ^2G_{7/2}$ could not be ascertained due to poor resolution of the crystal field split levels, whereas $\Omega_6$ increases with increase in $I_4/I_6$ of the transition $^4I_{9/2} \rightarrow ^4S_{3/2}, \ ^2F_{7/2}$. Increase of $I_4/I_6$ indicates an increase in covalency of the Nd-O bond. The relationship between the intensity parameter $\Omega_6$ and the intensity ratio $I_4/I_6$ ($I_4 = 747 \text{ nm}$ and $I_6 = 742 \text{ nm}$) since the intensity of the transition $^4I_{9/2} \rightarrow ^4S_{3/2}, \ ^2F_{7/2}$ is determined by $\Omega_6$, it is an indicator of the covalency of the RE-O bond. In the present system, the transition $^4G_{5/2}^+^2G_{7/2} \leftrightarrow ^4I_{9/2}^-$ is the most intense (Fig. 2) and it also satisfies the selection rules of hypersensitive transition such as $J = 2; \Delta L \leq 2$ and $\Delta S = 0$. The peak wavelength of the hypersensitive transition of Nd$^{3+}$ ion shifts from 582 to 590 nm and this red shift is indicative of an increase in the covalent nature of the neodymium-oxygen (Nd-O) bond. The substitution of B$_2$O$_3$ by Bi$_2$O$_3$ converts three coordinated boron (B$_3$) to four coordinated boron (B$_4$) resulting in the conversion of boroxol units to pentaborate groups. The fraction of B$_3$ in the form of diborate units is maximum around 40 mol% in bismuth borate glasses. With further addition of Bi$_2$O$_3$, back conversion of B$_3$ to B$_4$ takes place with the formation of non-bridging oxygen ions. It has been reported$^{20}$ that in borate glasses, a rare earth ion is coordinated by four BO$_4$ tetrahedra so that the two sets of two opposite tetrahedral are in similar position relative to the rare earth ion and retain the eight-coordination of the metal ion by non-bridging oxygen ions (two oxygen ions contributed by each tetrahedron). Bi$_2$O$_3$ can form its own network without involving the borate groups. Usually, the BO$_4$ itself will tighten the structure and with the above heavy metal network, the glass has a very tight structure. Therefore, this close packing of the local structures provides an increased interaction between the rare earth and the non-bridging oxygen ions leading to the observed nephelauxetic shift. In comparison, the same nephelauxetic shift was observed in zinc bismuth borate (ZBS) glasses$^9$. Saisudha$^{et \ al.}^{17}$, observed that the transition $^4G_{5/2}^+^2G_{7/2} \leftrightarrow ^4I_{9/2}^-$ did not find any change in shape in the lead borate glasses with different lead ion concentrations. In the present study, similar shapes have been observed for the transitions in all the samples. This implies that the rare earth (RE) experiences similar environment in all the glass samples. The increase of $\Omega_2$ and hence, the asymmetry of the crystal field at the rare earth site with increase in Bi$_2$O$_3$ content for Nd$^{3+}$ ion indicates that the rare earth ion in present glass matrix might be surrounded only by bismuth groups. The appearance and disappearance of the borate groups do not affect the symmetry of the ligand field at the rare earth site. According to Jacobs$^{et \ al.}^{16}$., the emission intensity of Nd$^{3+}$ is mainly characterized by the $\Omega_4$ and $\Omega_6$ parameters. If the spectroscopic quality factor (SQF = $\Omega_4/\Omega_6$) is greater than 1, then the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition will be more intense than the $^4F_{9/2} \rightarrow ^4I_{11/2}$ transition. In the present system, SQF is greater than 1, therefore $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition is found to be more prominent. Table 3 lists the J-O intensity parameters reported for Nd$^{3+}$ ions in different borate glasses for comparison.

To predict the lasing performance of the Nd$^{3+}$ ions in ZBN glasses, the computed Judd-Ofelt intensity parameters ($\Omega_i$) have been used to estimate the radiative emission properties. The spontaneous emission probability ($A_{rad}$), total radiative transition
rate ($A_\lambda$), radiative life time ($\tau_\lambda$) and branching ratio ($\beta$) of emission transitions $^4F_{3/2} \rightarrow ^4I_{15/2, 13/2, 11/2}$, and $9/2$ have been calculated and the obtained values are given in Table 4. The radiative properties of Nd$^{3+}$ ions mainly depend on the $\Omega_4$ and $\Omega_6$ parameters. Therefore, the ratio, $\Omega_6/\Omega_4$ (SQF) can be used to describe the emission transitions in the Nd$^{3+}$ doped systems. The condition $\Omega_4 >> \Omega_6$ favours the transition $^4F_{3/2} \rightarrow ^4I_{11/2}$ at 1.06 μm and $\Omega_6 << \Omega_4$ results the more probability for the emission $^4F_{15/2}$ transition $^4F_{3/2} \rightarrow ^4I_{9/2}$ at around 890 μm. The calculated values of SQF in the present glasses are in the range 1.03-1.25 (Table 3) and satisfy the second condition (i.e. $\Omega_6 << \Omega_4$). Hence, the present Nd$^{3+}$ doped zinc bismuth borate glass system is favourable to the lasing transition $^4F_{9/2} \rightarrow ^4I_{9/2}$ at 890 μm in the near IR wavelength. The probable lasing transitions of the Nd$^{3+}$ ions are shown in Fig. 5.

Table 4 shows that the values of transition probabilities, $A_{rad}$ (s$^{-1}$) for emission transition $^4F_{9/2} \rightarrow ^4I_{11/2}$ are larger than the other three transitions and $A_{rad}$ increases with increase in Bi$_2$O$_3$ content. However, the branching ratio of the emission transitions is approximately the same for all the transitions. The radiative life time of the emission level ($^4F_{3/2}$) is obtained from the reciprocal of the total radiative rate to all the lower energy level for Nd$^{3+}$ ions and is found to decrease with increase in Bi$_2$O$_3$ content in the present glasses. The stimulated emission cross-section is given by:

$$\sigma = \frac{\lambda^4 A_{rad}}{8\pi c n^2 \Delta \lambda_{eff}} \quad \ldots (3)$$

![Fig. 5 — Lasing transitions of Nd$^{3+}$ ($^4F_{3/2} \rightarrow ^4I_{15/2, 13/2, 11/2, 9/2}$) ions in ZBN glasses](image)
where $\Delta \lambda_{\text{eff}}$ is the effective band width which is calculated by integrating the intensity of the emission line shape and dividing by the intensity at the maximum wavelength. $\sigma$ for the fluorescence lines of Nd$^{3+}$ ions can be calculated from the fluorescence spectra using radiative transition probability. The $\sigma$ of the fluorescence line of Nd$^{3+}$ ions in bismuth borate glasses has been calculated and is found to be large. This large $\sigma$ is attractive feature for low-threshold, high-gain application and is utilized to obtain continuous wave (CW) laser action. In tellurite and lead borate glasses, doped with Nd$^{3+}$, the radiative transition probabilities are large and hence, the stimulated emission cross-sections facilitates laser action. The radiative transition probabilities in the present zinc bismuth borate glasses are of the same order as those reported for tellurite glasses and hence, can be utilized as active laser host material. The present glasses can be doped heavily with rare earth ions and utilized for high-concentration mini-laser.

The infrared spectra of all the glass samples are shown in Fig. 6. It is observed from Fig. 6 that with the increase in Bi$_2$O$_3$ content, the intensity of the band at 510 cm$^{-1}$, arising due to Bi–O–Bi vibration of the distorted (BiO$_6$) octahedral units, increases and shifts to lower wave number. Since (BiO$_3$) polyhedra vibration band at 840 cm$^{-1}$ does not appear in the IR spectra, therefore, it can be concluded that only (BiO$_6$) octahedral units build up the bismuthate structure of the investigated glasses. Bending vibration of B–O–B in (BO$_3$) units is observed at 680 cm$^{-1}$ for ZBN1 sample and it shifts up to 690 cm$^{-1}$ for ZBN5 glass sample. This shift is introduced by the electrostatic field of the strongly polarizing Bi$^{3+}$ ions. The spectral range of 900-950 cm$^{-1}$ is typical for the stretching vibration of [BO$_4$] units. The existence of (BO$_3$) units indicates that the increase in Bi$_2$O$_3$;B$_2$O$_3$ ratio leads to progressive conversion of (BO$_3$) units to (BO$_4$) units. Band in the range 1200-1300 cm$^{-1}$ is assigned to the stretching vibration of (BO$_3$) units. Further, with the increase in Bi$_2$O$_3$ content, the intensity of both the bands decreases and are shifted to lower wave numbers. It is assumed that new bridging Bi–O–B bonds are formed due to the increase in concentration of strongly polarizing Bi$^{3+}$ ions. Since the stretching force constant of Bi–O bonding is substantially lower than that of the B–O bonding, therefore, the stretching frequency of Bi–O–B bond tends to be lower.

4 Conclusions

Using the Judd-Ofelt theory, the three intensity parameters, spontaneous emission probability and radiative life time of Nd$^{3+}$ ions doped in zinc bismuth borate glasses are determined. The change in position and intensity parameters of the transitions in the optical absorption spectra of the Nd$^{3+}$ ions are correlated to the structural change in the host matrix. The shift of the hypersensitive bands of Nd$^{3+}$ ions shows that the covalency of the rare earth oxygen (RE-O) bond increases with Bi$_2$O$_3$ content, due to the increased interaction between the rare earth ions and non bridging oxygen ions. The variation of the intensity parameter $\Omega_2$ with Bi$_2$O$_3$ content for Nd$^{3+}$ ions implies that the crystal field parameter plays an important role in determining the intensity while the $\Omega_6$ mainly depends on nephelauxetic effect for Nd$^{3+}$ ions. The radiative emission probability is high as in tellurite glasses, which have been successfully used as laser host material. This indicates that the zinc bismuth borate glasses may be useful as laser host materials. Spectroscopic quality factor (SQF) ratio shows that the laser emission takes place at 890 μm. From IR spectra, it is predicted that with addition of Bi$_2$O$_3$, conversion of B$_2$ to B$_4$ to takes place with the formation of non-bridging oxygen ions and the band near 510 cm$^{-1}$ shifts to lower wave-number.
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References