Absorption And Energy Band Gap Studies Of Nd$^{3+}$-Er$^{3+}$ Ions Doped Zinc Alumino Bismuth Borate Glasses

V. R. L Murty, P. Rekha rani, M. Venkateswarlu, K. Swapna, Sk. Mahamuda, M. V. V. K Srinivas Prasad

Abstract:— Barium lead aluminofluoroborate (BaPbAlFB) glasses doped with different concentrations of co-doping of neodymium and erbium are prepared by using melt quenching technique to study their structural and optical properties. Oscillator strength are evaluated for the corresponding transitions from ground state to the excited states like $^4D_{5/2}$, $^4G_{9/2}$, $^4G_{11/2}$, $(^2G, ^4F_{2H})_{9/2}$, $^2P_{1/2}$, $^5F_{5/2}$, $^4F_{7/2}$, $^4H_{11/2}$, $^4G_{5/2}$, $^4F_{3/2}$, $^4S_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4I_{13/2}$ and $^4I_{11/2}$ respectively, with the help of the absorption spectra. To know the nature of the bonding between the ligands, we have evaluated Judd-Ofelt intensity parameters by using oscillator strengths. And also optical direct and indirect bandgap values are calculated from the absorption spectra. To study the structural disorders and defects of the as prepared glasses, urbach energy values are estimated from the absorption spectra. To understand the From the absorption spectra we have evaluated oscillator strengths.

Keywords: Absorption spectra, Neodymium glasses, Judd-Ofelt intensity parameters, optical band gap, Spectroscopic properties, spectrometer, urbach energy,
1. Introduction

Optical integrated(IO) circuits will lay the foundation for multitudinous applications in the area of photonics such as computing and data communication, chemical/biological sensing, biomedical instrumentation, space applications etc., as they offers compact size, protection from thermal drift, moisture and vibration, low power requirements and low cost due to the possibility of batch fabrication [1], [2], [3], [4]. Typically, to generate a IO circuit we need waveguides, modulators, switches, and other active optical functions onto various substrates. Among them, Optical waveguides are the fundamental component in IO devices that perform not only guiding but also coupling, switching, splitting, multiplexing and de-multiplexing of optical signal [5], [6], [7], [8], [9], [10]. Usually, in optical wave guides glasses can be used as substrates because of its light transmitting properties. Day-by-day, there is a tremendous swift in the evolution of telecommunication and the broadcasting of new data transmission services such as virtual-reality application, cloud computing and high-definition three-dimensional television, the wavelength-division-multiplexing (WDM) system etc., fairly WDM is now facing with the demand for explosive transmission traffic[11], [12], [13], [14], [15]. Hence, in communication network system, it is a requisite to configure the high speed network for the development of optical fibres and wave guides and also to enhance the transmission speed and expand the gain bandwidth of the optical fibres [16], [17], [18], [19], [20], [21].

Fortunately, fiber fabrication technology has brought the availability of silica glass transmission fiber with minimized OH- groups, which thus extends the low-loss transmission region to the wavelength range of 1200-1700 nm. Therefore, developing the corresponding fiber amplifier with broadband and flat gain spectrum, which can fully utilize this 1200-1700 nm low-loss window of silica glass fiber, attracts great attentions. Recent years, trivalent rare-earth (RE3+)-doped materials have attracted much attention to develop optical devices such as solid-state lasers, optical sensors and optical amplifiers to meet the incessant demands in basic science research, medicine, and telecommunications. The trivalent erbium ions (Er3+) doped glasses are attractive for various applications such as microchip lasers, broadband erbium-doped fiber amplifiers (EDFAs), eye safe laser systems, waveguide amplifiers and lidar transmitters and also efficient to generate green and red up-conversion emissions under the diode laser excitation at 808 and 980 nm. In particular, the near-infrared (NIR) emission of the trivalent erbium (Er3+) ion around 1.53 mm corresponding to 4I_{13/2}to 4I_{15/2} transition has been used in telecommunication for optical amplification applications. The commercially available erbium doped fiber amplifiers (EDFA) are made of silica glass, exhibiting a relatively narrow bandwidth (~35 nm) that limits broadband transmission. In this aspect, Nd3+ ions -doped glasses co-doped with Er3+ ions have been received great attention and studied in different host matrices. Therefore, it is necessary to search for a new host matrix and for RE ions to exhibit relatively higher bandwidth and longer lifetimes for optical amplification in telecommunications. In recent years, researchers focused on oxy-fluoride glasses due to their combined advantages of both oxide and fluoride matrices having high stability and low phonon energies, respectively. Oxy-fluoride glasses doped with trivalent rare-earth (RE3+) ions exhibit attractive luminescence properties, with high transparency, and are found to be potential materials for up-conversion luminescence and optical amplification. Fluoride glasses always stand solitary for its uniqueness because of distinct features such as extensive manufacture compatibility, low OH contents, tremendously soluble with RE ions , wide transmission range, long fluorescence lifetime and the foremost merit of fluoride compared with other glasses is that they can be easy to draw into fiber. The borate glasses act as a glass former but it possesses high phonon energies (~1300-1500 cm\(^{-1}\)). These borate glasses have non radiative emission process very much and cannot acts as good laser host due to high phonon energies. So that to reduce the phonon energies of borate glasses, fluoride and heavy metal oxides were added to B\(_2\)O\(_3\) while preparing the glasses matrices hence it reduces the phonon energies of prepared samples [8]. The doping of alkali/alkaline earth metals like BaF\(_2\) into B\(_2\)O\(_3\) converts the boron coordination and the structural groups from one to another and its varying on the nature and concentration of the alkali/alkaline earth oxide/fluoride. Among the oxide and mixedoxo-fluoride glass compositions, lead borate glasses doped with RE ions seems to be very attractive systems for applications in laser technology. In the present study, we aim to prepare the Nd\(^{3+}\)-Er\(^{3+}\) co-doped BaPbAlFB glasses followed by melt quenching technique in order to perform the structural and optical analysis to understand the suitability for optical communication system.

2 Experimental details

2.1 Glass preparation

He present glass matrix have prepared by taking the sigma Aldrich analar grade chemicals with the chemical composition 20 BaF\(_2\) + 5 Al\(_2\)O\(_3\) + (63.5-x)\(\text{B}_2\)O\(_3\) + 10 PbF\(_2\) + 1.0 \(\text{Nd}_2\)O\(_3\) (x=0.5, 1, 1.5, 2, 2.5 mol%) by using conventional melt quenching technique at room temperature. These glasses are designated as Glass-A to E depending on the Er\(^{3+}\) ions concentration from 0.5 to 2.5 mol% respectively. Analar grade chemicals BaF\(_2\), Al\(_2\)O\(_3\), H\(_3\)BO\(_3\), \(\text{Nd}_2\)O\(_3\) and Er\(_2\)O\(_3\) were used as starting materials to prepare the glasses. All the chemicals in the proportions as mentioned in the formula were crushed in an agate mortar until a homogeneous mixture was obtained. This homogeneous mixture taken into a alumina crucible was then heated at 1150\(^{0}\)C in an Indiffur electric furnace for about 45 minutes to get homogeneously mixed melt thereafter such melt was quenched suddenly on a pre-heated brass mould and pressed quickly by another pre-heated brass mould. Before
recording the absorption spectra, the glass samples are polished with emiri paper to get smooth surfaces. XRD spectrum was recorded for an undoped glass using Bruker X-ray diffractometer (model D8 Advance) at 40 KV voltage and 40 m. amp current. The absorption spectra for the prepared glasses were recorded from 300-1600 nm wavelength range on a UV-VIS-NIR Spectrophotometer Perkin-Elmer Lambda 950, having double beam and double monochromator facility.

2.2. XRD SPECTRAL MEASUREMENTS
To confirm the glassy nature of the prepared glasses an Fig.1 shows the XRD spectrum of an undoped BaPbAlFB glass. If XRD spectrum shows sharp peaks, those prepared samples confirmed as crystalline materials[23-25]. But the spectrum does not show any sharp peaks and it has a broad hump which is the characteristic feature of a glassy material. Hence prepared samples confirmed as glassy materials[26].

![Fig 1: XRD spectrum of an undoped BaPbAlFB glass](image)

The absorption spectra of Nd-Er doped glasses were measured in the wavelength range of 300-1600 nm and presented in the inset figure of Fig.2. All absorption peaks in the spectrum, corresponding to the Er3+ and Nd3+ ions transitions from their ground state to higher excited levels respectively, are denoted. The absorption spectra shown in inset of Fig. 2, are clearly represents that there is no appreciable change in the intensity of absorption peaks of various concentrations of Nd-Er co-doped as prepared glasses. The absorption spectra of Nd-Er co-doped BaPbAlFB glasses consist of fifteen absorption peaks at about 357, 365, 377, 407, 432, 450, 487, 521, 583, 650, 748, 804.5, 878.3, 976 and 1533 nm, each of which were corresponding to transitions at $^{4}D_{5/2}$, $^{4}G_{9/2}$, $^{4}G_{11/2}$, $^{2}G, ^{2}F_{11/2}$, $^{2}P_{1/2}$, $^{2}F_{5/2}$, $^{4}F_{7/2}$, $^{4}H_{11/2}$, $^{2}G_{5/2}$, $^{2}F_{9/2}$, $^{2}S_{3/2}$, $^{2}F_{5/2}$, $^{2}F_{3/2}$, $^{1}I_{11/2}$ and $^{1}I_{13/2}$ respectively, shown in Fig.2. In them, the absorption peaks ascribed at around 357, 365, 377, 407, 432, 450, 487, 521, 583, 976 and 1533 nm are obtained to the transition from the ground state $^{4}I_{15/2}$ of Er3+ to the excited states of $^{4}D_{5/2}$, $^{4}G_{9/2}$, $^{4}G_{11/2}$, $^{2}G, ^{2}F_{11/2}$, $^{2}P_{1/2}$, $^{2}F_{5/2}$, $^{4}F_{7/2}$, $^{4}H_{11/2}$, $^{2}G_{5/2}$, $^{2}F_{9/2}$, $^{2}S_{3/2}$, $^{2}F_{5/2}$, $^{2}F_{3/2}$, $^{1}I_{11/2}$ and $^{1}I_{13/2}$ respectively. The absorption peaks centered at around 650, 748, 804.5 and 878.3 nm are assigned to the absorption transition from the ground state $^{4}I_{13/2}$ of Nd3+ to the excited states of $^{4}F_{9/2}$, $^{4}S_{9/2}$, $^{2}F_{5/2}$ and $^{4}F_{3/2}$ respectively. Further, with the help of the Judd-Ofelt (J-O) theory, several spectroscopic parameters of RE doped host glasses can be predicted from the absorption spectra. According to the Judd–Ofelt theory, the experimental oscillator strength ($f_{exp}$) for each absorption band is obtained by the following expression:

$$f_{exp} = 4.32 \times 10^{-29} \epsilon(u) dv$$  \hspace{1cm} (1)

where $\epsilon(u)$ denotes molar absorptivity at a particular frequency v (cm$^{-1}$). The J-O intensity parameters ($\Omega_{l}$, ($\lambda = 2, 4, 6$)) and calculated oscillator strengths (fcal) of the titled glasses have been evaluated using the $f_{exp}$ values and J-O theory with the help of the following formula and least square fit method.

$$f_{cal} = \frac{8m^{2}cnu}{5h(2j+1)} \Omega_{l}(\psi||\psi')^{2}$$ \hspace{1cm} (2)

where m is the electron mass, c is light velocity in vacuum, v signifies the wave number of a specific transition in cm$^{-1}$, h represents the Planck’s constant, n is the refractive index, $\Omega_{l}$ are the J-O intensity parameters and $||\psi||^{2}$ are the squared doubly reduced matrix elements of the unit tensor operator of the rank $\lambda = 2, 4$ and 6. In order to estimate the quality of the fit between the experimental and calculated oscillator strengths, the root mean square deviation (rms) values have been obtained using the following expression:

$$\delta_{rms} = \frac{\sum(f_{exp}-f_{cal})^{2}}{N-3}^{1/2}$$ \hspace{1cm} (3)

The calculated and experimental oscillator strengths (fcal & fexp) along with the root mean square deviation values (rms) are presented in Table.2 From Table.2, the shorter magnitudes of $\delta_{rms}$ values obtained for the titled glasses exposed the good fit between measured and calculated oscillator strengths. Among all absorption transitions, the two hypersensitive transitions $^{4}I_{15/2} \rightarrow ^{4}G_{11/2}$ and $^{2}F_{5/2}$ possess higher values of oscillator strengths, which indicate the higher asymmetry Er$^{3+}$ ions around Nd$^{3+}$ ions. The J-O intensity parameters reveals the nature of the glass symmetry and covalent bonding of rare earth Nd$^{3+}$ ions, in which the parameter $\Omega_{2}$ is strongly affected by the chemical bonding between Nd$^{3+}$ and ligand anion, and the asymmetry of local environment around Nd$^{3+}$, while the parameter $\Omega_{6}$ is inversely proportional to the covalency of Nd-O bond. The remaining two J-O intensity parameters such as $\Omega_{4}$ and $\Omega_{6}$ reveal about the bulk properties such as viscosity and rigidity of the host medium in which the Nd3+ ions are situated. The evaluated J-O intensity parameters are presented in Table.2 along with some other reported values [27-30]. For the titled glasses, the $\Omega_{2}$ value is larger compared to $\Omega_{4}$ and $\Omega_{6}$ with the trend $\Omega_{2} > \Omega_{6} > \Omega_{4}$. Therefore, the trend of the parameters will be different based on the host matrix. Further, the JO intensity parameters trend could be varied due to the large and more sensitive values of oscillator strengths of two hyper sensitive transitions (HSTs).
Nd3+ and Er3+ ions doped BaPbAlFB glasses. Here in Table 3, the EU increases by increasing the concentration of Nd-Er. This due to the shifting of non-bridging oxygen atoms towards the conduction band. The Urbach energy (EU) can be obtained by plotting a graph between $\ln(\alpha)$ and hν shown in Fig 5. The obtained results are listed in Table 3. Urbach energy represents the defects produced due to lack of long-range order during the changes in the spectroscopic properties of glasses. Such defects lead to the creation of NBOs and hydroxyl groups. Sometimes these defects also act as activators (dopant ions) and changes the properties of glasses. Here in Table 3, the EU increases by increasing the concentration of Nd-Er. This shows that the structural disorders and defects are less at low concentrations which shows the suitability for optical applications.

**Table 2**: Comparison of Judd-Olfet intensity parameters $\Omega_2$, $\Omega_4$ and $\Omega_6$ (10-20 m$^2$) of Nd3+ ions doped BaPbAlFB glasses with the reported values.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\Omega_2$</th>
<th>$\Omega_4$</th>
<th>$\Omega_6$</th>
<th>Trend</th>
<th>$\chi=\Omega_2/\Omega_6$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaPbAlFBNd1.0</td>
<td>4.7</td>
<td>1.6</td>
<td>2.01</td>
<td>$\Omega_2 &gt; \Omega_6$</td>
<td>0.835</td>
<td>Present work</td>
</tr>
<tr>
<td>ZBLAN</td>
<td>7.1</td>
<td>3.1</td>
<td>5.09</td>
<td>$\Omega_2 &gt; \Omega_6$</td>
<td>0.612</td>
<td>[27]</td>
</tr>
<tr>
<td>Phosphate</td>
<td>6.3</td>
<td>4.0</td>
<td>4.30</td>
<td>$\Omega_2 &gt; \Omega_4$</td>
<td>0.93</td>
<td>[28]</td>
</tr>
<tr>
<td>SPB1</td>
<td>4.8</td>
<td>1.9</td>
<td>3.94</td>
<td>$\Omega_2 &gt; \Omega_6$</td>
<td>0.5</td>
<td>[28]</td>
</tr>
</tbody>
</table>

**Table 3**: Optical direct and indirect bandgap energies and urbach energy values of Nd-Er co-doped glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Direct bandgap (eV)</th>
<th>Indirect bandgap (eV)</th>
<th>Urbach energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass A</td>
<td>3.64</td>
<td>3.09</td>
<td>0.50</td>
</tr>
<tr>
<td>Glass B</td>
<td>3.635</td>
<td>3.08</td>
<td>0.51</td>
</tr>
<tr>
<td>Glass C</td>
<td>3.63</td>
<td>3.06</td>
<td>0.52</td>
</tr>
<tr>
<td>Glass D</td>
<td>3.623</td>
<td>3.04</td>
<td>0.53</td>
</tr>
<tr>
<td>Glass E</td>
<td>3.61</td>
<td>3.02</td>
<td>0.54</td>
</tr>
</tbody>
</table>

**Fig. 3** Direct optical bandgap of Nd-Er co-doped BaPbAlFB glasses.
Fig. 4 Indirect optical bandgap of Nd–Er co-doped BaPbAlFB glasses.

Fig. 5 Urbach energy bandgap of Nd–Er co-doped BaPbAlFB glasses.

Conclusion
In the present prepared transparent BaPbAlFB glasses doped with Nd3+–Er3+ ions with varying concentrations were prepared by melt quenching technique and characterized by using various spectroscopic techniques such as optical absorption. Using absorption spectra we have calculated oscillator strengths in turn to use to evaluate the Judd-Ofelt theory applied to the absorption spectral features allows us to estimate the phenomenological J-O parameters \( \Omega (\lambda = 2, 4, 6) \) to understand the nature of the bonds between ligands. Optical band gap also calculated by using absorption spectra (both direct and indirect band gaps). Urbach energy (EU) values calculated with the help of absorption spectra satisfies the amorphous condition of glasses under investigation.

Acknowledgements
The authors, Dr. K. Swapna (File Number: ECR/2015/000335), Dr. Sk. Mahamuda (File Number: ECR/2016/000376) and Prof. A. S. Rao (EMR/2016/007766) are thankful to Department of Science and Technology (DST), Govt. of India, New Delhi for the award of major research projects to them under DST-SERB.

REFERENCES

The authors, Dr. K. Swapna (File Number: ECR/2015/000335), Dr. Sk. Mahamuda (File Number: ECR/2016/000376) and Prof. A. S. Rao (EMR/2016/007766) are thankful to Department of Science and Technology (DST), Govt. of India, New Delhi for the award of major research projects to them under DST-SERB.


[22] M. Venkateswarlu a, Sk. Mahamuda a, K. Swapna a, M.V.V.K.S. Prasad a, A. Srinivasa Rao a,b,† A. Mohan Babu c, Suman Shakya d, G. Vijaya Prakash “Spectroscopic studies of Nd$^{3+}$ doped lead tungsten tellurite glasses for the NIR emission at 1062 nm”, Optical Materials 39 (2015) 8–15