Upconversion luminescence in Er\(^{3+}\)/Yb\(^{3+}\) codoped PbO-Bi\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-B\(_2\)O\(_3\) glasses

B Appa Rao*, Y Raja Rao, K Krishnamurthy Goud and M Srinivas
Department of Physics, Osmania University, Hyderabad-500 007, India

apparao.bojja@gmail.com Mobile: +91 9391060524

Abstract. Er\(^{3+}\)/Yb\(^{3+}\) co-doped glasses with the composition PbO-Bi\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-B\(_2\)O\(_3\) were prepared by melt quenching method. Optical absorption (OA) and photoluminescence (PL) and FT-IR spectra of all the glasses were recorded at room temperature. Green and red up-conversion emissions centered at 525, 545 and 654 nm corresponding to \(^2\)H\(_{11/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\), \(^4\)S\(_{3/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\) and \(^4\)F\(_{9/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\) transitions of Er\(^{3+}\) ions have been obtained under the excitation of 980 nm laser at room temperature. From emission spectra it was observed that the intensity of red emission increases with increasing the concentration of Er\(^{3+}\) ions upto 0.8 mol% and decreases with the further increase in the concentration of Er\(^{3+}\) ions. The spectra have been analyzed in the light of structural modifications in the vicinity of the dopant rare earth ions, due to relative variations in the concentration of Al\(_2\)O\(_3\) and B\(_2\)O\(_3\) in the glass network.

1. Introduction

In recent years, the upconversion of infrared light to visible light by rare earth ion doped glasses has been investigated extensively because of their potential applications in optoelectronics, such as three dimensional volumetric display, optical data storage, medical diagnostics, sensors, undersea optical communication. Among various rare earth ions Er\(^{3+}\) is identified as one of the most efficient rare earth ions for obtaining NIR laser emission, frequency upconversion in the glass hosts [1].

Among various glass systems, heavy metal oxide based glass systems (like lead bismuth oxide based systems) find potential applications in non-linear optical devices, because of their high refractive index and low phonon energy [2, 3]. In view of such qualities these glass systems offer suitable environment to rare earth ions for laser emission with high quantum efficiency. In the present study, we have investigated luminescence spectra and up-conversion phenomenon in Er\(^{3+}\)/Yb\(^{3+}\) co-doped PbO–Bi\(_2\)O\(_3\)–Al\(_2\)O\(_3\)–B\(_2\)O\(_3\) glass system. Al\(_2\)O\(_3\) is added because it participates in the glass network with AlO\(_4\) and AlO\(_6\) structural units and alternate with BO\(_4\)/BO\(_3\) units; strengthen the glass network and increase the mechanical strength of the glasses.

For the present study, glasses of composition [100-(x+y)][0.5PbO-0.25Bi\(_2\)O\(_3\)-0.20Bi\(_2\)O\(_3\)-0.05Al\(_2\)O\(_3\)]-xEr\(_2\)O\(_3\)-yYb\(_2\)O\(_3\) with \(y=0\) for \(x=0\); \(y=0.2\) for \(x=0.2\) to 1.0 (step 0.2) are chosen and the glasses are labelled as A0, A2, A4, A6, A8 and A10 respectively. The details of methods of preparation of glasses, techniques adopted for recording OA, PL and IR spectra were reported in our earlier paper [4].
2. Results and discussion

2.1 Optical absorption

The optical absorption spectra of the co-doped glasses (Fig. 1) exhibited a prominent overlapping band at 980 nm due to $^4I_{15/2} \rightarrow ^4I_{11/2}$ and $^2F_{7/2} \rightarrow ^2F_{5/2}$ transitions of Er$^{3+}$ and Yb$^{3+}$ ions respectively. The spectra also exhibited other absorption bands in the visible and the NIR regions due to at $^4I_{15/2} \rightarrow ^4F_{7/2}$, $^4H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^2H_{9/2}$ and $^1I_{13/2}$ transitions of Er$^{3+}$ ions at 525, 554, 660, 808 and 1540 nm respectively. From Fig. 1 it can be seen that the absorption edge shifts towards longer wavelength side with doping of the rare earth ions. From Fig. 1 it can be seen that, for almost all the glasses, there is an exponential rise of spectra towards the edge. The spectra further indicated that the cut-off wavelength shifts towards longer wavelength with increasing the concentration of Er$^{3+}$ ions up to 0.8 mol%. From the absorption edges we have evaluated optical band gap ($E_o$) by drawing the Tauc plots between $(\alpha h\omega)^{1/2}$ vs $h\omega$; the value of $E_o$ is found to decrease with increasing the concentration of Er$\text{O}_3$ up to 0.8 mol% and found to increase for further increase in the concentration of Er$\text{O}_3$.

![Fig. 1 Optical absorption spectra for [100-(x+y)][0.5PbO-0.25B\text{}_2O_3-0.20Bi\text{}_2O_3-0.05Al\text{}_2O_3]-xEr\text{O}_3-yYb\text{O}_3$ glass system](image)

2.2 FTIR spectra

To have some structural assessment of these glasses we have also recorded the IR spectra of these glasses. The IR spectra of the titled glasses recorded in 1600-400 cm$^{-1}$ region exhibited four characteristic groups of bands (I-IV). The first group of bands in the region (400-650cm$^{-1}$) has been identified PbO$_4$, as well as borate rings deformation vibrations. This region may also consist of bands due to AlO$_4$ structural units. The second group of bands (II) observed in the region 650-850cm$^{-1}$ is attributed to B-O-B bending and AlO$_4$ structural units [5]. The third group of bands (III) is associated with B-O stretching vibration of tetrahedral BO$_4$ group (850-1050cm$^{-1}$) [6-8]. The fourth group of bands (IV) centered at about 1300 cm$^{-1}$ is due to the antisymmetric O-B stretching vibration of the trigonal BO$_3$ group. Out of these bands the AlO$_4$ participates in the network forming and alternate with BO$_4$ structural units, whereas, AlO$_6$ structural units act as modifiers and induce non-bridging oxygens. With increase in the concentration of Er$\text{O}_3$ (up to 0.8 mol%) all the asymmetrical bands are observed to grow at the expense of symmetrical bands. Thus the analysis of IR spectra reveal that the degree of disorder in the glass network increases with increase in the concentration of Er$\text{O}_3$ up to 0.8 mol%.
Table 1 Frequencies and their assignments for FT-IR spectra

| Wavenumber (cm^{-1}) | IR assignments |
|----------------------|----------------|
| ~490                 | B-O-B and Pb-O-B bending vibration as well as borate rings deformation. This region may also consist of bands due to AlO_6 structural units |
| ~706, ~730           | Due to the B–O–B bending and AlO_4 structural units |
| ~935, ~970, ~990     | B-O stretching vibration of tetrahedral BO_4 group |
| ~1270, ~1280         | Antisymmetric B-O stretching vibration of the trigonal BO_3 group |

2.3 Upconversion spectra

The room temperature up-conversion spectra of Er^{3+}/Yb^{3+} co-doped [100-(x+y)][0.5PbO-0.25B_2O_3-0.20Bi_2O_3-0.05Al_2O_3]-xEr_2O_3-yYb_2O_3 glasses under 980 nm excitation are shown in Fig. 2. The spectra exhibited three up-conversion bands centered at 525, 544 and 654 nm corresponding to ^2H_{11/2} \rightarrow ^4I_{15/2}, ^4S_{3/2} \rightarrow ^4I_{15/2} (green) and ^4F_{9/2} \rightarrow ^4I_{15/2} (red) transitions of Er^{3+} ions, respectively [9,10]. The close examination of the spectra indicated that the intensity of red emission was much stronger than that of the green emission.

Fig. 3 shows the up-conversion mechanisms of green and red emission. Up-conversion excitation mechanisms has been proposed to be involved in the population of the relevant excited state emitting levels of the Er^{3+}/Yb^{3+} co-doped glass as shown in Fig. 3. Firstly Er^{3+} ions excited from the ground state ^4I_{15/2} to the excited state ^1I_{11/2} through one of the following three processes under 980nm excitation: (i) Ground-State Absorption (GSA) ^4I_{15/2} (Er^{3+}) + a photon → ^4I_{11/2} (Er^{3+}), (ii) Phonon-Assisted Energy Transfer (PAET) from the Yb^{3+} ^2F_{5/2} state: ^2F_{5/2} (Yb^{3+}) + ^4I_{15/2} (Er^{3+}) → ^2F_{7/2} (Yb^{3+}) + ^4I_{11/2} (Er^{3+}), and (iii) Energy Transfer (ET) from the ^4I_{11/2} state of adjacent Er^{3+}. Among the above three processes, PAET from Yb^{3+} is the dominant one, due to the larger absorption cross section of Yb^{3+} at around 980 nm. Next the ions at the populated ^4I_{11/2} state are promoted to the ^4F_{7/2} state by the one of the following processes.

Fig. 2 Upconversion fluorescence spectra of PbO-B_2O_3- Bi_2O_3-Al_2O_3; Er_2O_3/Yb_2O_3 glass system recorded at room temperature

(i) Excited state absorption (ESA): ^4I_{11/2} (Er^{3+}) + a photon → ^4F_{7/2} (Er^{3+}), (ii) Phonon-Assisted Energy Transfer (PAET) from the Yb^{3+}: ^2F_{5/2} (Yb^{3+}) + ^4I_{11/2} (Er^{3+}) → ^2F_{7/2} (Yb^{3+}) + ^4F_{7/2} (Er^{3+}), and (iii) Energy Transfer (ET) from the ^4I_{11/2} state of adjacent Er^{3+}: ^4I_{11/2} + ^4I_{11/2} → ^4F_{7/2} + ^4I_{15/2}. Er^{3+} ions at the populated ^4F_{7/2} state can relax non-radiative relaxation (NR) very fast to the intermediate state of ^2H_{11/2} due to a multiphonon relaxation process (MPR), the ^2H_{11/2} → ^4I_{15/2} transition shows the 525 nm...
green emission. Er$^{3+}$ ion at the $^4F_{7/2}$ state can also decay rapidly down to the $^4S_{3/2}$ state, and finally, the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition reveals green upconversion at 545 nm. For the red-upconversion emission at 654 nm, Er$^{3+}$ ion is first excited from the ground state $^4I_{15/2}$ to the excited $^4I_{11/2}$ through the above mentioned three processes under 980 nm excitation.

Upconversion luminescence intensities of red emission as a function Er$^{3+}$ concentration at fixed Yb$^{3+}$ (0.2 mol%) is shown in Fig. 4. From Fig. 4 it is clearly observed that the glass containing 0.8 mol% of Er$^{3+}$ ions is the best upconversion emission intensity of present glass system. When Er$^{3+}$ concentration is less than 0.8 mol%, the intensity of red emission is decreased. This stronger red emission is due to the Energy Transfer between the excited Er$^{3+}$ ions, when the distance between the two excited Er$^{3+}$ ions is short at higher concentration. When Er$^{3+}$ concentration is beyond 0.8 mol%, the intensity decreases. This may be due to increase in back energy transfer from Er$^{3+}$ to Yb$^{3+}$, i.e., $^4I_{11/2} (Er^{3+}) + ^2F_{7/2} (Yb^{3+}) \rightarrow ^4F_{15/2} (Er^{3+}) + ^2F_{5/2} (Yb^{3+})$.

![Graph showing upconversion luminescence intensities (I_R) vs Er$^{3+}$ concentration with fixed Yb$^{3+}$ (0.2 mol%)](image)

**Fig. 4** Upconversion luminescence intensities (I_R) vs Er$^{3+}$ concentration with fixed Yb$^{3+}$ (0.2 mol%)

### 3. Conclusions

The studies on up-conversion phenomenon in Er$^{3+}$/Yb$^{3+}$ co-doped lead bismuth alumina borate glasses have indicated that the up-conversion is more prominent in the glasses containing 0.8 mol% of Er$^{3+}$. When Er$^{3+}$ concentration is beyond 0.8 mol%, the intensity decreases. This may be due to increase in back energy transfer from Er$^{3+}$ to Yb$^{3+}$.

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