Intense upconversion fluorescence in Tm$^{3+}$/Yb$^{3+}$ codoped alumina lead borate glasses

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Abstract. The Tm$^{3+}$/Yb$^{3+}$ codoped alumina lead borate glasses were prepared by the conventional melt quenching technique. Optical absorption and FTIR spectra were recorded. The upconversion fluorescence spectra exhibited weak blue (480 nm) and intense red (660 nm) emissions due to $^4G_4 \rightarrow ^3H_6$ and $^4G_4 \rightarrow ^3H_4$ transitions, respectively. The results concluded that both emissions are due to three photon absorption process. It has been observed that in the upconversion efficiency increases with the increase in the concentration of Yb$^{3+}$ ions. The strong red upconversion fluorescence indicate that Tm$^{3+}$/Yb$^{3+}$ codoped alumina lead borate glasses can be used as potential host material for upconversion lasers.

1. Introduction

The optical properties of rare-earth doped glasses have been investigated extensively over the last several years. In particular, significant effort has been devoted to develop optimized glasses for broadband fiber amplifier, efficient lasing, and frequency upconversion due to their potential applications in various photonics devices [1, 2]. Some rare earth ions up-convert infrared light to visible light. This phenomenon is of great interest because it can be utilized to build a new laser system. In recent year, particularly, high-power laser diodes have been employed as pumped sources with a view to develop compact up-conversion visible laser systems. Most of oxide glasses have large phonon energies (>1000 cm$^{-1}$) owing to the lattice vibration of network-forming oxides [3].

Among the various rare earth ions, the Tm$^{3+}$ is very attractive since it has two stable excited levels, $^4G_4$ and $^3H_6$. Through $^4G_4 \rightarrow ^3H_6$ transmission, blue upconversion luminescence near 476 nm can be obtained which can be used in color displays, high density optical data storage and reading, biomedical diagnostic, etc. [4-7]. Through $^3H_4 \rightarrow ^3H_6$ transmission, 794 nm near infrared upconversion luminescence can be obtained which can be applied in the amplifier of the first communication window of quartz optical fiber [8, 9]. The Yb$^{3+}$ ions can greatly increase the upconversion luminescence efficiency [10].

In previous researches, Tm$^{3+}$/Yb$^{3+}$ codoped fluoride, silicate and tellurite glasses were investigated under excitation of 980 nm laser diode and were shown to be effective blue luminescence materials through the Tm$^{3+}:^4G_4 \rightarrow ^3H_6$ transition [11]. In Tm$^{3+}$/Yb$^{3+}$ codoped glasses, Yb$^{3+}$ ion absorbs the energy and transfers it to the Tm$^{3+}$ or Er$^{3+}$ ion. i.e., Yb$^{3+}$ ion acts as an effective sensitizer. When the Tm$^{3+}$ and Yb$^{3+}$ ions are simultaneously introduced into the glass matrix, a material emitting blue and red upconversion luminescence can be obtained. Spectroscopic properties of the three rare earth ions doped fluoride and tellurite glasses were reported in previous researches [12, 13].

PbO–Bi$_2$O$_3$–Ga$_2$O$_3$ system has recently been investigated as a potential host for broadband fiber-optic amplifiers and all-solid-state upconversion lasers especially due to its advantages [14-16]. In this paper, the influence of the concentrations of the rare earth ions on visible upconversion luminescence
in Tm\(^{3+}/\text{Yb}^{3+}\) codoped Pb\(_2\)O\(_4\)−Al\(_2\)O\(_3\)−B\(_2\)O\(_3\) glasses was studied under the excitation of 980 nm laser diode. The addition of aluminium in to the glass matrix produce greater enhancement on fluorescence of rare-earth ions including Tm\(^{3+}\) and Yb\(^{3+}\) when incorporated in the glass hosts [17]. The results obtained are discussed quantitatively based on the energy transfer between Yb\(^{3+}\) and Tm\(^{3+}\) ions.

2. Experimental

Series of Rare earth codoped Alumina Lead Borate glasses 35Pb\(_2\)O\(_4\)−[5−(x+y)]Al\(_2\)O\(_3\)−60B\(_2\)O\(_3\)−x Tm\(_2\)O\(_3\)−yYb\(_2\)O\(_3\) were prepared by the rapid melt quenching technique using AR-grade Pb\(_2\)O\(_4\), B\(_2\)O\(_3\), Al\(_2\)O\(_3\), Yb\(_2\)O\(_3\), Tm\(_2\)O\(_3\). The required amounts of chemicals were mixed and thoroughly ground in a mortar. The mixer was then taken in a porcelain crucible and was placed in a vertical furnace. The temperature of the furnace was increased in steps of 50°C, until the mixture melted at about 950°C and the melt was kept at that temperature for thirty minutes to ensure its homogeneity. The melt was then quenched quickly using the quenching device. Circular brass discs of 2 mm thickness and having hole of diameter 1.5 mm at the centre was used to get the glass samples of uniform shape. The glass samples prepared were annealed at about 300°C, for about four hours and were cooled to room temperature gradually to avoid internal mechanical stresses.

In doped samples Al\(_2\)O\(_3\) was partially substituted by Yb\(^{3+}\), Tm\(^{3+}\) ions in various concentrations (x = 1 to 0 and y = 0 to 1 in steps of 0.2 mol%). Total seven samples were prepared in various concentrations and they are given in table 1. ALBTOY0 is pure one and ALBTOY10 is doped with 1 mol% Yb\(^{3+}\) only where as ALBTOY10 is doped with 1 mol% of Tm\(^{3+}\) only.

The XRD spectra were recorded using Rigaku Mini-flex table top diffractometer. Optical absorption spectra were recorded at room temperature in the wavelength region 350 nm-2000 nm using JASCO Model V-670 UV–VIS–NIR Spectrophotometer, by using xenon arc lamp. The FTIR transmission spectra in the frequency region 4000cm\(^{-1}\) - 400cm\(^{-1}\) were recorded using KBr pellet disc technique. The luminescence spectra and lifetime measurements were carried out at room temperature using JOBIN YVON Fluorolog-3 spectrophotofluorimeter using xenon arc lamp as radiation source.

Table 1. 35Pb\(_2\)O\(_4\)−[5−(x+y)]Al\(_2\)O\(_3\)−60B\(_2\)O\(_3\)−x Tm\(_2\)O\(_3\)−yYb\(_2\)O\(_3\) glass compositions and sample codes used.

| S. No. | x (mol%) | y (mol %) | Sample code |
|--------|----------|-----------|-------------|
| 1      | 0        | 0         | ALBTOY0     |
| 2      | 1        | 0         | ALBTOY10    |
| 3      | 0.8      | 0.2       | ALBTSY2     |
| 4      | 0.6      | 0.4       | ALBTSY4     |
| 5      | 0.4      | 0.6       | ALBT4Y6     |
| 6      | 0.2      | 0.8       | ALBT2Y8     |
| 7      | 0        | 1         | ALBTOY10    |

3. Results and Discussion

3.1. X-Ray Diffraction

The X-ray diffraction analysis was carried out using using Rigaku Mini-flex table top diffractometer. The XRD patterns shows the absence of sharp peaks, confirming the Non-crystalline nature of the studied glass samples. The X-ray diffraction patterns of ALB glasses are shown in figure 1.
3.2. Optical absorption spectra
The optical absorption spectra were recorded using JASCO Model V-670 UV–VIS–NIR spectrophotometer in the wavelength range 350–2000 nm. Figure 2 shows the absorption spectra of \(35\text{Pb}_2\text{O}_5\cdot[5-(x+y)]\text{Al}_2\text{O}_3\cdot60\text{B}_2\text{O}_3\cdot x\text{Tm}_2\text{O}_3\cdot y\text{Yb}_2\text{O}_3\) glass system. The absorption band centered at 975 nm is attributed to transitions from the ground state \(^2F_{7/2}\) to excited state \(^2F_{5/2}\) of Yb\(^{3+}\) ions. The other absorption bands centered at 476 nm (\(^3\text{H}_6 \rightarrow ^1\text{G}_4\)), 692 nm (\(^3\text{H}_6 \rightarrow ^3\text{F}_{2,3}\)), 798 nm (\(^3\text{H}_6 \rightarrow ^3\text{H}_4\)), 1215 nm (\(^3\text{H}_6 \rightarrow ^3\text{H}_3\)) and 1661 nm (\(^3\text{H}_6 \rightarrow ^3\text{F}_4\)) are attributed to transitions from the ground state to excited states of Tm\(^{3+}\) ions [18].

From optical absorption spectra, it was observed that with the increase of rare earth ion concentration the intensity of spectral bands increases without shift in the spectral band positions.
Figure 2 shows that with the addition of rare earth ions the absorption edge shifts towards higher wavelength side. Using standard relations the values of optical band gap and the Urbach energy are calculated [19, 20].

The $E_{opt}$ values were determined from the curves representing $(\alpha hv)^{1/2}$ as a function of photon energy $hv$ by extrapolation of the linear region of the plots to $(\alpha hv)^{1/2} = 0$. The logarithm of the absorption coefficient was plotted as a function of photon energy. The values of Urbach energies ($\Delta E$) were calculated by taking the reciprocals of the slopes of the linear portion in the lower photon energy region of these curves. Urbach energy indicates the degree of disorder in materials [21]. The obtained values of $E_{opt}$ and Urbach energy values are presented in Table 2.

| Glass sample | Cut off wavelength (nm) | $E_{opt} \pm 0.01$ (eV) | $\Delta E \pm 0.01$ (eV) |
|--------------|-------------------------|--------------------------|--------------------------|
| ALBT0Y0      | 366                     | 3.37                     | 0.329                    |
| ALBT10Y0     | 380                     | 3.25                     | 0.273                    |
| ALBT8Y2      | 382                     | 3.23                     | 0.251                    |
| ALBT6Y4      | 385                     | 3.21                     | 0.249                    |
| ALBT4Y6      | 387                     | 3.19                     | 0.243                    |
| ALBT2Y8      | 390                     | 3.16                     | 0.237                    |
| ALBT0Y10     | 395                     | 3.12                     | 0.231                    |

From the values of cut off wavelength and optical band gap it was observed that with the addition of Yb$^{3+}$ ions cut off wavelength shifts towards higher wavelength side and the value of optical band gap decreases.

The relation between $(\alpha hv)^{1/2}$ and $hv$, points out that the optical band gap is caused by amorphous optical absorption edge. This indicates the fact that the disordered amorphous glass materials have prevailingly the direct transitions between the valence band and the conduction band and the absence of the indirect inter-band transitions like in the case of the crystals (i.e. the transitions in the different points of the Brillouin zone). Some deviations observed from this dependence are understood due to trapping of some disordered states within the energy gap.

The decrease in the optical band gap with the increase in the concentration of Yb$_2$O$_3$ suggests increasing degree of depolymerization or concentration of bonding defects and non-bridging oxygens (NBO) in the glass network as also observed in IR spectra. Probably in this concentration range the aluminium ions may take network forming positions with AlO$_4$ structural units and alternate with BO$_4$ units. Such linkages may cause a decrease in the rigidity of the glass network and leads to the decrease in the optical band gap as observed.

### 3.3. FTIR spectral analysis

The FTIR spectra of ALB glass system doped with Tm$^{3+}$/Yb$^{3+}$ was obtained using Bruker FT-IR–TENSOR27 spectrophotometer in the range 4000–400 cm$^{-1}$. Infra red spectra of ALB glass system in the range 1400–400 cm$^{-1}$ is shown in Figure 3. The FTIR spectra of ALB glass system shows characteristic bands corresponding to the different vibration modes of the various functional groups present in the glass system.
Figure 3. FTIR spectra of ALB glass system doped with Tm$^{3+}$/Yb$^{3+}$.

A band cited in the region ~480 cm$^{-1}$ is identified due to the presence of PbO$_4$ units. This region may also consist of bands due to network modifying AlO$_6$ octahedral groups. A band cited in the region ~700 cm$^{-1}$ is identified due to vibrations of B-O-B linkages and also due to network forming AlO$_4$ tetrahedral groups. The band in the region ~980 cm$^{-1}$ which are due to B–O bond stretching of the tetrahedral BO$_4$ units. The band at ~1325 cm$^{-1}$ due to stretching vibrations of B–O bond of trigonal BO$_3$ units [22, 23].

Table 3. Various functional groups present in the infra red spectra of ALB glass system.

| Wave number (cm$^{-1}$) | IR assignments |
|------------------------|----------------|
| ~480                   | Due to the presence of PbO$_4$ units. This region may also consist of bands due to AlO$_6$ structural units. |
| ~700                   | Vibrations of B-O-B linkages and due to AlO$_2$ structural units |
| ~980                   | B–O bond stretching of the tetrahedral BO$_4$ units. |
| ~1325                  | Stretching vibrations of B–O bond of trigonal BO$_3$ units. |

With increase in the concentration of Yb$^{3+}$ in the glass matrix, the intensity of the band around 700 cm$^{-1}$ is increased. Generally every AlO$_2$/BO$_4$ structural unit in alumino borate glasses is associated with two similar units and one oxygen from each unit with a metal ion. This type of arrangement give rise to construction of long chain of tetrahedra. When Ln$_2$O$_3$ is introduced in to the glass network, it acts as modifier (Shelby 1994) and breaks the tetrahedral bonds. Such kind of breaking leads to coordinated defects known as dangling bonds. In the process of breaking of tetrahedral bonds there can be a break of different structural units viz. BO$_4$, PbO$_4$ and AlO$_4$ units. The infra red spectra of these glasses shows the decreasing trend of intensities of BO$_4$ and PbO$_4$ structural units indicating the reduction of BO$_4$ and PbO$_4$ units [24, 25].
3.4 Photoluminescence

The upconversion fluorescence spectra was recorded at room temperature using JOBIN YVON Fluorolog-3 spectrofluorimeter using xenon arc lamp as radiation source in the wavelength range 300-700 nm. The spectra exhibited the bands at 480 nm and 660 nm due to $^1G_4 \rightarrow ^3H_6$ (blue) and $^1G_4 \rightarrow ^3H_4$ (Red) transitions of Tm$^{3+}$ ions, respectively [26, 27]. The intensity of blue emission is very small when compared with the intensity of red emission. Hence figure 4 represents the upconversion fluorescence spectra of intense red emission under the excitation of 975 nm laser diode at room temperature.

![Figure 4](image)

**Figure 4.** Upconversion fluorescence spectra of ALB glass system doped with Tm$^{3+}$/Yb$^{3+}$ at room temperature.

From the spectra it was clearly observed that, the blue emission at 480nm is much weaker than the red emission at 660 nm. It is also observed that the intense red upconversion fluorescence is bright enough to be observed by the naked eye at lower excitation power. This is may be due to the integrated intensity of $^1G_4 \rightarrow ^3H_6$ transition occupies maximum percentage of the total emitted light in the spectral region studied. The results showed that the dominant emission is the red emission. In an upconversion, the upconversion emission intensity ($I_{up}$) increases in proportion to the $n^{th}$ power of infrared excitation intensity ($I_{IR}$), i.e.,

$$I_{up} \propto I_{IR}^n$$

where $n$ is the number of IR photons absorbed per visible photon emitted [28]. A plot of log $I_{up}$ vs. log$I_{IR}$ yields a straight line with slope $n$. Figure 5 and figure 6 shows such a plot for the 480 and 660 nm emissions under 975nm excitation, respectively. From figure 5 and figure 6 the slope values ($n$) for the 480 and 660 nm emission bands were calculated and got less than three. The values of $n$ less than three for the blue and red emissions are due to the saturation effect. When the pump beam was focused into the sample as a result saturation effect takes place. This indicates radiative and non-radiative recombinations at intermediate excitation stages. The results shows that a three photon upconversion process is responsible for the blue (480 nm) and red (660 nm) emissions from the $^1G_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3H_4$ transitions, respectively [29]. In order to understand the upconversion mechanism under 975 nm laser diode, the energy level diagram for Tm$^{3+}$/Yb$^{3+}$ codoped alumina lead borate glasses is shown in figure 7 [30]. When the glass sample is excited with 975 nm laser diode, Tm$^{3+}$ ions cannot absorb
energy directly due to lack of the matched energy level. First Yb$^{3+}$ ions absorb the energy efficiently and transfer it to Tm$^{3+}$.

**Figure 5.** Dependence of upconversion fluorescence intensity of blue emission on excitation power under 975 nm laser diode for ALB glass system doped with Tm$^{3+}$/Yb$^{3+}$.

**Figure 6.** Dependence of upconversion fluorescence intensity of red emission on excitation power under 975 nm laser diode for ALB glass system doped with Tm$^{3+}$/Yb$^{3+}$.

**Figure 7.** Upconversion fluorescence spectra of ALB glass system doped with Tm$^{3+}$/Yb$^{3+}$ at room temperature.

The excitation process for the $^1G_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3H_4$ transitions can be explained as follows. First Yb$^{3+}$ ions in the ground level absorbs a photon and excites to the higher level ($^2F_{7/2} \rightarrow ^2F_{5/2}$) then Yb$^{3+}$ transfers their energy to the Tm$^{3+}$ ions which are in ground level ($^3H_4$). This step is involved by energy transfer (ET) mechanism of excited Yb$^{3+}$ to Tm$^{3+}$: $(Yb)^{3+}F_{5/2} + (Tm)^{3+}H_6 \rightarrow (Yb)^{3+}F_{7/2} + (Tm)^{3+}H_5$. Actually the energy gap between (Yb)$^3F_{5/2}$ and(Yb)$^3F_{7/2}$ is in a wide range and the low energy edge is near the high energy edge of the energy gap between (Tm)$^3H_4$ and (Tm)$^3H_6$. Thus the energy transfer from Yb$^{3+}$ becomes efficient [31].
In the second step, Tm$^{3+}$ in the ($^1$H$_4$) excited state relaxes nonradiatively to the metastable level ($^3$H$_4$) by the cooperation of the phonons in the alumina lead borate glasses. Tm$^{3+}$ in the $^3$H$_4$ level is excited to $^3$F$_{2,3}$ level by ET from Yb$^{3+}$ and absorption a photon. Thus, the population of $^3$F$_{2,3}$ level is based on the processes as follows: ET from Yb$^{3+}$: (Yb)$^2F_{5/2}$ + (Tm)$^3$H$_4$ $\rightarrow$ (Yb)$^3F_{7/2}$ + (Tm)$^3$F$_{2,3}$ and excited state absorption (ESA): (Tm)$^3$H$_4$ + a photon $\rightarrow$ (Tm)$^3$F$_{2,3}$. Then the $^3$F$_{2,3}$ states also relaxes by a multiphonon assisted process to the $^3$F$_1$ level [32]. Finally, Tm$^{3+}$ in the $^3$F$_1$ level is excited to $^1$G$_4$ level by ET from Yb$^{3+}$ and absorption a photon. Therefore, the population of $^1$G$_4$ is based on the processes as follows: ET from Yb$^{3+}$: (Yb)$^2F_{5/2}$ + (Tm)$^3$F$_1$ $\rightarrow$ (Yb)$^3F_{7/2}$ + (Tm)$^3$G$_4$ and ESA: (Tm)$^3$F$_1$ + a photon $\rightarrow$ (Tm)$^3$G$_4$. From the $^1$G$_4$ level, the Tm$^{3+}$ ions decay radiatively to the $^3$H$_4$ ground state, generating the intense red emission around 660 nm. The major contribution to the blue emission is attributed to the $^1$G$_4$ $\rightarrow$ $^3$H$_6$ transition. The transition probability involved in the blue emission process is small compared to red emission process. Hence the observed blue emission is weak. From the above results it can be concluded that Tm$^{3+}$ and Yb$^{3+}$ showed a dominating role in the energy absorption and energy transfer in visible region. Because three photon upconversion fluorescence is more sensitive to pump energy. Intense red emission has been observed when the excitation power rise to the value above 50 mW. It proven that commercial 975 nm laser diode is a power full pumping source for upconversion fluorescence in Tm$^{3+}$/Yb$^{3+}$ codoped alumina lead borate glasses.

4. Conclusions

Tm$^{3+}$/Yb$^{3+}$ codoped alumina lead borate glasses have been prepared and characterized. Based on optical absorption optical band gap energy and urbach energy were calculated. FTIR spectra revealed the presence of AlO$_4$ and AlO$_6$ functional groups. Intense red and weak blue emissions corresponding to the $^1$G$_4$ $\rightarrow$ $^3$H$_6$ (blue) and $^1$G$_4$ $\rightarrow$ $^3$H$_4$ (Red) transitions of Tm$^{3+}$ ions, respectively, were observed at room temperature under the excitation of 975 nm laser diode. From the results it can be concluded that weak blue and intense red emissions are due to three photon absorption process. The strong red upconversion fluorescence indicate that Tm$^{3+}$/Yb$^{3+}$ codoped alumina lead borate glasses can be used as potential host material for upconversion lasers.

5. References

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