

Spectroscopic Properties and Energy Transfer in Lead Bismuth Gallium Borate Glasses Codoped with Tm^{3+} and Yb^{3+}

K Krishna Murthy Goud*,
Dept. of Physics, UCE (A),
Osmania University,
Hyderabad-500007 (T.S), India.

Ch Ramesh
Dept. of Physics, M G University,
Nalgonda (T.S), India.

B Appa Rao
Dept. of Physics,
Osmania University,
Hyderabad-500007 (T.S), India.

Abstract— Lead bismuth gallium borate (GTY) glasses codoped with $\text{Tm}^{3+}/\text{Yb}^{3+}$ were prepared by melt quenching technique. The glasses were characterized by X-ray diffraction spectra. Optical absorption, FTIR and photoluminescence spectra of these glasses have been studied. The optical absorption spectra exhibits a band at 980 nm due to transitions from the ground states $^4\text{I}_{15/2}$ and $^2\text{F}_{7/2}$ to excited states of Yb^{3+} . The other absorption bands at 658 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_2$), 686 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_3$), 792 nm ($^3\text{H}_6 \rightarrow ^3\text{H}_4$), 1211 nm ($^3\text{H}_6 \rightarrow ^3\text{H}_5$) and 1663 nm ($^3\text{H}_6 \rightarrow ^3\text{F}_4$) are attributed to 4f-4f transitions of Tm^{3+} ions, respectively. Judd-Ofelt theory has been applied to the f \leftrightarrow f transitions for evaluating Ω_2 , Ω_4 and Ω_6 parameters. Radiative properties like branching ratio β_r and the radiative life time τ_R have been determined on the basis Judd-Ofelt theory. Upconversion emissions have been observed under 980nm laser excitation at room temperature. The spectra exhibited two emission bands centered at 468 nm and 654 nm due to $^1\text{G}_4 \rightarrow ^3\text{H}_6$ (blue) and $^1\text{G}_4 \rightarrow ^3\text{H}_4$ (red) transitions, respectively. The results obtained are discussed quantitatively based on the energy transfer between Yb^{3+} and Tm^{3+} .

Keywords— Optical absorption, FTIR, Luminescence

I. INTRODUCTION

The visible upconversion luminescence of rare earth ions exhibits extensive applications in color display, high density optical data storage and reading, biomedical diagnostics and optical communications, etc. [1–6]. Among various glass systems, heavy metal oxide based glass systems find potential applications in non-linear optical devices because of their high refractive index and low phonon energy compared with other glasses [7].

Glasses based on heavy metal oxides (HMO), especially $\text{Ga}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-PbO}$ glasses, are becoming important and attractive materials for optical amplifier and planar waveguide due to their high refractive index and low phonon energies [8-11]. Moreover, their excellent thermal stability and mechanical properties are advantageous for drawing fibers [12, 13]. The reduced phonon energy effectively improves the quantum efficiency of luminescence from excited states of rare-earth (RE) ions in these matrices and provides the possibility of developing more efficient lasers and fiber optics amplifiers at longer wavelengths.

Among the rare earth ions, the Tm^{3+} is very attractive since it has two stable excited levels, $^1\text{G}_4$ and $^3\text{H}_4$. Through $^1\text{G}_4 \rightarrow ^3\text{H}_6$ 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. [14-17]. Through $^3\text{H}_4 \rightarrow ^3\text{H}_6$ 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 [18, 19].

In previous researches, $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped fluoride and tellurite glasses were investigated under 980 nm laser diode (LD) excitation and were shown to be effective blue luminescence materials through the $\text{Tm}^{3+}: ^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition [20, 21]. In this investigation, a series of $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped lead bismuth gallium borate glasses have been prepared. The XRD, optical absorption, FTIR and upconversion fluorescence spectra have been measured for these samples and the results are discussed in detail.

II. EXPERIMENTAL

For the present study, glasses with the composition $[(100-(x+y))][0.5\text{PbO}-0.25\text{B}_2\text{O}_3-0.20\text{Bi}_2\text{O}_3-0.05\text{Ga}_2\text{O}_3]-x\text{Tm}_2\text{O}_3-y\text{Yb}_2\text{O}_3$ with $y = 0$ for $x = 0, 0.2$ and $y = 0.2$ for $x = 0$ to 1.0 (step 0.2 mol%) are chosen and the glass samples are labelled as GT0Y0, GT2Y0, GT0Y2, GT2Y2, GT4Y2, GT6Y2, GT8Y2 and GT10Y2 respectively. Appropriate amounts of AR grade reagents of PbO , B_2O_3 , Bi_2O_3 , Ga_2O_3 , Tm_2O_3 and Yb_2O_3 powders were weighed by using digital electronic balance. These chemicals were mixed and thoroughly ground in a mortar to get a homogeneous mixture and melted in a porcelain crucible in the temperature range of 900 to 950 °C in a programmable electrical furnace for thirty minutes until bubble free liquid is formed. The resultant melt is poured in a brass mould and subsequently annealed at 300 °C for about four hours in order to avoid these internal mechanical stresses. After annealing, both surfaces of the samples were optically polished to the dimensions of 1 cm \times 1 cm \times 0.2 cm in order to meet the requirements for optical measurements.

The structure of the samples was tested by means of X-ray diffraction using Rigaku miniflex table top X-ray diffractometer with Cu K α radiation at room temperature. The diffractograms have been measured in the range of 10°-80° with a scanning speed of 2.4°/min. The optical absorption spectra were obtained with the JASCO Model V-670 UV-VIS-NIR spectrophotometer in the wavelength range 350–1600 nm with a spectral resolution of 0.1 nm. The FTIR spectra of glass samples were recorded on a BRUKER OPTICS, TENSOR-27 infrared spectrometer in the range 4000 – 400 cm^{-1} . These measurements were made on glass

powder dispersed in KBr pellets. The visible upconversion fluorescence spectra were recorded using JOBIN YVON Fluorolog-3 spectrofluorimeter in the wavelength range 300-700 nm under the excitation of 980 nm laser diode.

III. RESULTS AND DISCUSSION

A. X-ray Diffraction

The short and medium range orders in the prepared samples were tested by means of X-ray diffraction. The obtained diffraction patterns (Fig. 1) have proved the vitreous character of these samples.

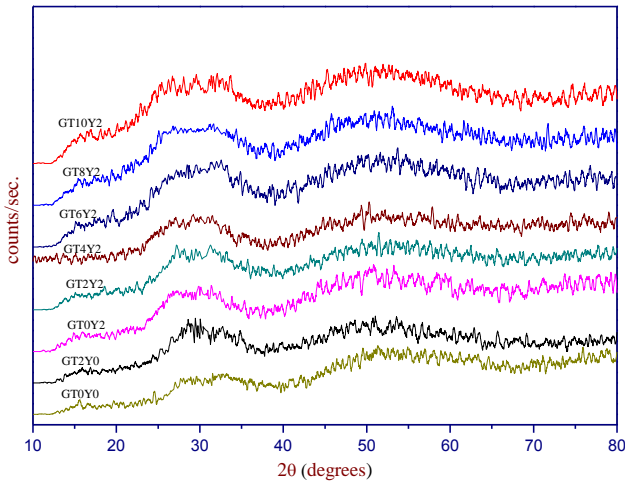


Fig. 1. XRD spectra of GTY glass system

B. Optical Absorption

The optical absorption spectra of all the prepared glass samples were shown in figure 2. The spectra exhibits an absorption band at 980 nm due to ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions. The other absorption bands at 658 nm (${}^3H_6 \rightarrow {}^3F_2$), 686 nm (${}^3H_6 \rightarrow {}^3F_3$), 792 nm (${}^3H_6 \rightarrow {}^3H_4$), 1211 nm (${}^3H_6 \rightarrow {}^3H_5$) and 1663 nm (${}^3H_6 \rightarrow {}^3F_4$) are attributed to 4f-4f transitions of Tm^{3+} ions, respectively [22-24]. Assignments to the various observed bands made by comparing their band positions with the previously reported transitions of Tm^{3+} ions in other glass systems. The intensities of all absorption bands attributed to Tm^{3+} were found to increase with increase in the concentration of Tm^{3+} ions and no significant shift is observed in the band positions.

From the spectra it was observed that cut-off wavelength value increases upto 0.6 mol% (GT6Y2) of Tm^{3+} ions and decreases further with increase in the concentration of Tm^{3+} ions. Using standard relations the values of optical band gap and the Urbach energy are calculated [25, 26]. From the data (Table 1) the value of E_{opt} was found to decrease upto 0.6 mol% (GT6Y2) of Tm^{3+} ions and increases further with increase in the concentration of Tm^{3+} ions. The decrease in the optical band gap with the increase in the concentration of Tm_2O_3 up to 0.6 mol% suggests increasing degree of depolymerization or concentration of bonding defects and non-bridging oxygens (NBO) in the glass network up to this concentration of Tm_2O_3 . Probably in this concentration range the gallium ions may take network forming positions with GaO_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.

Table 1. Values of cut off wavelength, optical band gap and urbach energy of GTY glass system codoped with $\text{Tm}^{3+}/\text{Yb}^{3+}$.

S.No.	Sample code	Cut-off wavelength (nm)	E_{opt} (eV) ± 0.01	ΔE (eV) ± 0.001
1	GT0Y0	420	3.07	0.147
2	GT2Y0	423	3.06	0.149
3	GT0Y2	426	3.05	0.152
4	GT2Y2	430	3.05	0.153
5	GT4Y2	439	3.03	0.157
6	GT6Y2	457	2.99	0.164
7	GT8Y2	454	3.00	0.162
8	GT10Y2	441	3.02	0.159

The Judd-Ofelt theory helps in the analysis of the radiative transitions within in the $4f^N$ configuration of a rare earth ion. The Judd-Ofelt parameters Ω_2 , Ω_4 and Ω_6 [27, 28] can be determined by obtaining the experimental ground state oscillator strengths of the absorption transitions via an integration of the absorption coefficients for each band. The values of Judd-Ofelt intensity parameters are found to be $\Omega_2 = 1.86 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.09 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 1.14 \times 10^{-20} \text{ cm}^2$, respectively. The Judd-Ofelt theory has often been used to calculate the spectroscopic parameters, such as radiative lifetime, oscillator strength and branching ratios (β_r) using standard equations [29-34]. The results are summarized in Table 2 and Table 3.

Table 2. Experimental and calculated oscillator strength of Tm^{3+} in GT2Y0 glass.

Transition from ${}^3H_6 \rightarrow$	$f_{exp}(\times 10^{-6})$	$f_{cal}(\times 10^{-6})$
3F_4	3.987	4.102
3H_5	3.451	3.598
3H_4	5.684	5.578
3F_3	6.981	7.115
3F_2	7.284	7.561
r.m.s. deviation	± 0.281	

Table 3. Radiative life time (τ_R) and branching ratios (β_r) of Tm^{3+} in GT2Y0 glass.

Transitions	β_r (%)	τ_R (ms)
${}^1G_4 \rightarrow {}^3H_6$	63.11	0.118
${}^1G_4 \rightarrow {}^3F_4$	28.09	0.197

According to literature [35-37], Ω_2 is related with the symmetry of the rare earth site while Ω_6 is inversely proportional to the covalency of Tm-O bond. The Tm-O bond is assumed to be dependent on the local basicity around the rare-earth (RE) sites, which can be adjusted by the composition or structure of the glass hosts. It is well established that an emission level with β_r value above 50% becomes a potential laser emission. Referring to the data on emission transitions in the present glass system, the transition ${}^1G_4 \rightarrow {}^3H_6$ has the highest value of β_r among various transitions. This transition may therefore considered as a possible laser transition. From the values of Judd-Ofelt parameters it was found to be in the order $\Omega_2 > \Omega_6 > \Omega_4$.

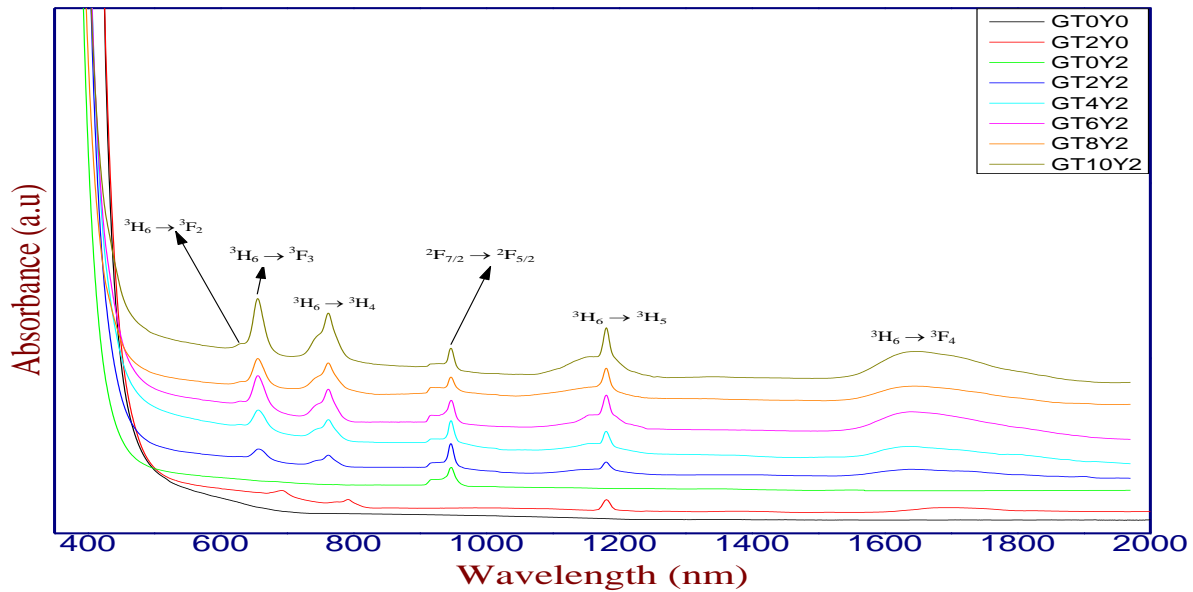


Fig. 2. Optical absorption spectra of GTY glass system.

C. FTIR

The experimental FT-IR spectra of GTY glass system in the range 1600-400 cm^{-1} are presented in Fig. 3. The FTIR spectra of these glasses shows characteristic bands corresponding to the different vibration modes of the various functional groups present in the glass system [38-41]. The assignment of the absorption bands detected is summarized in Table 4.

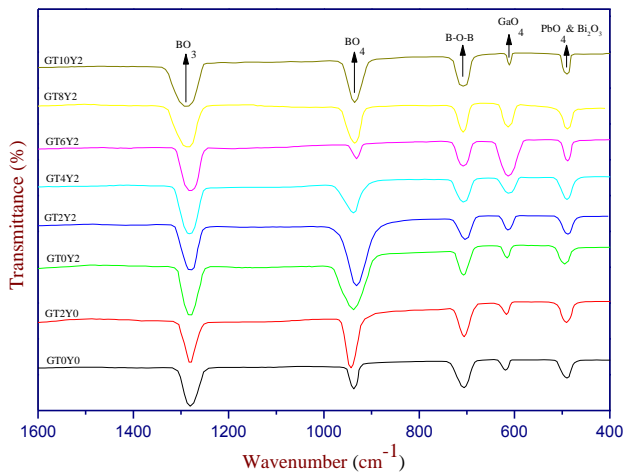


Fig. 3. FTIR spectra of GTY glass system.

A band cited in the region $\sim 490 \text{ cm}^{-1}$ is identified due to bending vibrations of Bi_2O_3 pyramidal units and also due to the presence of PbO_4 structural units. A band cited in the region $\sim 610 \text{ cm}^{-1}$ is identified due to network forming GaO_4 tetrahedral groups. The band cited at $\sim 707 \text{ cm}^{-1}$ and is attributed to the vibrations of B-O-B linkages. A band cited in the region $\sim 930 \text{ cm}^{-1}$ is assigned to asymmetric stretching vibrations of B-O bands in BO_4 units. The band cited in the region $\sim 1280 \text{ cm}^{-1}$ is identified due to asymmetric stretching modes of borate triangles BO_3 and BO_2O^- .

PbO in addition to participating in the glass network with PbO_4 structural units, it may also enter as modifier. Ga_2O_3 is considered to act as a network former if Ga^{3+} ions take preferentially fourfold coordination in oxide glasses. The excess negative charge on GaO_4 tetrahedra is compensated either by localization of a modifier ion nearby or by generation of threefold oxygens. The GaO_4 tetrahedrons may enter the glass network and alternate with BO_4 tetrahedrons. In some of the glass networks, the gallium ions are also found to be in modifier positions with GaO_6 structural units [42].

Table 4. Absorption bands and their assignments for FT-IR spectra.

Wave number (cm^{-1})	IR assignments
~ 490	Bending vibrations of Bi_2O_3 pyramidal units, PbO_4 bending vibrations.
~ 610	Due to network forming GaO_4 tetrahedral groups.
~ 707	Vibrations of B-O-B linkages.
~ 930	Asymmetric stretching vibrations of B-O bands in BO_4 units.
~ 1280	Asymmetric stretching modes of borate triangles BO_3 and BO_2O^- .

From the spectra it was observed that intensity of band corresponding to GaO_4 tetrahedral groups increases from 0 mol% of Tm^{3+} ions (GT0Y0) to 0.6 mol% of Tm^{3+} ions (GT6Y2) beyond this concentration trend is reverse. This is due to the fact that Ga^{3+} ions go into substitutional positions with GaO_4 structural units and alter the glass network upto 0.6 mol%. Within this concentration Ga^{3+} ions, isolate the rare-earth ions from RE-O-RE bonds and form Ga-O-RE bonds. Such declustering effect leads to the larger spacing between RE ions and may contributes for the enhancement of fluorescence emission.

D. Upconversion

Figure 4 represents the upconversion emission spectra of Tm^{3+}/Yb^{3+} codoped GTY glass system in the wavelength range of 500 –700 nm under the excitation of 980 nm laser diode at room temperature. The spectra exhibited two emission bands centered at 468 nm and 654 nm due to $^1G_4 \rightarrow ^3H_6$ (blue) and $^1G_4 \rightarrow ^3H_4$ (red) transitions, respectively [43, 44].

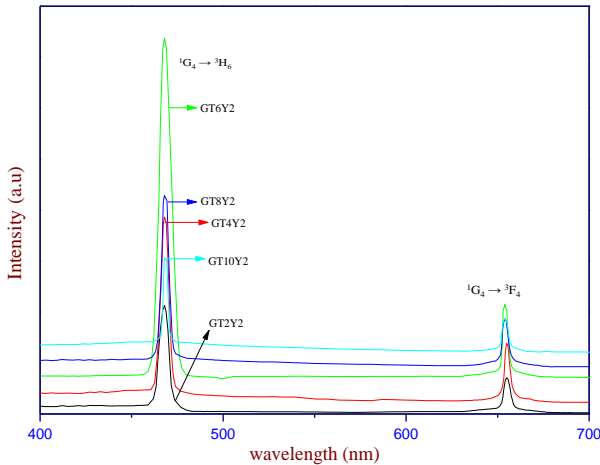


Fig. 4. Frequency upconversion emission spectra of Tm^{3+}/Yb^{3+} codoped GTY glass system.

From the spectra it was observed that the upconversion luminescence intensity of blue emission (468 nm) is higher than the upconversion luminescence intensity of red emission (654 nm). It is also important to point out that the red emission is very weak and blue emission is very prominent to be observed by the naked eye at low excitation power for Tm^{3+}/Yb^{3+} codoped GTY glass system at room temperature. From the spectra it can be concluded that the intensity of blue and red emissions increases with increase in the concentration of Tm^{3+} ions upto 0.6 mol% (GT6Y2) and decreases with further increase in the concentration of Tm^{3+} ions in Tm^{3+}/Yb^{3+} codoped glass samples.

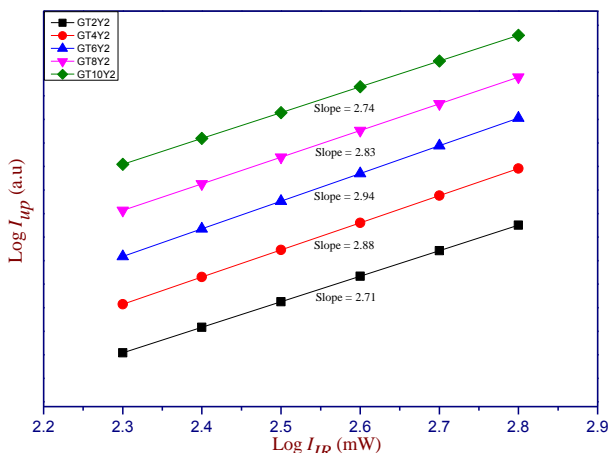


Fig. 5. (a) Dependence of upconversion fluorescence intensity of blue emission (468 nm) on excitation power under 980 nm excitation.

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 [45].

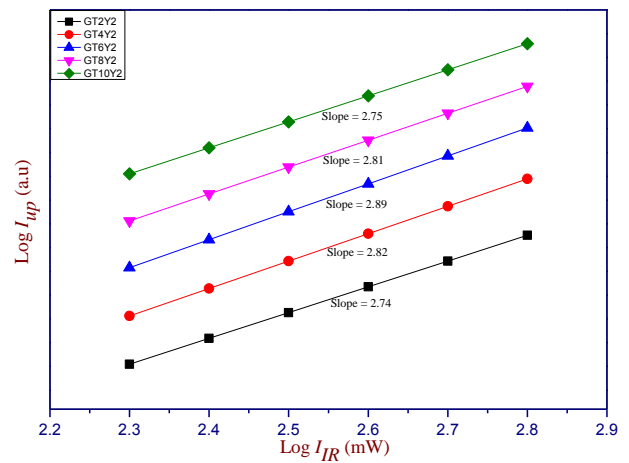


Fig. 5. (b). Dependence of upconversion fluorescence intensity of red emission (654 nm) on excitation power under 980 nm excitation.

A plot of $\log I_{up}$ versus $\log I_{IR}$ yields a straight line with slope 'n'. Figure 5 shows such a plot for the 468nm and 654 nm emissions under 980 nm excitation. From figure 5 the slope value (n) for the 468 nm and 654 nm emission bands was calculated and got around three. The results shows that a three photon upconversion process is responsible for the blue and red emissions from $^1G_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3H_4$ transitions, respectively.

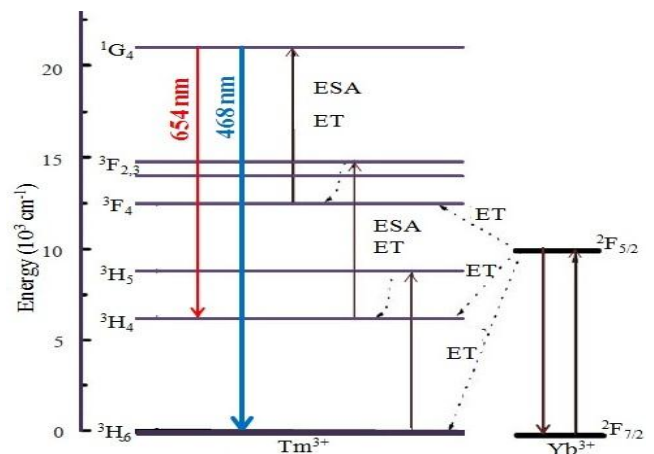


Fig. 6. Energy transfer process between Yb^{3+} and Tm^{3+} ions in GTY glass system.

Figure 6 represents the energy transfer mechanism between Yb^{3+} and Tm^{3+} ions. 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_5). This step is involved by energy transfer (ET) mechanism of excited Yb^{3+} to Tm^{3+} : $(Yb) ^2F_{5/2} + (Tm) ^3H_6 \rightarrow (Yb) ^2F_{7/2} + (Tm) ^3H_5$. Actually the energy gap between $(Yb) ^2F_{5/2}$ and $(Yb) ^2F_{7/2}$ is in a wide range and the low energy edge is near the high energy edge of the energy gap between $(Tm) ^3H_6$ and $(Tm) ^3H_5$. Thus the energy transfer from Yb^{3+} becomes efficient [46].

In the second step, Tm^{3+} in the (3H_5) excited state relaxes nonradiatively to the metastable level (3H_4) by the cooperation of the phonons in the alumina lead borate glasses. Tm^{3+} in the 3H_4 level is excited to $^3F_{2,3}$ level by ET from Yb^{3+} and absorption a photon. Thus, the population of $^3F_{2,3}$ level is based on the processes as follows: ET from Yb^{3+} : $(Yb) ^2F_{5/2} + (Tm) ^3H_4 \rightarrow (Yb) ^2F_{7/2} + (Tm) ^3F_{2,3}$ and excited state absorption (ESA): $(Tm) ^3H_4 + a \text{ photon} \rightarrow (Tm) ^3F_{2,3}$. Then the $^3F_{2,3}$ states also relaxes by a multiphonon assisted process to the 3F_4 level [47]. Finally, Tm^{3+} in the 3F_4 level is excited to 1G_4 level by ET from Yb^{3+} and absorption a photon. Therefore, the population of 1G_4 is based on the processes as follows: ET from Yb^{3+} : $(Yb) ^2F_{5/2} + (Tm) ^3F_4 \rightarrow (Yb) ^2F_{7/2} + (Tm) ^1G_4$ and ESA: $(Tm) ^3F_4 + a \text{ photon} \rightarrow (Tm) ^1G_4$.

It might be ascribed to the fact that the relaxations of 3H_5 to 3H_4 and $^3F_{2,3}$ to 3F_4 need the assistance of multiphonon relaxation, and the density of high energy phonon states is comparatively low in this glass. From the 1G_4 level, the Tm^{3+} ions decay radiatively to the 3H_6 ground state, generating the intense blue emission around 468 nm. This is a process that involved three photons. So the 468 nm emission presents nearly a cubic dependence on the excitation power. Though the phonon energy of the matrix is about 1000 cm^{-1} , the blue luminescence of Tm^{3+}/Yb^{3+} codoped samples can be seen by naked eye under excitation power as low as 70 mW. The red emission around 654 nm is due to the radiative decay of Tm^{3+} ions from the 1G_4 level to the 3H_4 level. The major contribution to the blue emission is ascribed to the $^1G_4 \rightarrow ^3H_6$ transition. The transition probability involved in the blue emission process is very high compared to red emission process. Hence the observed red 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 blue emission has been observed when the excitation power rise to the value above 70 mW. It proven that commercial 980 nm laser diode is a power full pumping source for upconversion fluorescence in Tm^{3+}/Yb^{3+} codoped alumina lead borate glasses. Moreover, as mentioned before, the phonon energy also plays an important role and it can affect the upconversion intensity: with the increase of the phonon energy in Tm^{3+}/Yb^{3+} co-doped glasses the blue emission increases more than the red by means of the process described above.

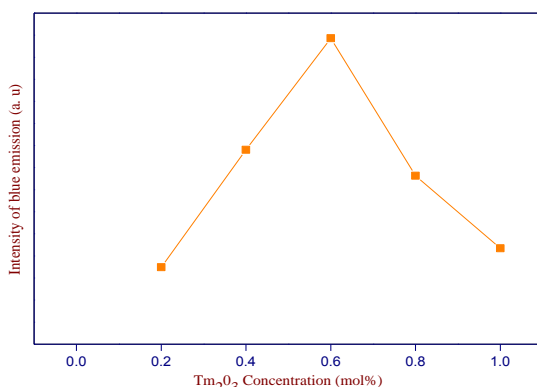


Fig. 7. Intensity of blue emission as a function of Tm_2O_3 concentration at fixed Yb_2O_3 concentration.

Figure 7 shows the intensity of blue emission as a function of Tm_2O_3 concentration in GTY glass system. From the figure it was observed that as the concentration of Tm_2O_3 is increased the blue emission band is observed to grow gradually up to 0.6 mol% and decreases further increasing the concentration of Tm_2O_3 . A similar behavior is also observed in cut-off wavelengths of these glasses. This is due to the fact that Ga^{3+} ions (like any other III A group elemental ions), isolate the rare-earth ions from RE-O-RE bonds and form Ga-O-RE bonds. Such declustering effect which seems to be dominant in the glasses containing higher concentrations of Tm_2O_3 , leads to the larger spacing between RE ions and contributes for the enhancement of fluorescence emission.

Above 0.6 mol% of Tm_2O_3 there is a decrease in the emission intensity which may be due to optical quenching. For the Yb^{3+}/Tm^{3+} codoped glass, the 468 nm blue luminescence can be quenched by the following process: $Tm^{3+} : ^1G_4 + Tm^{3+} : ^3H_6 \rightarrow Tm^{3+} : ^3H_4 + Tm^{3+} : ^3H_5$. However, when the concentration of Tm^{3+} ions is not too high, this quenching process is not notable because the 3H_4 and 3H_5 energy levels are still the interim states for the blue upconversion emission. Tm^{3+} ions in 3F_4 or 3H_4 can be sensitized again to 1G_4 . It is just like a cycle. However, when the concentration of Tm^{3+} ions increases 3F_4 and 3H_4 states are depopulated by the energy transfer and the cycle breaks. Hence, luminescence quenching takes place resulting the decrease in the upconversion intensity.

IV. CONCLUSIONS

We have prepared and characterized Tm^{3+}/Yb^{3+} codoped lead bismuth gallium borate (GTY) glasses. Infrared spectra revealed the presence of various functional groups present in the glass system. With the help of optical absorption spectra and Judd-Ofelt theory, we have calculated the Ω_t ($t = 2, 4, 6$) intensity parameters, the oscillator strengths, branching ratios (β_r), and the radiative lifetimes of Er^{3+} doped glass. The upconversion luminescence was recorded and investigated under the excitation of 980 nm laser diode. The intense blue (468 nm) and weak red (654 nm) emissions are observed at room temperature.

The blue emission is more influenced than the red emission. With increasing in the concentration of Tm^{3+} upto 0.6 mol% (GT6Y2) the intensity of red (654 nm) increases slightly, while the blue (468 nm) emission intensity increases very much more than that of red emission. From the values of branching ratio it was found that the transition $^1G_4 \rightarrow ^3H_6$ (468 nm) has the highest value of β_r among various transitions. This transition may therefore considered as a possible laser transition. The intense blue upconversion luminescence of GT6Y2 glass can act as potential materials for developing upconversion optical devices.

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