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Upconversion and Spectroscopic Properties of Rare Earth Codoped Lead Borate Glass Matrix

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Abstract

To develop efficient upconversion laser materials in the visible region an active lead borate glasses doped with Er^{3+}/Yb^{3+} rare earth ions (GEY) has been studied extensively. In this investigation characterization techniques like Optical absorption, FTIR and photoluminescence were recorded and the data was analyzed. To evaluate the values of Ω_2, Ω_4 and Ω_6 Judd-Ofelt theory has been applied to the f $\leftrightarrow$ f transitions. Based on Judd–Ofelt theory branching ratio(βr) oscillator strength and the radiative life time(T_R) values were determined. The upconversion spectra exhibited three emission bands at around 525 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$), 545nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) and 660nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$). The energy transfer mechanism between Yb^{3+} and Er^{3+} was discussed very clearly. Comparing the data obtained in other Er^{3+}/Yb^{3+} doped materials, the lead bismuth gallium borate glasses doped with 0.6 mol% of Er_2O_3/0.2 mol% of Yb_2O_3 ions are suitable materials for developing red upconversion lasers in the visible region.

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Glasses, Optical Absorption, FTIR, Photo Luminescence.

Introduction

The addition of rare earths to the base glass matrix created a great interest in the researchers because of upconversion of infrared light to visible light. This feature leads to various applications like upcoversion lasers, sensors, and optical displays[1-3]. Among different oxide glass compositions, the lead borate glass matrix doped with *f* block elements are suitable systems for applications in optical devices of laser technology. The absorption and emission properties of rare earth ions in lead borate glass matrix are well reported in the literature[4-6]. Among various glass systems, heavy metal oxide glasses are good enough for the applications in non-linear optical instruments[7].

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The physical properties like thermal expansion coefficient, refractive index, glass transition temperature, chemical resistance and infrared transmittance of the glasses changes when heavy metal oxides like, Ga_2O_3 is introduced in to the glass matrix. The addition of heavy metal oxides makes the glass matrix good enough for the applications in photonic devices[8,9]. Er_2O_3 is universally considered as an effective ion among different rare-earth ions that produce upconversion, and gives rather high efficiency. Energy transfer and excited state absorption mechanisms are most efficient in the case of Er_2O_3 [10]. Because of efficient energy transfer from Yb^{3+} to Er^{3+} ions, the sensitization of Er^{3+} doped materials with Yb^{3+} ions is a well-known method for increasing the optical pumping efficiency[11]. In this task, we presented the spectral properties of Er^{3+}/Yb^{3+} codoped lead bismuth gallium borate (GEY) glasses.

Experimental

Glasses with [100-(x+y)] [0.5PbO-0.25B_2O_3-0.20Bi_2O_3-0.05Ga_2O_3] -xEr_2O_3 -yYb_2O_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 for this investigation and the glass samples are marked as GE0Y0, GE2Y0, GE0Y2, GE2Y2, GE4Y2, GE6Y2, GE8Y2 and GE10Y2, respectively. All glasses were processed by universally accepted melt quenching method.

With the help of JASCO Model V-670 UV–VIS–NIR spectrophotometer, optical absorption spectra of the present glass matrix were reported in the wavelength range 350– 2000 nm. The FTIR spectra of glass samples were recorded on a BRUKER OPTICS, TENSOR-27 infrared spectrometer in the range 4000– 400 cm^{-1}. Using JOBIN YVON Fluorolog-3 spectrofluorimeter, upconversion fluorescence spectra were obtained in the wavelength range 300-700 nm upon the incitement of 980 nm laser diode.

Results and Discussion

The optical absorption spectra of all prepared glasses was shown in Figure 1. The spectra exhibits intense absorption band at 980 nm because of $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions of Er^{3+} and Yb^{3+}, respectively. The supplementary absorption bands are due to the contribution of 4f-4f transitions of Er^{3+} ions from the ground ($^4I_{15/2}$) level to the higher levels at 488nm ($^4F_{7/2}$), 521nm ($^2H_{11/2}$), 545nm ($^4S_{3/2}$), 652nm ($^4F_{9/2}$), 798nm ($^4I_{9/2}$) and 1510nm ($^4I_{13/2}$)[12,23]. With the augmentation in the enrichment of Er^{3+} ions, the enhancement in the intensities of all bands was noticed to increase.

The enhancement in the value of cut-off wavelength upto 0.6 mol% of Er_2O_3 ions and decrement beyond this concentration of Er_2O_3 was noticed in the

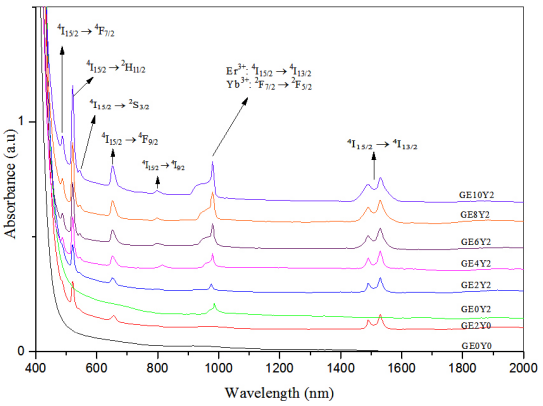

Fig. 1: Optical absorption spectra of GEY glasses.

Figure 1. Optical band gap energy(E_{opt}) and Urbach energy (ΔE)values are measured applying standard relations[13,14]. From the data (Table 1) the value of E_{opt} was found to decrease upto 0.6 mol% of Er^{3+} ions and enhances thereafter with augmentation in the enrichment of Er^{3+} ions.

The decrement in the value of E_{opt} with the rise in the enrichment of Er_2O_3 up to 0.6 mol% refers to the

Table 1: Values of cut off wavelength, E_{opt} and ΔE of GEY glasses codoped with Er^{3+}/Yb^{3+}.

S. No.	Sample code	Cut-off wave-length (nm)	E_{opt} (eV) ±0.01	ΔE (eV) ±0.001
1	GE0Y0	400	3.02	0.152
2	GE2Y0	408	2.96	0.148
3	GE0Y2	409	2.95	0.148
4	GE2Y2	419	2.89	0.144
5	GE4Y2	425	2.85	0.139
6	GE6Y2	431	2.8	0.135
7	GE8Y2	427	2.83	0.138
8	GE10Y2	423	2.86	0.141

amplification of bonding artifacts and NBOs in the glass network up to 0.6 mol% of Er_2O_3. More likely in this concentration region the Ga^{3+} ions may take network establish locations with GaO_4 units and interchange with BO_4 units. Such concatenation may incur a decrement in the firmness of the glass network and causes the decrease in the optical band gap as noticed. Judd-Ofelt theory helps in the analyzation of the radiative transitions within the confines of $4f^n$ configuration of a rare earth ion. The Judd-Ofelt parameters Ω_λ (λ = 2, 4 and 6) and different spectroscopic parameters, in particular radiative lifetime, oscillator strength and branching ratios (β_r) were determined by applying standard equations[15-22]. The values of various radiative parameters are presented in Table 2 and Table 3.

According to literature[23,24], Ω_2 is associated with the symmetry of the rare earth site while Ω_6 is inversely proportional to the covalency of Er-O bond. The Er-O bond is supposed to be dependent on the local basicity around the rare-earth sites, which can be adjusted by the configuration or complex of the host material. It is strongly entrenched that an emission level with β_r value above 50% turn into a possible laser radiation. Based on info on radiative transitions in the present glasses, the transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ has the high degree of β_r apart from different transitions. As a result this transition may be treated as a acceptable laser transition. The order of Judd-Ofelt parameters in the present glass system is $\Omega_2 > \Omega_4 > \Omega_6$.

Table 2: Radiative life time (T_R) and branching ratios (β_r) of Er^{3+} in GEY glasses.

Transitions	β_r (%)	T_R (ms)
$^2H_{11/2} \rightarrow {}^4I_{15/2}$	14	0.74
$^4S_{3/2} \rightarrow {}^4I_{15/2}$	16	0.8
$^4F_{9/2} \rightarrow {}^4I_{15/2}$	52	2.76

Table 3: Experimental and evaluated oscillator strength values of Er_2O_3 in GEY glass system.

Transition from $^4I_{15/2} \rightarrow$	f_{exp}(x 10^{-6})	f_{cal}(x 10^{-6})
4I13/2	0.982	0.976
4I11/2	0.549	0.558
4I9/2	0.446	0.441
4F9/2	1.207	1.219
4S3/2	0.328	0.312
2H11/2	4.435	4.442
4F7/2	1.163	1.171
r.m.s. deviation	±0.091	

The FTIR spectra of GEY glass system codoped with Er^{3+}/Yb^{3+} was shown in figure 2. The band cited at ~482 cm^{-1} is attributed to the bending vibrations of Bi_2O_3 pyramidal units and also because of the presence of PbO_4 units[25]. The band indicated at ~613 cm^{-1} is because of network forming GaO_4 tetrahedral groups[26]. A band was identified at ~707 cm^{-1}, which is produced by the vibrations of B-O-B linkages. Asymmetric stretching vibrations of B-O bands in BO_4 units produces a band at ~930 cm^{-1}. The band identified at ~1250 cm^{-1} is because of asymmetric stretching vibrations of BO_3 units[27].

From figure 2 it was noticed that, the intensity of band corresponding to GaO_4 tetrahedral groups increases from 0 mol% of Er_2O_3 to 0.6 mol% of Er_2O_3, beyond 0.6 mol% of Er_2O_3 the trend is

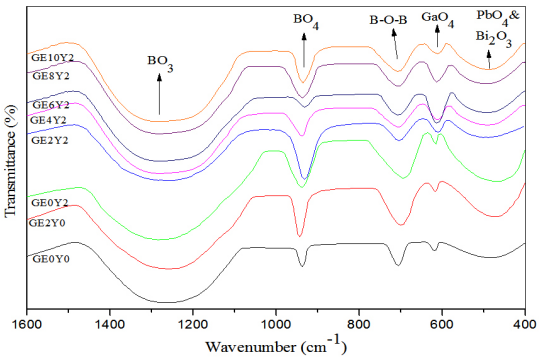

Fig. 2: FTIR spectra of GEY glass matrix.

reverse. This is due to the fact that Ga^{3+} ions go into alternative positions with GaO_4 structural units and alter the glass structure upto 0.6 mol%. Within this concentration Ga^{3+}, separate the rare-earth ions from rare earh-O-rare earh bonds and convert into Ga-O-rare earh. Like that declustering effect leads to the large gap between rare earth ions and may favors the increment of fluorescence emission.

Figure 3 represents the upconversion emission spectra of present glasses obtained in the wavelength region 500 –700nm upon the incitement of 980nm laser source. Three emission bands at 525nm, 545 nm and 660nm were exhibited by the spectra. It was noticed that the upconversion luminescence intensity of red emission (660nm) is higher than the upconversion luminescence intensity of green emission (525 and 545nm). It was also noticed that the green radiation is feeble and red radiation is of high intense.

The results showed that the intensity of green and red radiations increases with increase in the

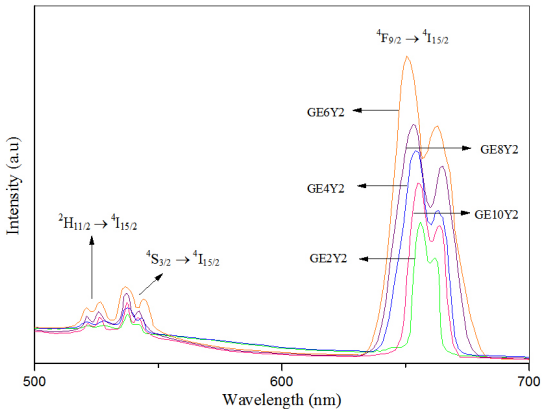

Fig. 3: Frequency upconversion emission spectra of Er^{3+}/Yb^{3+} codoped glasses.

concentration of Er_2O_3 upto 0.6 mol% and beyond this concentration decrease in the intensity was observed. As per literature in an upconversion, the increment in the intensity of emitted radiation (I_{up}) increases in proportion to the nth power of infrared excitation intensity (I_{IR}), i.e.,

where n represents the number of infrared photons absorbed to emit one photon in the visible region[28]. The value of 'n' can be determined from plot of log I_{up} versus log I_{IR}. This plot gives a straight line and the slope of this straight line represents the value of 'n'.The log-log plot for the 525 nm, 545 nm and 660 nm emission was shown in figure 4 (a), (b) and (c), respectively. From figure 4 (a), (b) and (c),the value of 'n' for 525 nm, 545 nm and 660 nm emission bands was calculated and got around two. Hence, two photon absorption is responsible for green and red radiations[29].

Figure 5 illustrates the energy transfer mechanisms for the emisions in the Er^{3+}/Yb^{3+} codoped glasses

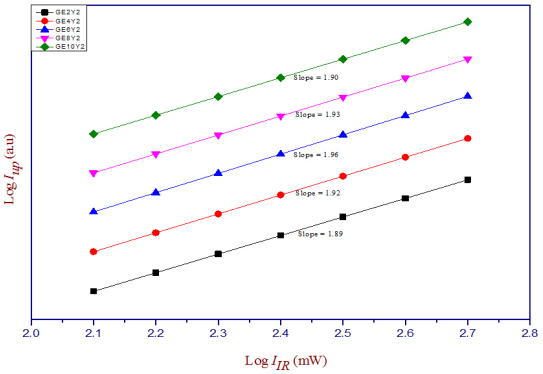

Fig. 4: (a) log-log plot for the green emission (525 nm) upon the incitement of 980 nm laser source.

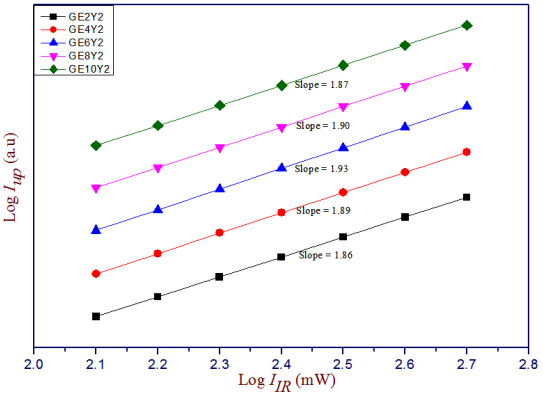

Fig. 4: (b). log-log plot for the green emission (545 nm) upon the incitement of 980 nm laser source.

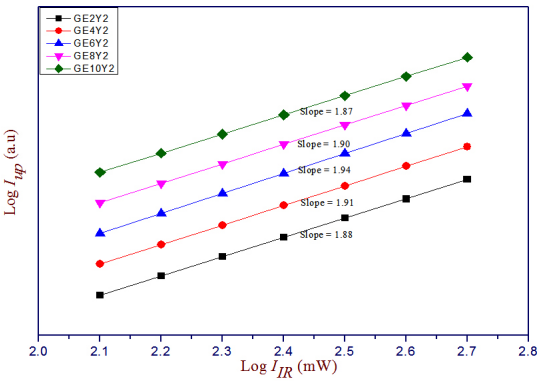

Fig. 4: (c). log-log plot for the red emission (660 nm) upon the incitement of 980 nm laser source.

upon the incitement of 980 nm laser source[30].The energy transfer mechanism between Er_2O_3 and Yb_2O_3 mainly involves ground state absorption (GSA), energy transfer (ET) and excited state absorption (ESA). The energy transfer mechanism which is responsible for the green and red emissions was explained in detail in our previous papers[31, 32].

From the Upconversion spectra, it was noticed that the intensity of green emissions centered at 525 nm

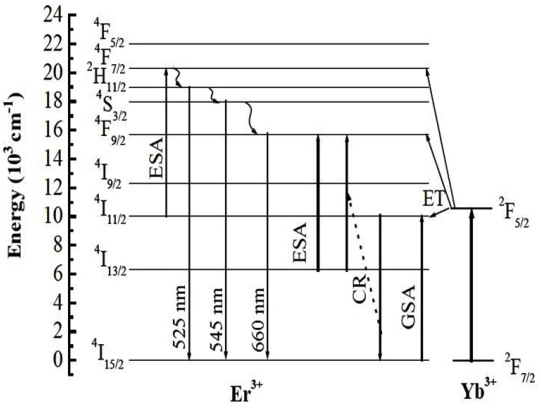

Fig. 5: Energy transfer mechanism between Er^{3+}/Yb^{3+} in GEY glasses[35].

and 545 nm are very small. This may be due to the radiation less transition of the erbium ions at $^4S_{3/2}$ level to $^4F_{9/2}$ level in large number.

The $^4I_{13/2}$ level is populated owing to the radiation less transition from the upper $^4I_{11/2}$ level. In addition to this, the radiation less transition from $^4S_{3/2}$ level, which is populated by means of the mechanism explained earlier, to the $^4F_{9/2}$ level also contributes to the red emission. As per the discussion made earlier, the phonon energy also plays a significant role and it can affect the upconversion intensity: with the increase of the phonon energy in Er^{3+}/Yb^{3+} co-doped glasses the red emission increases more than that of green by means of the mechanism explained above. The previous researchers reported that Ga_2O_3 influences the increase in the intensity of red emission than that of green emission[33,34].

Conclusions

For the investigation of spectroscopic properties at room temperature, lead bismuth gallium borate glasses were prepared with different dopant (Er^{3+}/Yb^{3+}) ion concentrations. The incorporation of Er^{3+}/Yb^{3+} in the present glass matrix was evidenced by the studied characterization techniques. The Judd–Ofelt intensity parameters Ω_t (t=2,4,6), oscillator strength, branching ratio (β_r), and the radiative lifetime values were calculated and analyzed. For the transition $^4F_{9/2} \rightarrow ^4I_{15/2}$ at 660nm, the branching ratio (β_r) showed highest value among other transitions. Therefore, this transition is considered as suitable transition for the development of upconversion lasers. The upconversion bands representing to weak green and intense red emissions at around 525nm, 545 nm and 660nm, respectively, were detected upon the incitement of 980nm laser source. ESA and the ET were primarily connected with the upconversion processes. It was noticed that the increment in the energy transfer efficiency takes place with Er^{3+} content, and reaches maximum for the 0.6 mol% Er^{3+}/0.2 mol% Yb^{3+} co-doped glass. From the upconversion spectra it was found that, the red emission is more influenced than the green emission. Two-photon absorption process is responsible for the green and red emissions. The probability of radiation less transition of Er^{3+} ions from $^4F_{11/2} \rightarrow ^4I_{13/2}$ is enough higher than the probability of upconversion to the upper $^4F_{7/2}$ level as a result of the longer lifetime of the $^4I_{13/2}$ level compared to the lifetime of the $^4I_{11/2}$ level, which influences the radiation less transition ($^4I_{11/2} \rightarrow ^4I_{13/2}$) to take place more easily. Hence, the intensity of red emission is intensified than that of green emission. With increase in the concentration of Er^{3+} upto 0.6 mol%, the intensity of green emission increased slightly, while the red emission intensity increases to a larger extent when compared with that of green emission. The results obtained provide useful information for choice of Er and Yb concentration as well as for modelling and optimising the performance of upconversion lasers based Er^{3+}/Yb^{3+} codoped lead bismuth gallium borate glasses.

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