

## **NIR EMISSION SPECTRA OF (Er<sup>3+</sup>: Yb<sup>3+</sup>) DOPED SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> SOL-GEL GLASSES**

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**Abstract:** The present paper reports the near infrared (NIR) emission spectra of Er<sup>3+</sup>: Yb<sup>3+</sup> co-doped SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> sol-gel glasses. Upon optical pumping either with 980nm(Diode Laser) or 488nm (Ar<sup>+</sup> ion laser), the NIR emission transition (<sup>4</sup>I<sub>13/2</sub>→<sup>4</sup>I<sub>15/2</sub>) at 1550nm of (Er<sup>3+</sup>:Yb<sup>3+</sup>) glasses have revealed an improved intensity by many times compared with the Er<sup>3+</sup> singly doped sol-gel glass. The dependence of the emission intensity and lifetimes on the Yb<sup>3+</sup>/Er<sup>3+</sup> values and also the Er<sup>3+</sup> concentration change has been investigated.

**Keywords:** (Er<sup>3+</sup>:Yb<sup>3+</sup>) sol-gel glasses-emission spectra

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### **Introduction**

In recent years, NIR emission from the Er<sup>3+</sup>-doped thin films and bulk materials has generated a great deal of interest due to its applications in the optical communications. Er<sup>3+</sup>-doped fiber amplifier (EDFA) has already been proved to be a key component in modern optical communication systems,

especially for the wavelength division multiplexing (WDM) systems. However, an EDFA has relatively been a larger in size and hence that has not been found suitable for the integration of several functions like in the case of integrated optics on a single chip. Therefore,  $\text{Er}^{3+}$ -doped waveguide amplifiers (EDWA) that are a few centimeters long have now widely been developed. The  $\text{Er}^{3+}$  content in the material for EDWA is normally maintained at higher concentration compared with a fiber. In the optical materials with such higher  $\text{Er}^{3+}$  content, cooperative up-conversion and fast energy migration between the  $\text{Er}^{3+}$  ions could become apparent and hence the emission intensity quenching takes place at still higher concentration that results in a lower emission efficiency [1-2]. This drawback could be overcome to a great deal by co-doping with the  $\text{Yb}^{3+}$  ions along with the  $\text{Er}^{3+}$  ions in the glasses as reported in literature [5-7]. In the past several years, many authors have reported the lasing transition from  $\text{Er}^{3+}$ - $\text{Yb}^{3+}$  doped materials including phosphate and silicate glasses [8-9] crystals [10-12]. Moreover, waveguide amplifiers and lasers made from phosphate glasses by an ion exchange have also been reported [13]. For  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped silica glasses obtained from a sol-gel process, a waveguide amplifier was made, but no net gain could be obtained. Therefore, there is a need to identify an optimized recipe as one of the main requirements for achieving an efficient amplification operation. In the present work we report the fluorescence properties of  $\text{Er}^{3+}:\text{Yb}^{3+}$  co-doped  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  sol-gel glasses. The objective has mainly been to optimize the recipe, for its applications as waveguide amplifiers and glass lasers. The  $\text{SiO}_2$  content has been used because of its low loss in the infrared range;  $\text{TiO}_2$  was incorporated in it in order to control the refractive index of the material and to develop waveguides. The function of  $\text{Al}_2\text{O}_3$  is to disperse the rare earth ions uniformly in the glass matrices and also in preventing the cluster formation trends in the glass networks. The dependence of the emission intensity and lifetimes on the  $\text{Er}^{3+}$  content as well as the  $\text{Er}^{3+}/\text{Yb}^{3+}$  ratio has been investigated, and the optimized composition of the glass has been identified based on the results presented here.

### Experimental

We have earlier reported the procedures relating to the production of rare earth doped SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glasses by a sol-gel technique [14], however a sample preparation is briefly summarized here. The TEOS [Si (OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>](TEOS means tetra ethyl ortho silicate) was diluted in ethanol and the de-ionized water hydrolyzed it with a little amount of HCl as the catalyst. The titanium salt [Ti((CH<sub>3</sub>)<sub>2</sub>CHO)<sub>4</sub>] was mixed with acetyl acetone [C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>] for decreasing its hydrolysis rate, then into the pre-hydrolyzed SiO<sub>2</sub> solution. The raw chemicals of high purity (99.99%, Aldrich) such as Al(NO<sub>3</sub>)<sub>3</sub>, Er(NO<sub>3</sub>)<sub>3</sub>, and Yb(CH<sub>3</sub>COO)<sub>3</sub> were used as precursors of Al<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and YbO<sub>2</sub> respectively. Al (NO<sub>3</sub>)<sub>3</sub>, Er (NO<sub>3</sub>)<sub>3</sub> were dissolved into ethanol and Yb(CH<sub>3</sub>COO)<sub>3</sub> into de-ionized water these solutions were mixed with SiO<sub>2</sub>-TiO<sub>2</sub> solution step by step after it was hydrolyzed for about 2 hours. The end solutions were aged at the room temperature in sealed bottles. In about two weeks time, dry gels were obtained in the bottles and these dried gels were annealed at high temperature to obtain transparent sol-gel optical glasses with homogeneous distribution of dopant rare earth ions in the glassy matrices undertaken in the present work. In order to obtain an optimized recipe for observing a strong NIR emission, fourteen samples were prepared and abbreviated as group-I (2 samples), group-II (7 samples) with a fixed Er<sup>3+</sup> (1mol) and a varied Yb<sup>3+</sup> content, and group-III (5 samples) with a fixed Yb<sup>3+</sup> (1mol) and a varied Er<sup>3+</sup> content. The NIR fluorescence spectra and lifetime were measured using a photoluminescence spectral measurement system developed by us at the laboratory with a diode laser (980nm) as the pump source. NIR emission spectra were also measured under an excitation at 488nm (Ar<sup>+</sup> ion laser) on group-I samples for a comparison between the two different pump sources. The chemical compositions of the three groups of glasses studied are

Group-I: 93SiO<sub>2</sub>-7TiO<sub>2</sub>-10AlO<sub>1.5</sub>: 1Er<sup>3+</sup> +XYb<sup>3+</sup> (X=0 & 1 mol)

Group-II: 93SiO<sub>2</sub>-7TiO<sub>2</sub>-15AlO<sub>1.5</sub>: 1Er<sup>3+</sup> +XYb<sup>3+</sup> (X=0.1,0.25,0.5,0.8,1.0,1.5 & 2mol)

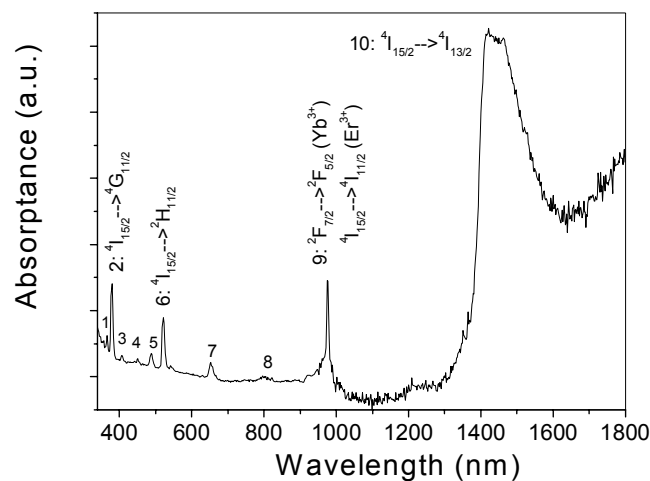
Group-III: 93SiO<sub>2</sub>-7TiO<sub>2</sub>-15AlO<sub>1.5</sub>: 1Yb<sup>3+</sup> +XEr<sup>3+</sup> (X=0.05,0.1,0.5,1.0 & 2.0 mol)

## Results and Discussion

Figure 1 describes the absorption spectrum of 1mol Er<sup>3+</sup> doped and co-doped with 2mol Yb<sup>3+</sup> in SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sol-gel glass and from this spectrum, the following absorption bands have been observed and assigned to the electronic transitions appropriately:

- ${}^4I_{15/2} \rightarrow {}^2G_{7/2}$  (358nm),  ${}^2K_{15/2}$  (363nm),  ${}^4G_{9/2}$  (366nm) (marked as level 1 in Fig. 1 )
- $\rightarrow {}^4G_{11/2}$  (382nm) (level 2)
- $\rightarrow {}^4F_{9/2}$  (411nm) (level 3)
- $\rightarrow {}^4F_{9/2}$  (452nm) (level 4)
- $\rightarrow {}^4F_{7/2}$  (502nm) (level 5)
- $\rightarrow {}^2H_{11/2}$  (524nm),  ${}^4S_{3/2}$  (544nm) (level 6)
- $\rightarrow {}^4F_{9/2}$  (660nm) (level 7)
- $\rightarrow {}^4I_{9/2}$  (812nm) (level 8)
- $\rightarrow {}^4I_{11/2}$  (986nm) (level 9)
- $\rightarrow {}^4I_{13/2}$  (1525nm) (level 10)

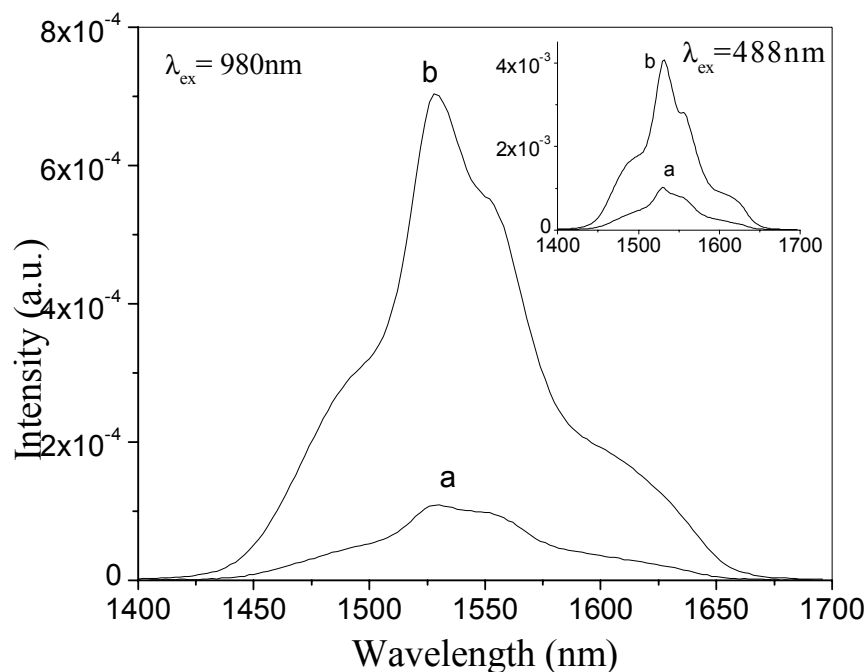
From the figure, it is clear that the Er-Yb glass sample has a strong absorption band ( ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ ) around 980nm and this is because the co-dopant Yb<sup>3+</sup> has also got its absorption peak ( ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ ) in the same wavelength region.



**Figure 1:** Absorption spectrum of 1(mol) Er<sup>3+</sup>+2(mol)Yb<sup>3+</sup> doped 93SiO<sub>2</sub>-7TiO<sub>2</sub>-10AlO<sub>1.5</sub> sol-gel glass (group I)

Therefore, in our NIR fluorescence emission measurement, a 980nm diode laser has been chosen for optical excitation. Also it can be seen that a broader absorption transition  ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$  has been measured and its position is slightly shifted in the sol-gel silica glass studied. Figure 2 shows

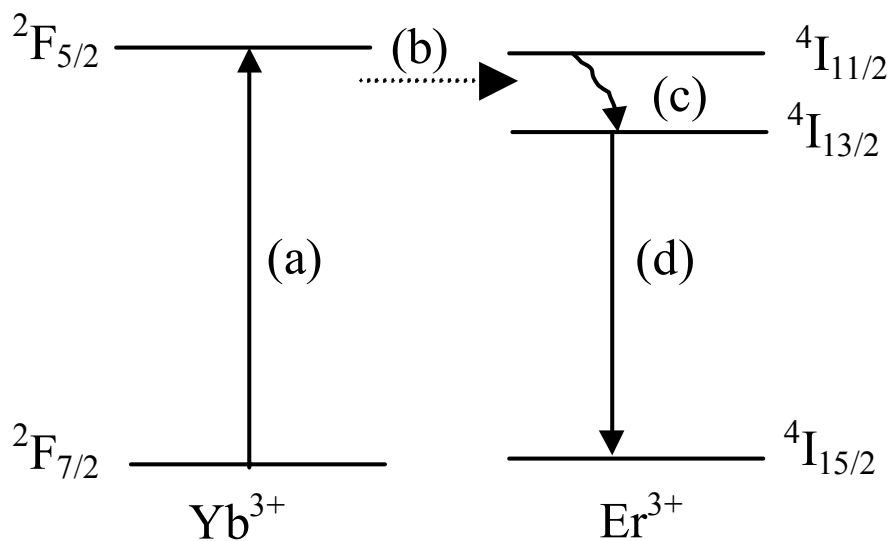
the emission spectra of group-I  $\text{Er}^{3+}$  glasses with and without  $\text{Yb}^{3+}$ . A comparison reveals that the emission strength of  $\text{Er}^{3+} + \text{Yb}^{3+}$  glass at the 1550nm band has been enhanced by at least seven times with respect to that of the  $\text{Er}^{3+}$  glass without  $\text{Yb}^{3+}$ .



**Figure 2:** NIR Fluorescence spectra of  $\text{Er}^{3+}$  (1 mol):  $93\text{SiO}_2$ - $7\text{TiO}_2$ - $10\text{AlO}_{1.5}$  sol-gel glasses (group I) excited at 980nm (Diode Laser) and 488nm ( $\text{Ar}^+$  ion laser) (a) Without the co-dopant  $\text{Yb}^{3+}$  and (b) with the co-dopant  $\text{Yb}^{3+}$

In the same figure, the emission spectra measured with an  $\text{Ar}^+$  laser (488nm) as the pump source have also been shown for a comparison purpose. It can be seen that an argon ion laser at 488nm is also suitable for inducing NIR fluorescence emission from the samples. Interestingly, it can be observed that the emission enhancement is less for the 488nm-excitation source. A simple explanation is due to the strong absorption at 980nm existing for both dopant erbium ion and co-dopant ytterbium ion in the glass and relatively a weak absorption at 488nm. Also due to the fact that the co-dopant  $\text{Yb}^{3+}$  encourages energy transfer onto the levels of  $\text{Er}^{3+}$  in a quite significant manner and also back transfer from the erbium ion to the ytterbium levels. In fact, the  $^2\text{F}_{5/2}$  excited state of  $\text{Yb}^{3+}$  is about 1.2-1.3eV above the ground state ( $^2\text{F}_{7/2}$ ), the energy difference is thus just right for the absorption of 980nm photons (1.27eV). As for a 488nm photon, its energy is about 2.5eV, although there is a nearly

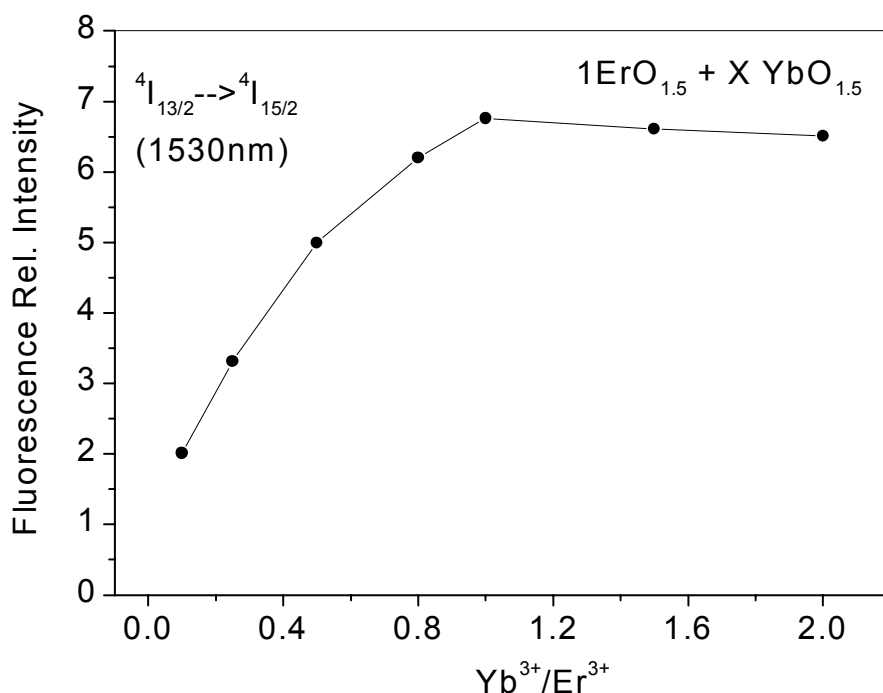
matched transition from  ${}^2F_{7/2}$  to  ${}^4I_{15/2}$ , the absorption strength as shown in Figure 1. It is believed that  $Yb^{3+}$  in  $SiO_2$  glasses could form some complexes with excited  $Yb^{3+*}$  centers and these centers could interact with 488nm photons, hence causing the energy transfer from such complex  $Yb^{3+*}$  excited centers to the  $Er^{3+}$  ions and resulting in with an emission enhancement. The weaker absorption by these complexes at 488nm has actually been reported for implanted  $SiO_2/Si$  films [3]. Figure 3 describes the energy transfer mechanism between  $Yb^{3+}$  and  $Er^{3+}$ .



**Figure 3:** Energy transfer process in  $Er^{3+}:Yb^{3+}:SiO_2-Al_2O_3-TiO_2$  sol-gel glass upon pumping with 980nm(Diode Laser)

The 1550nm-band emission enhancement from  $Er^{3+}+Yb^{3+}$  when excited by a 980nm photon can be summarized as the following: i) absorption of a 980nm pump photon from the ground state  ${}^2F_{7/2}$  to the excited  ${}^2F_{5/2}$  state of  $Yb^{3+}$  ii) energy transfer from the  $Yb^{3+}$  ( ${}^2F_{5/2}$ ) state to the  $Er^{3+}$  ( ${}^4I_{11/2}$ ) state iii) a non radiative decay from the  ${}^4I_{11/2}$  state to  ${}^4I_{13/2}$  state and iv) a radiative decay of  $Er^{3+}$  from  ${}^4I_{13/2}$  to  ${}^4I_{15/2}$  state (1532nm).Figure 4 presents the dependence of the emission intensity upon the  $Yb^{3+}/Er^{3+}$  ratio when the  $Er^{3+}$  content is fixed at 1mole (group-II samples). As can be seen that the fluorescence intensity obviously increases with the  $Yb^{3+}/Er^{3+}$  ratio when it is less than 1 and the fluorescence

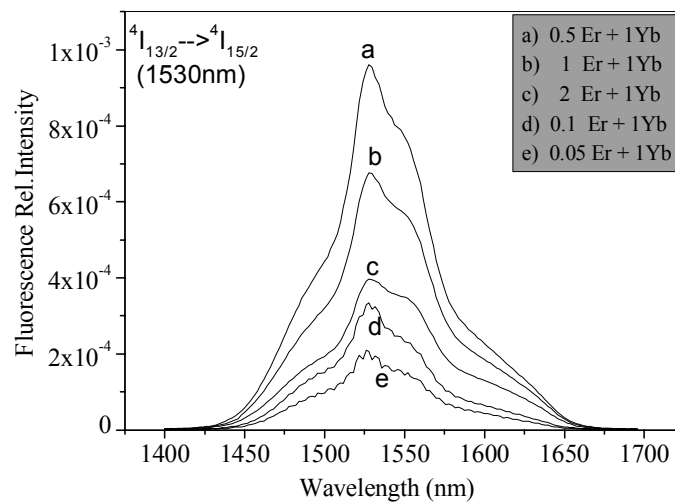
intensity shows more or less a saturation situation with the  $\text{Yb}^{3+}/\text{Er}^{3+}$  ratio for more than 1. That means the  $\text{Yb}^{3+}/\text{Er}^{3+}$  ratio should not be less than in the enhancement of fluorescence intensity



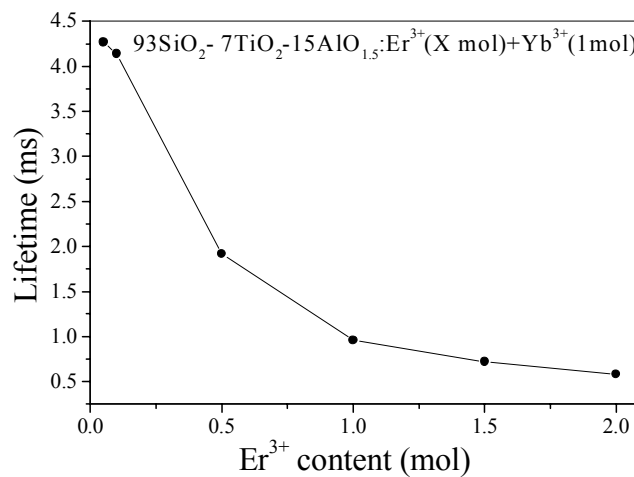
**Figure 4:** Dependence of NIR fluorescence intensity of  $\text{Er}^{3+}$  doped  $\text{Yb}^{3+}$  co-doped in  $93\text{SiO}_2\text{-}7\text{TiO}_2\text{-}15\text{AlO}_{1.5}$ :  $1\text{Er}^{3+} + \text{X}\text{Yb}^{3+}$  sol-gel glasses based on the  $\text{Yb}^{3+}/\text{Er}^{3+}$  ratio change

The lifetime of the 0.5mol, 1.0mol, 1.5mol and 2.0mol samples of this group are 0.989ms, 0.959ms, 0.75ms and 0.72ms respectively. So, the lifetimes show a decreasing trend with an increase of  $\text{Yb}^{3+}$  content. Thus, we conclude from the NIR emission intensity and lifetime results that the  $\text{Yb}^{3+}/\text{Er}^{3+}$  ratio should be higher than one but less than two. Figure 5 shows the dependence of the emission intensity upon the  $\text{Er}^{3+}$  content when the  $\text{Yb}^{3+}$  content is fixed at 1mol (group III samples). These results show that the sample with 0.5 mole  $\text{Er}^{3+}$  has revealed a strong emission. Initially, the emission intensity increases with  $\text{Er}^{3+}$  content up to 0.5mol; afterwards, any increase in  $\text{Er}^{3+}$  content is accompanied by a decrease in emission intensity due to concentration quenching. The lifetimes of the five group-III samples are shown in Figure 6. It can be seen that the lifetime decreases with an increment of the  $\text{Er}^{3+}$  content in the glasses. For the 0.5 mole  $\text{Er}^{3+}$  sample that has the strongest emission intensity, its lifetime is about 1.8 ms. As there is always a trade-off between the emission intensity and the lifetime and 1.8 ms, hence it could be suggested that the recipe of  $93\text{SiO}_2$ :

$7\text{TiO}_2:15\text{AlO}_{1.5}:0.5\text{ErO}_{1.5}:1\text{YbO}_{1.5}$  would be an ideal composition for optical waveguide amplifier and laser applications.



**Figure 5:** Dependence of NIR fluorescence intensity on the  $\text{Er}^{3+}$  content variation of  $93\text{SiO}_2\text{-}7\text{TiO}_2\text{-}15\text{AlO}_{1.5}\text{:}1\text{Yb}^{3+}\text{+}X\text{Er}^{3+}$  sol-gel glasses



**Figure 6:** Lifetime of the emission transition ( ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ ) at 1530nm as a function of the  $\text{Er}^{3+}$  content in  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{:}1\text{Yb}^{3+}\text{+}X\text{Er}^{3+}$  sol-gel glasses upon excitation with 980nm

## Conclusions

Sol-gel glasses doped with  $\text{Er}^{3+}\text{:Yb}^{3+}$  have been prepared in understanding the influence of  $\text{Yb}^{3+}$  on the NIR emission performance of  $\text{Er}^{3+}$  and also the  $\text{Er}^{3+}$  content effects on both the emission intensity and lifetimes. The experimental results confirm the fact that the mole ratio of  $\text{Yb}^{3+}/\text{Er}^{3+}$



should be in between one and two to enhance the fluorescence intensity significantly from  $\text{Er}^{3+}$  doped optical glasses at 1530nm window and in having the lifetime of the lasing transition ( $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ ) of  $\text{Er}^{3+}$  as high as possible for the sol-gel derived optical glasses. Our results show that with 0.5 mol of  $\text{Er}^{3+}$  and 1.0 mol of  $\text{Yb}^{3+}$  doped  $93\text{SiO}_2:7\text{TiO}_2:15\text{AlO}_{1.5}$  sol gel glass has been found to be exhibiting satisfactory NIR fluorescence intensities compared to other glass systems and hence this optical material could be suggested as suitable glassy compositions for the fabrication an optical waveguide for integrated optical applications.

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