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NIR EMISSION SPECTRA OF (Er^{3+}; Yb^{3+}) DOPED SiO_2-TiO_2-Al_2O_3 SOL-GEL GLASSES

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Abstract: The present paper reports the near infrared (NIR) emission spectra of Er^{3+}: Yb^{3+} co-doped SiO_2-Al_2O_3-TiO_2 sol-gel glasses. Upon optical pumping either with 980nm(Diode Laser) or 488nm (Ar^+ ion laser), the NIR emission transition ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) at 1550nm of ($Er^{3+}$:$Yb^{3+}$) glasses have revealed an improved intensity by many times compared with the Er^{3+} singly doped sol-gel glass. The dependence of the emission intensity and lifetimes on the Yb^{3+}/Er^{3+} values and also the Er^{3+} concentration change has been investigated.

Keywords: (Er^{3+}:Yb^{3+}) sol-gel glasses-emission spectra
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Introduction

In recent years, NIR emission from the Er^{3+}-doped thin films and bulk materials has generated a great deal of interest due to its applications in the optical communications. Er^{3+}-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, Er^{3+}-doped waveguide amplifiers (EDWA) that are a few centimeters long have now widely been developed. The 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 Er^{3+} content, cooperative up-conversion and fast energy migration between the 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 Yb^{3+} ions along with the 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 Er^{3+}-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 Er^{3+}/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 Er^{3+}: Yb^{3+} co-doped SiO_2-TiO_2-Al_2O_3 sol-gel glasses. The objective has mainly been to optimize the recipe, for its applications as waveguide amplifiers and glass lasers. The SiO_2 content has been used because of its low loss in the infrared range; TiO_2 was incorporated in it in order to control the refractive index of the material and to develop waveguides. The function of Al_2O_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 Er^{3+} content as well as the Er^{3+}/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_2-TiO_2-Al_2O_3 glasses by a sol-gel technique [14], however a sample preparation is briefly summarized here. The TEOS [$Si(OC_2H_5)_4$](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 [$Ti((CH_3)_2CHO)_4$] was mixed with acetyl acetone [$C_5H_8O_2$] for decreasing its hydrolysis rate, then into the pre-hydrolyzed SiO_2 solution. The raw chemicals of high purity (99.99%, Aldrich) such as $Al(NO_3)_3$, $Er(NO_3)_3$, and $Yb(CH_3COO)_3$ were used as precursors of Al_2O_3, Er_2O_3 and YbO_2 respectively. Al $(NO_3)_3$, Er $(NO_3)_3$ were dissolved into ethanol and $Yb(CH_3COO)_3$ into de-ionized water these solutions were mixed with SiO_2-TiO_2 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^{3+} (1mol) and a varied Yb^{3+}content, and group-III (5 samples) with a fixed Yb^{3+} (1mol) and a varied Er^{3+} 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^+ 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: $93SiO_2$-$7TiO_2$-$10AlO_{1.5}$: $1Er^{3+}$ +XYb^{3+} (X=0 & 1 mol)
Group-II: $93SiO_2$-$7TiO_2$-$15AlO_{1.5}$: $1Er^{3+}$ +XYb^{3+} (X=0.1, 0.25, 0.5, 0.8, 1.0, 1.5 & 2mol)
Group-III: $93SiO_2$-$7TiO_2$-$15AlO_{1.5}$: $1Yb^{3+}$ +XEr^{3+} (X=0.05, 0.1, 0.5, 1.0 & 2.0 mol)

Results and Discussion

Figure 1 describes the absorption spectrum of 1mol Er^{3+} doped and co-doped with 2mol Yb^{3+} in SiO_2-TiO_2-Al_2O_3 sol-gel glass and from this spectrum,the following absorptin 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^{3+} has also got its absorption peak ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) in the same wavelength region.

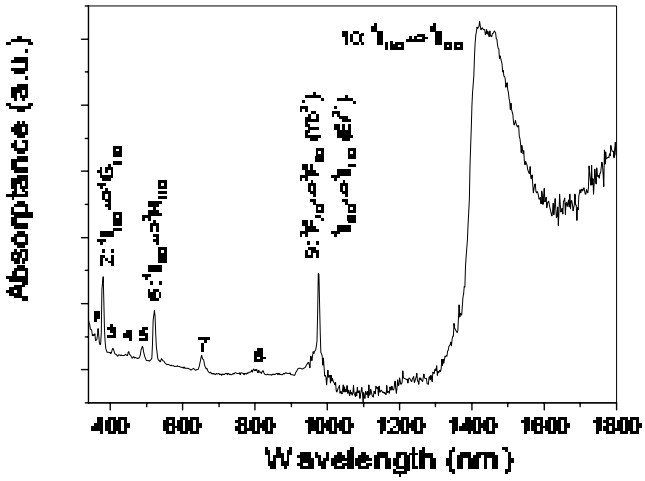

Figure 1: Absorption spectrum of 1(mol) Er^{3+}+2(mol)Yb^{3+} doped $93SiO_2$-$7TiO_2$-$10AlO_{1.5}$ sol-gel glass (group I)

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 positione is slightly shifted in the sol-gel silica glass studied. Figure 2 shows

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

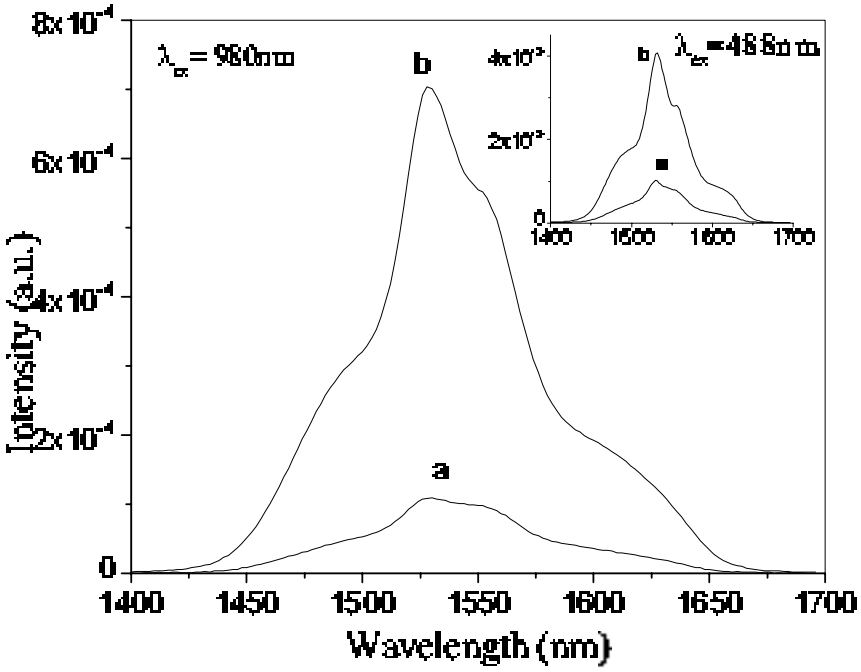

Figure 2: NIR Fluorescence spectra of Er^{3+} (1 mol): $93SiO_2$-$7TiO_2$-$10AlO_{1.5}$ sol-gel glasses (group J) excited at 980nm (Diode Laser) and 488nm (Ar^+ ion laser) (a) Without the co-dopant Yb^{3+} and (b) with the co-dopant Yb^{3+}

In the same figure, the emission spectra measured with an 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 Yb^{3+} encourages energy transfer onto the levels of Er^{3+} in a quite significant manner and also back transfer from the erbium ion to the ytterbium levels. In fact, the $^2F_{5/2}$ excited state of Yb^{3+} is about 1.2-1.3eV above the ground state ($^2F_{7/2}$), 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 $^4I_{11/2}$, 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+}.

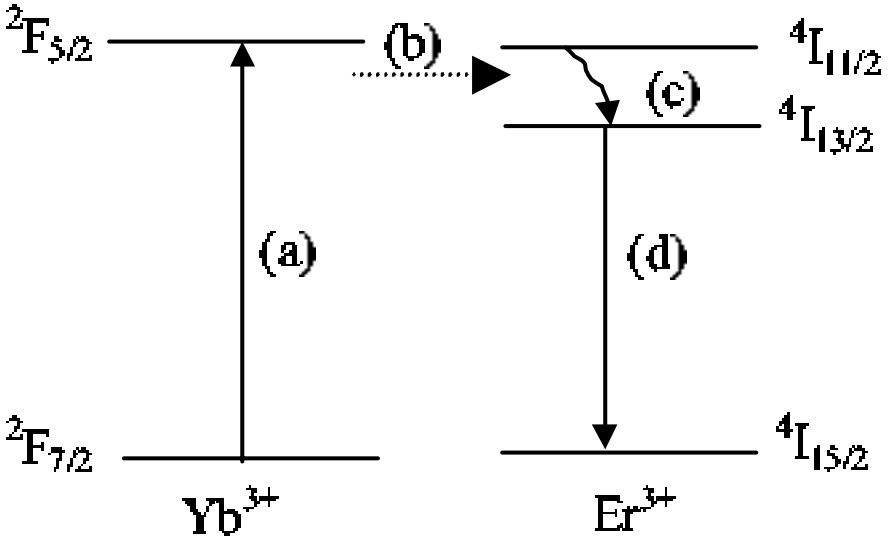

Figure 3: Energy transfer process in Er^{3+}:Yb^{3+}:SiO_2-Al_2O_3-TiO_2 sol-gel glass upon pumping with 980nm(Diode Laser)

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 Yb^{3+}/Er^{3+} ratio for more than 1. That means the Yb^{3+}/Er^{3+} ratio should not be less than in the enhancement of fluorescence intensity

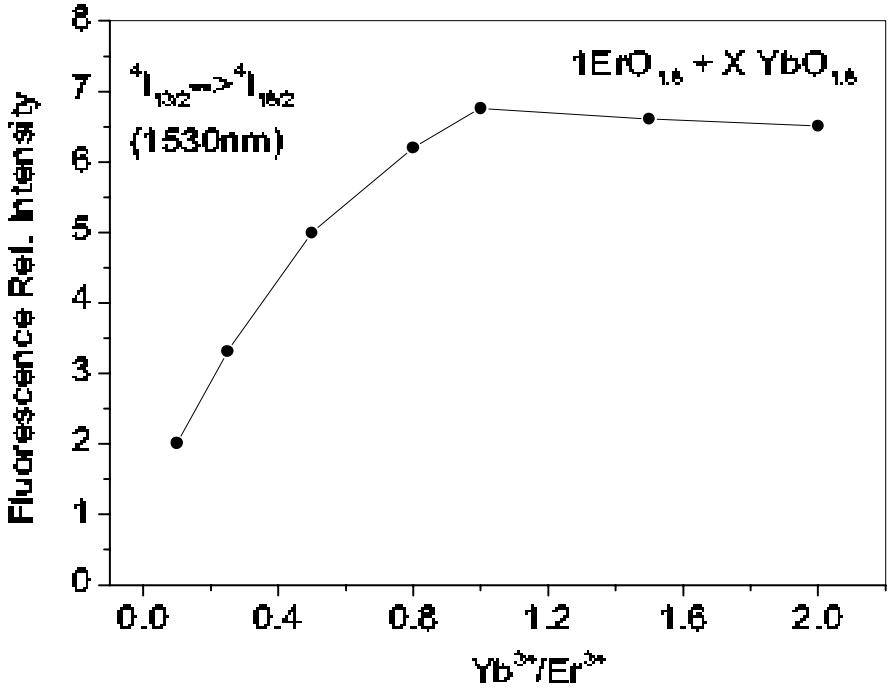

Figure 4: Dependence of NIR fluorescence intensity of Er^{3+} doped Yb^{3+} co-doped in $93SiO_2$-$7TiO_2$-$15AlO_{1.5}$: $1Er^{3+}$+XYb^{3+} sol-gel glassesbased on the Yb^{3+}/Er^{3+} ratio change

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 Yb^{3+} content. Thus, we conclude from the NIR emission intensity and lifetime results that the Yb^{3+}/Er^{3+} ratio should be higher than one but less than two. Figure 5 shows the dependence of the emission intensity upon the Er^{3+} content when the Yb^{3+} content is fixed at 1mol (group III samples). These results show that the sample with 0.5 mole Er^{3+} has revealed a strong emission. Initially, the emission intensity increases with Er^{3+} content up to 0.5mol; afterwards, any increase in 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 Er^{3+} content in the glasses. For the 0.5 mole 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 $93SiO_2$:

$7TiO_2$:$15AlO_{1.5}$:$0.5ErO_{1.5}$:$1YbO_{1.5}$ would be an ideal composition for optical waveguide amplifier and laser applications.

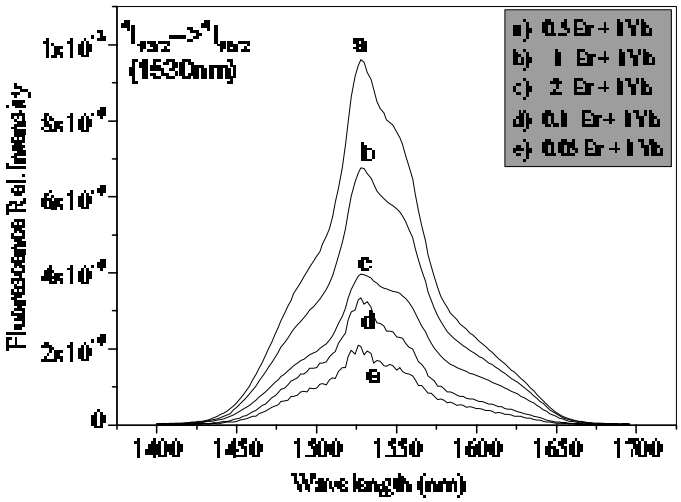

Figure 5: Dependance of NIR fluorescence intensity on the Er^{3+} content variationof $93SiO_2$-$7TiO_2$-$15AlO_{1.5}$:$1Yb^{3+}$+XEr^{3+} sol-gel glasses

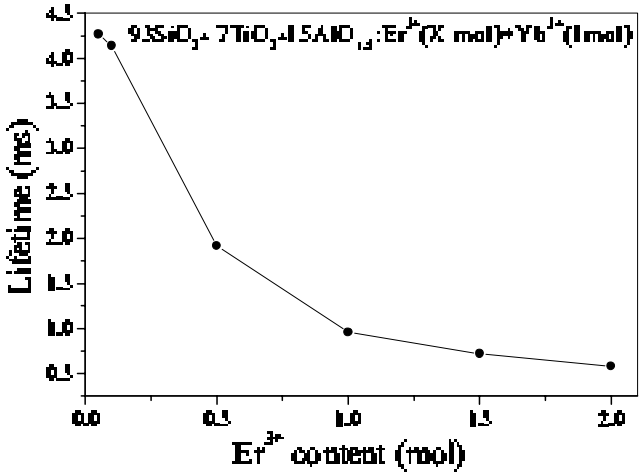

Figure 6: Lifetime of the emission transition ($^4I_{13/2}$→$^4I_{15/2}$) at 1530nm as a function of the Er^{3+} content in SiO_2-TiO_2-Al_2O_3:$1Yb^{3+}$+XEr^{3+} sol-gel glasses upon excitation with 980nm

Conclusions

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

should be in between one and two to enhance the fluorescence intensity significantly from Er^{3+} doped optical glasses at 1530nm window and in having the lifetime of the lasing transition ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) of Er^{3+} as high as possible for the sol-gel derived optical glasses. Our results show that with 0.5 mol of Er^{3+} and 1.0 mol of Yb^{3+} doped $93SiO_2$:$7TiO_2$:$15AlO_{1.5}$ 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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