Spectroscopic Properties of Yb^{3+}/Nd^{3+} Co-doped Ions in SiO_2-Al_2O_3-Na_2CO_3-SrF_2-CaF_2 Oxyfluoride Glasses for Photonic Applications

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Abstract—The Yb^{3+} and Yb^{3+}/Nd^{3+} co-doped SiO_2-Al_2O_3-Na_2CO_3-SrF_2-CaF_2 oxyfluorosilicate glasses have been prepared by a high temperature melt-quenching method. The prepared glasses are excited with 808 nm, and the near infrared emission bands are observed. The intensified emission band was centered at 1030nm ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) of Yb^{3+} ions. Stimulated emission cross-section was evaluated for the prominent $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ion by using the Mc-Cumber theory. The energy transfer from Nd^{3+} to Yb^{3+} ions in co-doped silicate based oxyfluoride glasses is described under the 514nm excitation wavelength.

Rare earth doped materials are widely used in lighting, display, lasers, optical amplifiers and communications [1-3]. Among the rare-earth ions, the Yb^{3+} has a two-level energy level diagram and also is very attractive for near infrared (NIR) applications. NIR lasers based on Yb^{3+} ions have several advantages over those of Nd^{3+} due to their simple energy level configuration. The Yb^{3+} ions are suitable for high energy mode-locked femtosecond lasers based on their high fluorescence lifetime along with the significance emission cross-section and broad emission profile. However, the Yb^{3+} ions are limited only for a pumping wavelength at 980nm. The Nd^{3+} ions act as an efficient sensitizer for Yb^{3+} ions in co-doped glasses, due to having more absorption bands from UV to the NIR region [4-6].

$Nd^{3+} \rightarrow Yb^{3+}$ energy transfer has been already considered and studied in several materials for different applications. The authors selected silicate based oxyfluoride glasses as a host material because of their favourable properties. They exhibit good thermal and chemical properties like oxide glasses and excellent optical properties like fluoride glasses [7]. The host glasses possess high thermal stability which could be useful for fibre drawing applications [7, 8].
The present article, discusses the optical and spectroscopic properties of Yb^{3+} and Yb^{3+}/Nd^{3+} co-doped ions in silicate based oxyfluoride glasses. The energy transfer mechanism from Nd^{3+} to Yb^{3+} has been described.

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A series of glasses doped with Yb^{3+} and co-doped with Yb^{3+}/Nd^{3+} ions were prepared from the high purity chemicals (~99.9%). The silicate based oxyfluoride glass samples with molar composition: (44-*x*) SiO_2-5Al_2O_3-17Na_2Co_3-18SrF_2-15CaF_2-1.0Yb_2O_3-*x*Nd_2O_3 (where *x*=0, 0.1, 0.5, 1.0 and 2.0) were prepared and denoted as Yb10, Yb10Nd01, Yb10Nd05, Yb10Nd10 and Yb10Nd20, respectively. Optical absorption spectra were recorded using a JASCO V770 spectrometer with a resolution of 0.1nm from a range of 300÷1100nm. The NIR fluorescence spectra were recorded by using FLS-980 fluorescence spectrophotometer) under the excitation of 514nm with a Xenon lamp.

Absorption and fluorescence spectra

The absorption spectra of the Yb10 single and Yb10Nd05 co-doped glasses in a range of 300÷1100nm are shown in Fig. 1. The optical absorption spectra of Yb10 have shown only one band at 977nm ($^2F_{7/2} \rightarrow {}^2F_{5/2}$). In the co-doped sample, the spectrum consists of Nd^{3+} bands which are assigned to transitions from $^4I_{9/2}$ to the excited states of $^2I_{11/2}$, $^4D_{5/2}$, $^2P_{1/2}$, $^4G_{11/2}$, $(^2D, {}^2P)_{3/2}$, $^4G_{9/2}$, $^4G_{7/2}+{}^2K_{13/2}$, $^4G_{5/2}+{}^2G_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}+{}^4S_{3/2}$, $^4F_{5/2}+{}^2H_{9/2}$ and $^4F_{3/2}$ of Nd^{3+} and ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) of Yb^{3+}. This band positions of Yb^{3+} and Nd^{3+} ions transitions are similar to the other co-doped glasses [5, 6].

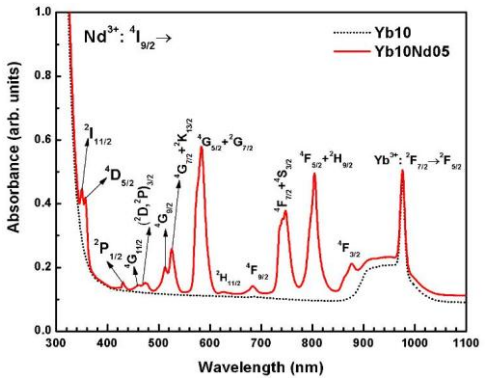

Fig. 1. Optical absorption spectra of Yb10 and Yb10Nd05 co-doped oxyfluoride glasses.

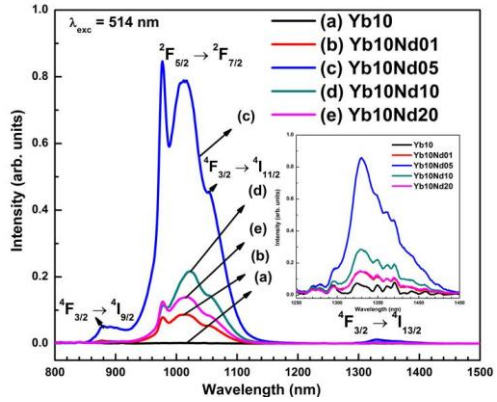

Fig. 2. Emisssion spectra of Yb10 and Yb10Nd*x* (*x*=0.1, 0.5, 1.0 and 2.0 mol%) co-doped oxyfluoride glasses using the excitation wavelength of 514nm.

The luminescence spectra of oxyfluorosilicate glasses doped withYb^{3+} ions and co-doped with Yb^{3+}/Nd^{3+} are shown in Fig. 2 under the excitation of 514nm. The Yb10 glasses did not show any emission bands from 800 to 1500nm. However, when introducing different concentrations of Nd^{3+} ions with 1.0 mol% of Yb^{3+} ions, the NIR emission bands were observed at 880, 1020, 1056 and 1330nm, which is attributed to the transitions of Nd^{3+} ions $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (880nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1056nm), $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1330nm), and also the strongest band $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (1020nm) is corresponding to the Yb^{3+} ions. The emission band intensity was increased with increasing Nd^{3+} ions concentration from 0.1 to 0.5mol% and then emission intensity decreased to 2.0mol% of Nd^{3+} ion. This may be due to the effect of concentration quenching of Nd^{3+} ions and energy transfer from Nd^{3+} to Yb^{3+} ions.

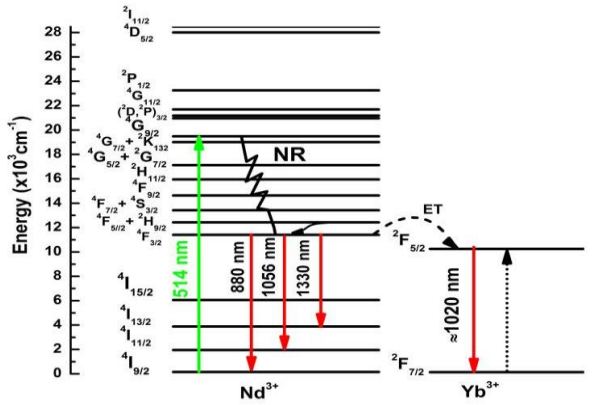

Fig. 3. Simplified energy level diagram of $Nd^{3+}$and Yb^{3+} ions in Yb^{3+}/Nd^{3+} co-doped silicate based oxyfluoride glasses (λ_{exc}=514nm).

Mechanism of energy transfer in Yb^{3+}/Nd^{3+} system

A simplified energy level diagram of Yb^{3+}/Nd^{3+} co-doped oxyfluoride glasses is shown in Fig. 3. This is helpful in understanding the energy transfer mechanisms of Nd^{3+} ions sensitization of Yb^{3+} ions under the 514nm excitation. When the the co-doped samples are excited under 514nm, Nd^{3+} ions are excited to $^4G_{9/2}$ and then depopulated to $^4F_{3/2}$ of Nd^{3+} ions. The well populated state ($^4F_{3/2}$) partially depopulated to the $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ of Nd^{3+} ions and gives radiative emissions: 880,1056, 1330 nm, respectively. And the Yb^{3+}($^2F_{5/2}$) state was activated through energy transfer from Nd^{3+} ions and then radiated to the ground state of Yb^{3+} ions as Yb^{3+}: $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (1020nm) emission transition. The strong NIR emission (Yb: 1020nm) intensity of co-doped samples was increased with increasing concentration from 0.1 to 0.5mol% and then decreased to 2.0mol% of Nd^{3+} ions. The results indicate that the ET from Nd^{3+} to Yb^{3+} is high for 0.5 mol% of Nd^{3+} ions in co-doped glasses.

McCumber Theory

The laser performance in Yb^{3+}-glasses can be accessed from the effective absorption and emission cross-sections of Yb^{3+} ions transitions. The absorption cross-section (σ_{abs}) for the Yb^{3+}: $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition can be calculated by using Beer Lambert's Law [9]:

$$\sigma_{abs}(\lambda) = \frac{2.303 \cdot OD}{Cl}, \qquad (1)$$

where OD is the optical density, *C* is the concentration of Yb^{3+} ions and *l* is the thickness of Yb10 and Yb10Nd05 glasses.

The emission cross-section of Yb^{3+}: $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition can be calculated from the absorption cross-section, with the well-known McCumber theory [10]. The stimulated emission cross-sections (σ_{emi}) and absorption cross-sections (σ_{abs}) are related by:

$$\sigma_{emi}(\lambda) = \sigma_{abs}(\lambda)\frac{Z_l}{Z_u}\exp\left[\left(\frac{E_{zl} - hc\lambda^{-1}}{KT}\right)\right], \qquad (2)$$

where Z_l and Z_u are denoted as partition functions of the lower ($^2F_{7/2}$) and upper ($^2F_{5/2}$) levels of Yb^{3+} ions. The zero line energy (E_{zl}) is defined to be the energy separation between the lowest components of the upper and lower states accomplished with the highest absorption peak in Yb^{3+} ion. Please note that *h* is Plank's constant, *k* is the Boltzmann constant and λ is the wavelength of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ (~976nm) transition of Yb^{3+} ions. The absorption and emission cross-sections of Yb10 and Yb10Nd05 glasses for the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ (~976nm) transitions are presented in Fig. 4. Thickness, concentration of (Yb^{3+} ions), absorption and emission cross-section values are calculated and presented in Table 1. The σ_{abs} ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) increases from 0.786 to 0.796×10^{-20}cm^2, and the σ_{emi} ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) is also found to increase from $1.168\div1.213\times10^{-20}$cm^2 in the co-doped samples.

Table 1. Thickness, concentration, absorption and emission cross-sections of Yb10 and Yb10Nd05 co-doped oxyfluoride glasses.

Parameters	**Yb10**	**Yb10Nd05**
Thickness (cm)	0.268	0.279
Concentration of Yb^{3+} (ions/cc)	4.154	4.088
σ_{abs} at 976 nm (x 10^{-20} cm^2)	0.786	0.796
σ_{emi} at 976 nm (x 10^{-20} cm^2)	1.168	1.213
σ_{abs} at 1020 nm (x 10^{-20} cm^2)	0.041	0.048
σ_{emi} at 1020 nm (x 10^{-20} cm^2)	0.512	0.619

The σ_{emi} of the present oxyfluoride glasses (Yb10Nd05) is higher than the value of $0.80\times10^{-20}cm^2$ (Yb-YAG) [11] and lower than the value of $1.35\times10^{-20}cm^2$ (lead phosphate glass) [12]. The σ_{emi} (1020nm) increased in co-doped samples due to the enhancing pumping energy from Nd^{3+} ions (875nm). The results concluded that the Nd^{3+} was also one of the efficient sensitizers for Yb^{3+} ions and the presented glasses were suitable for fiber drawing application.

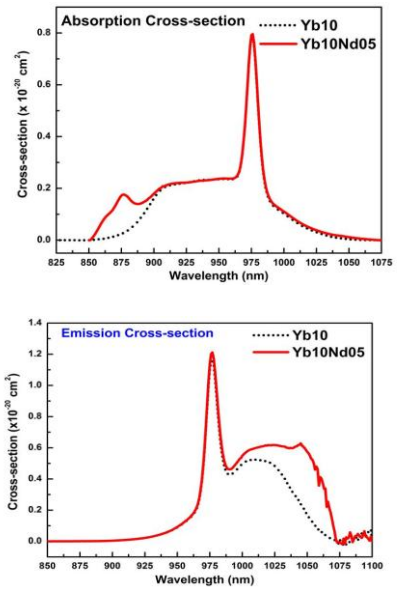

Fig. 5. The absorption and emission crosssections of Yb10 and Yb10Nd05 glasses.

In the present paper, the spectroscopic properties of Yb^{3+} doped and Yb^{3+}/Nd^{3+} co-doped oxyfluorosilicate glasses were investigated. The prepared glasses exhibit good thermal stability and may be suitable for fibre laser applications. The introduction of Nd^{3+} ions increases the pumping efficiency at 875nm and enhances the emission cross-section at 1020nm. The energy transfer from Nd^{3+} to Yb^{3+} ions is high for optimized Yb10Nd05glass. The emission cross-section (σ_{emi}) has been found to be $1.21\times10^{-20}cm^2$ for the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. The designed new oxyfluoride glasses are very promising materials for fibre laser applications.

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