ENERGY TRANSFER BETWEEN CO-DOPED YB\(^{3+}\)/ER\(^{3+}\) IONS IN POTASSIUM NIOBATE SILICATE GLASSES

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ABSTRACT
This paper focuses on the energy transfer process in co-doped Yb\(^{3+}\)/Er\(^{3+}\) ions in potassium niobate silicate glass (KNbSi). Absorption spectra of KNbSiEr\(_{0.5}\)/Yb\(_{10}\) glass has been recorded in UV, Vis and IR regions. The visible and IR emission spectra of different concentrations of KNbSi glasses has been recorded under 380 and 980 nm excitation, respectively. The intensity of IR emission spectra of Er\(^{3+}\) ions increased with the addition of Yb\(^{3+}\) ions due to efficient energy transfer from Yb\(^{3+}\) to Er\(^{3+}\) ions and exhibited broad emission band and larger emission cross sections at 1.54 µm corresponding to \(^4\)I\(_{13/2}\) → \(^4\)I\(_{15/2}\) transition. The lifetimes of \(^4\)I\(_{11/2}\) level increased when compare to Er\(^{3+}\) doped KNbSi glass. The increase of lifetime in the presence of Yb\(^{3+}\) ions confirmed that efficient energy transfer from Yb\(^{3+}\) to Er\(^{3+}\) ions.

Keywords: Er\(^{3+}\) ions; Yb\(^{3+}\) ions; Emission; Lifetime

INTRODUCTION
Rare-earth-doped glasses are very important materials for the development of optical fiber amplifiers and waveguide lasers [1, 2]. Singly doped Er\(^{3+}\) and co-doped Er\(^{3+}\)/Yb\(^{3+}\) glasses have received great attention due to their potential applications in compact optical amplifiers, telecommunication devices and sensors [3-10]. Co-doping of Yb\(^{3+}\) ions with Er\(^{3+}\) ions greatly enhances the luminescence intensity of Er\(^{3+}\) ions owing to the energy transfer from \(^2\)F\(_{5/2}\) (Yb\(^{3+}\)) to \(^4\)I\(_{11/2}\) (Er\(^{3+}\)) state, because both the Yb\(^{3+}\) and Er\(^{3+}\) ions posses absorption bands around 980 nm and the absorption cross-section of \(^2\)F\(_{5/2}\) state level is much larger than that of \(^4\)I\(_{11/2}\) level [11–13]. The selection of host material is a fundamental issue, since it plays a key role in the performance of practical devices. Among different host glasses, silicate glasses doped with Er\(^{3+}\) ions are more suitable for fiber amplifiers due to their good chemical durability, ion-exchangeability, high gain coefficient and wide bandwidth capability.

Spectral properties of rare earth ions activated materials, such as absorption photoluminescence, excited state lifetimes and radiative quantum efficiencies are very important and essential to improve the efficiency of optical devices. In this paper, spectroscopic properties of co-doped Er\(^{3+}\)/Yb\(^{3+}\) ions in silicate glasses are characterized by the absorption, emission and decay time measurements. The effect of co-doping Yb\(^{3+}\) ions on the visible and IR emissions of Er\(^{3+}\) ions has been studied.

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OBJECTIVES

- To prepare potassium niobate silicate (KNbSi) glasses doped with Er\(^{3+}\) and Er\(^{3+}/Yb\(^{3+}\) ions.
- To characterize and optimize the prepared glasses by the conventional spectroscopic techniques like absorption, emission and lifetime measurements.
- To identify the optimum concentrations of dopant ions for efficient emission and lifetime.

Experimental Details

Co-doped Er\(^{3+}/Yb\(^{3+}\) silicate glasses with a chemical composition of 30 K\(_2\)O - 25 Nb\(_2\)O\(_5\) - (43.5 - x) SiO\(_2\) - 0.5 Er\(_2\)O\(_3\) - xYb\(_2\)O\(_3\) (x = 0, 0.1, 0.5, and 1.0) were prepared by conventional melt quenching technique and are referred as KNbSiEr\(_{0.5}\), KNbSiEr\(_{0.5}/Yb\(_{0.1}\)), KNbSiEr\(_{0.5}/Yb\(_{0.5}\)) and KNbSiEr\(_{0.5}/Yb\(_{1.0}\)) glasses, respectively. The starting materials of K\(_2\)CO\(_3\), Nb\(_2\)O\(_5\), SiO\(_2\), Er\(_2\)O\(_3\) and Yb\(_2\)O\(_3\) (99.9%) with the batch quantities of \~15 g were mixed and grinded in agate mortar for homogeneity. The mixtures were taken in a platinum crucible and melted in an electric furnace at 1350°C for about 2-3 hr. Then the melts were poured onto a preheated brass plate and annealed at 450°C for 12 hr to remove the thermal stress and strain.

Optical absorption spectrum of KNbSiEr\(_{0.5}/Yb\(_{1.0}\)) glass was recorded using a Perkin Elmer Lambda-950 UV-Vis-NIR spectrophotometer in the wavelength range of 350-1600 nm. The visible emission was recorded by exciting the samples at 378 nm using Jobin Yvon Fluorolog-3 spectrofluorimeter with xenon arc lamp as an excitation source. The NIR emission spectra were measured using Dongwoo monochromator (Monora511i) with the InGaAs detector. The decay curves were measured by exciting the glass samples with the 980 nm radiation of diode laser by monitoring at 1.54 µm emission and the signal was acquired by a digital oscilloscope (LeCroy 200 MHz Oscilloscope).

RESULTS AND DISCUSSION

Absorption spectra

Figs. 1(a) & 1(b) shows the absorption spectra of co-doped KNbSiEr\(_{0.5}/Yb\(_{1.0}\)) glass in the UV-VIS and NIR regions, respectively. The absorption bands of Er\(^{3+}\) ions located at 357, 365, 378, 407, 451, 488, 544, 651, 977, and 1532 nm, correspond to the transition from the ground state \(^{4}I\(_{15/2}\)\) to the excited states \(^{4}G\(_{7/2}\), \(^{4}G\(_{9/2}\), \(^{4}G\(_{11/2}\), \(^{2}G\(_{11/2}\), \(^{2}F\(_{5/2}\), \(^{2}F\(_{7/2}\), \(^{2}H\(_{11/2}\), \(^{4}S\(_{3/2}\), \(^{4}F\(_{9/2}\), \(^{4}I\(_{11/2}\), \(^{4}I\(_{13/2}\), respectively. It is observed that the absorption band of Yb\(^{3+}\) ions near 980 nm corresponding to the \(^{2}F\(_{5/2}\) \rightarrow \(^{2}F\(_{7/2}\) transition is more predominant.
Hence, the addition of Yb$_2$O$_3$ to glass can enhance the pumping efficiency of Er$^{3+}$ ions through the energy transfer (ET) from Yb$^{3+}$ to Er$^{3+}$. The energy transfer process acts as indirect pumping of Er$^{3+}$ ions. The absorption band around 980 nm has a strong optical intensity owing to the large spectral overlap between Yb$^{3+}$ emission ($^2$F$_{7/2} \rightarrow ^2$F$_{5/2}$) and Er$^{3+}$ absorption ($^4$I$_{15/2} \rightarrow ^4$I$_{11/2}$). Furthermore, Yb$^{3+}$ has a larger absorption cross-section than that of Er$^{3+}$ at this absorption band. However, the typical erbium absorption bands exhibit little dependence on the glass composition.

Visible and NIR emission spectra

The visible emission spectra for different concentration of KNbSiEr/Yb co-doped glasses are shown in Fig. 2. The spectra exhibit two distinct emission bands at 527 and 550 nm corresponding to the $^2$H$_{11/2}$, $^4$S$_{3/2} \rightarrow ^4$I$_{15/2}$ transitions, respectively. From emission spectra, it is noticed that there is no much variation in the intensities of the emission bands with the increase of Yb$^{3+}$ ions concentration. This may be due to the fact that Yb$^{3+}$ ions are not excited with 380 nm excitation wavelength.

Fig. 1. Absorption spectra of KNbSiEr0.5/Yb10 glass a) UV- VIS (b) IR regions

Fig. 2. Visible emission spectra of different concentrations Yb$^{3+}$ ions in KNbSiEr /Yb glasess
The IR emission spectra for the \(^4\!_{I_{13/2}} \rightarrow ^4\!_{I_{15/2}}\) transition of \(\text{Er}^{3+}\) ions in the co-doped \(\text{KNbSiEr}^{3+}/\text{Yb}^{3+}\) glasses under excitation at 980 nm are shown in Fig. 3. The partial energy level diagrams of \(\text{Yb}^{3+}\) and \(\text{Er}^{3+}\) ions along with emission transitions under the 380 and 980 nm excitations are shown in Fig. 4. The NIR emission intensities of co-doped \(\text{KNbSiEr/Yb}\) glasses increases due to the enhanced population of \(\text{Er}^{3+}\) ions through the energy transfer (ET) from \(\text{Yb}^{3+}\) ions to \(\text{Er}^{3+}\) ions as observed in Fig. 4.

![Graph showing emission spectra and energy levels](image)

**Fig. 3.** NIR emission spectra for \(\text{KNbSiEr/Yb}\) glasses under 980 nm laser excitation.

**Fig. 4.** Partial energy level diagram of \(\text{Yb}^{3+}/\text{Er}^{3+}\) ions in \(\text{KNbSiEr/Yb}\) glasses

**Excited state lifetime**

The lifetime of \(^4\!_{I_{13/2}}\) excited level of \(\text{Er}^{3+}\) ion is the key parameter in emission spectral analysis. The longer lifetime of \(^4\!_{I_{13/2}}\) level supports the population inversion between the \(^4\!_{I_{13/2}}\) and \(^4\!_{I_{15/2}}\) levels. The decay profiles of \(^4\!_{I_{13/2}}\) level for both \(\text{KNbSiEr0.5}\) and \(\text{KNbSiEr0.5/Y10}\)
glasses are shown in Fig.5 (a) & (b) and are fitted to single exponential function 

\[ \tau_{exp} = \frac{\int t \cdot I(t) dt}{\int I(t) dt} \]

where \( I(t) \) is intensity as a function of time.

The experimental lifetimes (\( \tau_{exp} \)) determine for \( ^4I_{13/2} \) level are 1.72, 3.89, 3.01, and 2.79 ms for KNbSiEr0.5, KNbSiEr0.5/Yb0.1, KNbSiEr0.5/Yb0.5 and KNbSiEr0.5/Yb10 glasses, respectively. The lifetimes of \( ^4I_{13/2} \) level in co-doped KNbSiEr/Yb glasses increased when compared with singly doped KNbSiEr0.5 glass due to energy transfer from \( \text{Yb}^{3+} \) to \( \text{Er}^{3+} \) ions.

**Fig. 5.** Decay curves of \( ^4I_{13/2} \) level for (a) KNbSiEr glass (b) different concentrations of \( \text{Yb}^{3+} \) ions in KNbSiEr/Yb glasses

**CONCLUSIONS**

Photoluminescence properties of co-doped \( \text{Er}^{3+}/\text{Yb}^{3+} \) ions in potassium niobate silicate glasses were studied. Dominant green emission has been observed owing to the \( ^2H_{11/2}, ^4S_{3/2} \rightarrow ^4I_{15/2} \) transitions of \( \text{Er}^{3+} \) ions at 527 and 550 nm, respectively. The NIR emission intensity of \( \text{Er}^{3+} \) ions increased with \( \text{Yb}^{3+} \) concentration up to 1.0 mol\%. The decay time of \( ^4I_{13/2} \) level of \( \text{Er}^{3+} \) ions increased in the presence of \( \text{Yb}^{3+} \) ions compared with that of singly doped KNbSiEr0.5 glass due to energy transfer efficiency from \( \text{Yb}^{3+} \) to \( \text{Er}^{3+} \) ions.

**FUTURE STUDY**

The results are compared with those of reported similar ion-doped systems to find the similarities/ differences/ improvements for the future scope of work in the field of \( \text{RE}^{3+} \)-doped systems.
REFERENCES