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### Fluorescence characteristics and energy transfer of ytterbium-sensitized erbium-doped fluorophosphate glass for amplifier applications



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#### ABSTRACT

 $Yb^{3+}/Er^{3+}$  codoped fluorophosphate glass has been investigated for developing broadband waveguide amplifier application. Spectroscopic properties and energy transfer microparameters of prepared glasses have been discussed. The spectral components of 1.55  $\mu$ m emission are analyzed and an equivalent four-level system is proposed to estimate the stark splitting for the  ${}^4I_{15/2}$  and  ${}^4I_{13/2}$  levels in  $Er^{3+}$  doped fluorophosphate glass. The results indicate that highly doped  $Yb^{3+}$  ions could transfer energy to Er ions efficiently in fluorophosphate glass and  $Er^{3+}/Yb^{3+}$  doped fluorophosphate glass is preferable for broadband  $Er^{3+}$ -doped waveguide amplifier application.

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#### 1. Introduction

Recently, many scientific works have been devoted to the investigation of different glass matrices containing  ${\rm Er}^{3+}/{\rm Yb}^{3+}$  ions due to their amplification as waveguide amplifiers near 1.5  $\mu$ m [1–4]. The  ${\rm Er}^{3+}$ -doped fiber amplifiers (EDFA) in 1.5  $\mu$ m have led to a revolution in high-speed optical telecommunications, which enables the deployment of high-capacity fiber-optic links on a global scale [2,3]. Generally, in order to achieve sufficient gain, gain medium must possess very high concentration of active ions [5]. As to EDFA system,  ${\rm Er}^{3+}/{\rm Yb}^{3+}$  codoped glass is particularly interesting system for 1.5  $\mu$ m emission because  ${\rm Yb}^{3+}$  ions have been proved to be an excellent sensitizer for  ${\rm Er}^{3+}$  ions [3,6]. However, there are only a few reports concerning 1.55 um emission in  ${\rm Er}^{3+}/{\rm Yb}^{3+}$  codoped fluorophosphate glass [5].

The choice of the host glass is as important as the decision of rare-earth ions. The optical spectra and transition probabilities of several Er<sup>3+</sup> doped silica and metaphosphate glasses have been investigated for potential application purposes. However, the gain bandwidth of silica-based EDFAs is limited to 30 nm [7], and silica glasses are not able to dissolve rare-earth ions with high concentration [5]. Phosphate glasses are particularly vulnerable to OH- contamination because they tend to absorb water easily during melting [8,9]. It is known that hydroxyl groups can increase the non-radiative decay rate and thereby reduce the stored energy in the Er<sup>3+</sup>:<sup>4</sup>I<sub>13/2</sub> state, which results in a corresponding degradation in the laser output energy. To solve the problem, sophisticated processing methods are used to dehydroxylate both the phosphate glass melting process and the raw materials [10,11]. In spite of these efforts, some residual hydroxyl groups remain in the phosphate glass typically at concentrations of about 100 ppm [12].

Fluorophosphate (FP) glasses are promising materials since they possess suitable combinations of properties, such as large-scale manufacture compatibility by conventional

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melting techniques, low nonlinear refractive index, low OH contents, high solubility for rare-earth ions, wide transmission range, broad absorption and emission bands, long fluorescence lifetime as well as adjustable optical and spectroscopic properties by the phosphate content [13–15]. Besides, in our previous work,  ${\rm Er}^{3+}$  doped FP glasses have shown potential laser applications in 2  $\mu$ m region and high solubility for rare-earth ions [16,17].

In this work, the fluorescence properties of  $1.55~\mu m$  emission as well as up-conversion emissions in highly Yb<sup>3+</sup>/Er<sup>3+</sup> doped fluorophosphate glasses are investigated under 980 nm excitation. The infrared transmission ability, absorption and emission spectra of prepared glass are measured. The spectral components emitting from the lowest and upper Stark levels of  $1.55~\mu m$  emission are distinguished by analyzing the spectra using a peak fitted procedure. Besides, absorption, emission and gain cross section of selective transitions is obtained based on the McCumber theory and absorption spectra measurement. Using the Förster–Dexter theory, the energy transfer microscopic parameters have been calculated and analyzed.

#### 2. Experimental

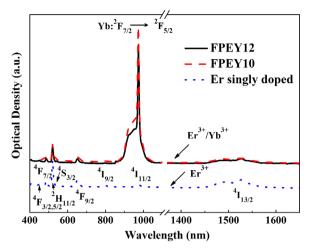
The investigated FP glasses with molar compositions:  $20Al(PO_3)_3 - 60RF_2 - 20NaF - 3ErF_3$ ,  $20Al(PO_3)_3 - 60RF_2 - 20NaF - 60RF_3 - 60RF_2 - 20NaF_3 - 60RF_3 - 60RF_3$ 1YbF<sub>3</sub>, 20Al(PO<sub>3</sub>)<sub>3</sub>-60RF<sub>2</sub>-20NaF-12YbF<sub>3</sub>, and 20Al(PO<sub>3</sub>)<sub>3</sub>- $60RF_2-20NaF-2NdF_3-3ErF_3-xYbF_3$  (x=10,12; R=Mg, Ca, Sr, Ba) which are hereafter denoted as FPE, FPY, FPY12, FPEY10 and FPEY12, have been prepared. All starting materials are of analytical grade. Batches of 25 g raw material were weighed and mixed in a special glove-box in order to minimize OH content. Then the mixture was melted in a platinum crucible in a furnace with two covers and a stream of dry air at 1000-1050 °C for 20 min. Then melts were cast on a preheated steel plate and annealed for several hours around the temperature of glass transition. All the annealed samples were fabricated and polished to the size of 20 mm ×  $10 \text{ mm} \times 1 \text{ mm}$  to meet the requirements of optical property measurements.

The absorption spectra were recorded using a JASCO V-570UV/VIS spectrophotometer at room temperature. The photoluminescence spectra were measured with a combined fluorescence lifetime and steady state spectrometer (FLSP 920) (Edingburg Co., England) and detected with a liquid-nitrogen-cooled PbS detector. The infrared transmittance spectrum was measured with a Perkin-Elmer 1600 series FTIR (PerkinElmer, USA) spectrometer in a wave number region between 2.5 and 5  $\mu m$ , with a resolution of 2 cm $^{-1}$ . All the measurements were performed at room temperature.

#### 3. Results

#### 3.1. Absorption and transmittance spectra

Fig. 1 shows the absorption spectra of prepared FP glasses in the wavelength region of 400–1650 nm. The corresponding absorption bands of Er and Yb are labeled in the figure. Apparently, except the absorption band around 980 nm, the position and shape of the absorption



**Fig. 1.** Absorption spectra of  $Er^{3+}$  singly and  $Er^{3+}/Yb^{3+}$  codoped samples.

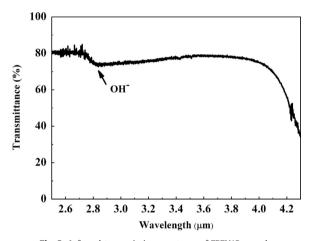


Fig. 2. Infrared transmission spectrum of FPEY12 sample.

bands in co-doped sample does not change obviously when compared with the  $\mathrm{Er}^{3+}$  singly doped one. The absorption band around 980 nm in codoped sample can be ascribed to the overlap of the  $\mathrm{Er}^{3+}$ : $^4\mathrm{I}_{15/2} \rightarrow ^4\mathrm{I}_{11/2}$  and  $\mathrm{Yb}^{3+}$ : $^2\mathrm{F}_{7/2} \rightarrow ^2\mathrm{F}_{5/2}$  absorption transitions. The spectra obtained for the codoped samples are similar, except for the absorption band centered around 980 nm varying depending on the  $\mathrm{Yb}^{3+}$  concentrations. It can be inferred that  $\mathrm{Er}^{3+}$  and  $\mathrm{Yb}^{3+}$  ions are homogeneously incorporated into the FP glassy network without cluster in the local ligand field. Due to large absorption band around 980 nm, the  $\mathrm{Er}^{3+}/\mathrm{Yb}^{3+}$  co-doped FP glass can be effectively excited by 980 nm LD.

Fig. 2 presents the infrared transmission spectrum of the  $Er^{3+}/Yb^{3+}$  doped sample. As is well known, the content of  $OH^-$  group has an important influence on fluorescence quantum efficiency, since residual  $OH^-$  group in glasses acts as the fluorescence-quenching center [18,19]. The  $OH^-$  content can be estimated from the infrared transmission spectrum using the following equation [18,20,21]:  $[OH^-](ppm, parts per million) = (1000/d) log(T_b/T)$ , where d is the sample thickness in millimeters,

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