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Short communication

Enhanced 2.7- and 2.9-μm emissions in Er^{3+}/Ho^{3+} doped fluoride glasses sensitized by Pr^{3+} ions

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ABSTRACT

In this report, $Er^{3+}/Ho^{3+}/Pr^{3+}$ tri-doped fluoride glass was prepared. The enhancement of 2.7 and 2.9 μm emissions from Er^{3+}/Ho^{3+}doped system were achieved successfully after the addition of Pr^{3+}. The combination of low OH^- concentration, low maximum phonon energy and high mid-infrared transmittance is beneficial to the realization of mid-infrared emissions. The energy transfer mechanism among Er^{3+}, Ho^{3+} and Pr^{3+} was investigated. The decay profiles of several levels were measured to further examine the enhanced mid-infrared emissions. Moreover, high stimulated emission cross sections at 2.7- and 2.9 μm ($1.08 \times 10^{-20}\,cm^2$ and $2.0 \times 10^{-20}\,cm^2$, respectively) were determined. $Er^{3+}/Ho^{3+}/Pr^{3+}$ tri-doped fluoride glass might provide a new choice for mid-infrared laser.

1. Introduction

In last decades, the development of efficient diode pumped mid infrared glass laser sources in 2–3 μm is of great importance for military system, medical applications, hazardous chemical detection, and pollution monitoring [1–3]. Among the rare-earth (RE) ions, trivalent erbium (Er^{3+}) and holmium (Ho^{3+}) have potential to yield emission at the 2–3 μm wavelength region due to the $^4I_{11/2} \rightarrow {}^4I_{13/2}$,$^5I_7 \rightarrow {}^5I_8$ and $^5I_6 \rightarrow {}^5I_7$ transitions. However, the efficiencies of these laser transitions in the range for the rare earth ions of Ho^{3+} and Er^{3+} are severely reduced by the self-saturation of the population-inversion [4]. The artificial depletion to avoid self-saturation can be achieved by suitable co-doping of the laser rare earth ion (donor) with other rare earth ions (acceptors), which makes use of the energy transfer between levels of the respective ions having equal energies.

From work in crystals, it is known that suitable codopants would be Pr^{3+} and Eu^{3+} for Ho^{3+} whereas Pr^{3+} for Er^{3+}. It has already been demonstrated suitable combination of Er^{3+} and Pr^{3+} ions in crystal and glasses for 3 μm laser [5]. It is known that special pump sources are needed for Ho^{3+} singly doped lasers other than the low cost and readily commercially available 800 or 980 nm laser diodes (LDs) since there is no energy level in Ho^{3+} matching with them [6]. It happens that Er^{3+} ions in the Er^{3+}/Ho^{3+} co-doped system can effectively absorb pumping energy and then transfer to Ho^{3+}: $^5I_6$ level due to absorption bands of Er^{3+} matching the commercially available 800 nm and 980 nm LDs. Moreover, Ho^{3+} ions are expected to deplete the Er^{3+}: $^4I_{13/2}$ level to obtain enhanced 2.7 μm emissions, which can be attributed to the energy transfer from the Er^{3+}: $^4I_{13/2}$ to Ho^{3+}: $^5I_7$ levels. Furthermore, Pr^{3+} can be utilized to further depopulate both Er^{3+}: $^4I_{13/2}$ and Ho^{3+}: $^5I_7$ level due to small energy mismatch between Pr^{3+}: $^3F_{3,2}$ and Er^{3+}: $^4I_{13/2}$ or Ho^{3+}: $^5I_7$ level [7,8]. In this case, the population inversion between Er^{3+}: $^4I_{11/2}$ and $^4I_{13/2}$ can be achieved as well as between Ho^{3+}: $^5I_6$ and $^5I_7$ levels. Thus, the 2.7 μm emission from Er^{3+}: $^4I_{11/2}$ to $^4I_{13/2}$ level and 2.9 μm luminescence from Ho^{3+}: $^5I_6$ to $^5I_7$ level can both be achieved. However, the enhanced 2.7 μm and 2.9 μm emissions from Er/Ho/Pr co-doped system are rarely reported to the best of our knowledge.

The choice of the host glass is as important as the decision of rare-earth ions. There is a growing interest in two families of special glasses for 2–3 μm lasers, namely chalcogenide and fluoride glasses due to their promising properties compared to heavy metal oxide glasses [9] or SiO_2. Chalcogenide glasses possess many unique optical properties, such as wide IR transparency, high refractive index, and low phonon energy, which make them as excellent host materials for amplifiers and infrared lasers [10,11].

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However, chalcogenide glasses have the disadvantages of poor solubility of rare earths and inferior thermal stability [11].

Fluoride glasses are promising materials since they possess suitable combinations of properties, such as large-scale manufacture compatibility by conventional melting techniques, low OH contents, large solubility for rare-earth ions, wide transmission range and long fluorescence lifetime [12,13]. Besides, in our previous work, Er^{3+} doped fluoride glasses have been shown potential laser applications in 2.7 μm region [14].

In this work, the fluorescence properties of mid infrared emissions and energy transfer mechanism in $Er^{3+}/Ho^{3+}/Pr^{3+}$ doped fluoride glass are investigated under 800 nm excitations. Enhanced 2.7 and 2.9 μm emissions are determined successfully in $Er^{3+}/Ho^{3+}/Pr^{3+}$ doped fluoride glass.

2. Experimental

The investigated fluoride glasses with following molar compositions: $50ZrF_4$-$33BaF_2$-$17(LaF_3+AlF_3+YF_3)$-$1ErF_3$, $50ZrF_4$-$33BaF_2$-$17(LaF_3+AlF_3+YF_3)$-$1HoF_3$, $50ZrF_4$-$33BaF_2$-$17(LaF_3+AlF_3+YF_3)$-$1PrF_3$, $50ZrF_4$-$33BaF_2$-$17(LaF_3+AlF_3+YF_3)$-$1ErF_3$-$1HoF_3$, $50ZrF_4$-$33BaF_2$-$17(LaF_3+AlF_3+YF_3)$-$1PrF_3$-$1ErF_3$-$1HoF_3$ which are hereafter denoted as ZE, ZH, ZP, ZHE and ZHEP, have been prepared by using a conventional melt-quenching technique in air atmosphere. All raw materials are of analytical grade. Batches of well-mixed 25 g raw material were placed into platinum crucible and melt at 900 °C for 30 min. Then melts were cast on a preheated steel plate and annealed for several hours around the glass transition temperature. All annealed samples were fabricated and polished to the size of 20 mm × 10 mm × 1 mm for property measurements.

The absorption spectra (400–2200 nm) were recorded using a UV/vis/NIR spectrophotometer at room temperature. The photoluminescence spectra in the range of 1100–3100 nm were measured by a combined fluorescence lifetime and steady state spectrometer (FLSP 920) (Edingburg Co., England) with a liquid-nitrogen-cooled PbS detector. The infrared transmittance spectrum was measured with a PerkinElmer 1600 series FTIR (PerkinElmer, USA) spectrometer in a wave number region between 2.5 and 9 μm, with a resolution of $2\,cm^{-1}$. The Raman spectrum of undoped glass sample was measured by a HORIBA Jobin Yvon HR800 Raman spectrometer with a 488 nm laser excitation source. All the measurements were performed at room temperature.

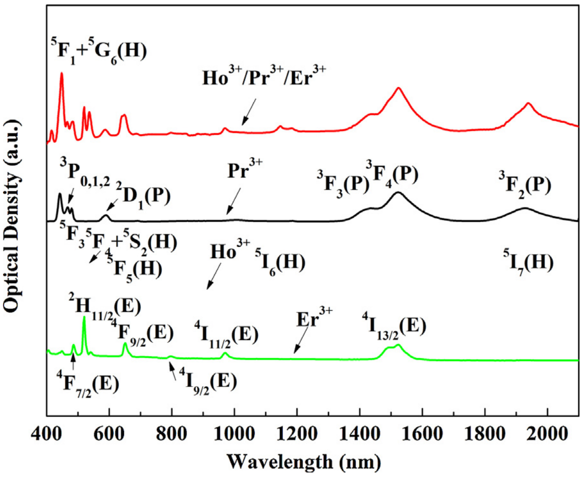

Fig. 1. Absorption spectra of $Er^{3+}/Ho^{3+}/Pr^{3+}$ doped fluoride glasses.

3. Results and discussion

Fig. 1 shows the absorption spectra of prepared fluoride glasses in the wavelength region of 400–2200 nm. The assigned transitions from the ground state of Er^{3+}, Ho^{3+} and Pr^{3+} ions to corresponding excited states are indicated in the figure. The observed absorption peaks are centered nearly to the wavelengths in other reported Er^{3+}, Ho^{3+} and Pr^{3+} singly-doped glasses, which suggests that rare earth ions should be homogeneously incorporated into the prepared fluoride glass network without cluster in the local ligand field. As is shown in the absorption spectrum of Ho^{3+} or Pr^{3+} singly-doped sample, no strong absorption bands correspond to the wavelength, i.e., 800 nm of readily available commercial laser diodes. However, it can be found that the available pumping wavelength of 800 nm is applicable to $Ho^{3+}/Er^{3+}/Pr^{3+}$ triply doped sample due to the addition of Er^{3+} ions. Thus, Er^{3+} ions can act as efficient sensitizers in prepared systems.

Fig. 2(a) shows the Raman spectrum of the undoped ZBLAY host. The maximum phonon energy is obtained to be $574\,cm^{-1}$, which can be assigned to the stretching vibrations of ZrF_7 and ZrF_8 polyhedra units [15]. This value is comparable to those of many other ZrF_4-based glasses [15].

Fig. 2(b) displays the infrared transmittance spectrum of prepared sample. The transmittance reaches as high as 86% at ~3 μm band under an uncontrolled atmosphere, which is beneficial for ~3 μm emissions. The absorption cut-off edge is up to 9 μm, apparently higher than those of silicate (5.1 μm) and fluorophosphate glasses (4.5 μm) [16]. In addition, the slight reduction of transmittance near 3 μm is attributed to the vibration absorption of OH^- groups [17]. The concentration of OH^- in glasses has a detrimental effect on the mid-infrared emission intensity or efficiency, since residual hydroxyl groups act as the fluorescence-quenching center [18]. As a result, the mid-infrared fluorescence can hardly be detected.

The hydroxyl content (in ppm, parts per million) can be estimated from the mid-infrared transmittance spectra, as shown in Fig. 2(b), using the following equation [19]

$$[OH^-](ppm) = \left(\frac{100}{d}\right)\log\left(\frac{T_b}{T}\right) \tag{1}$$

where d is the sample thickness in millimeters, T_b is the transmittance at the base line. T is the transmittance at the maximum of the OH^- band. The OH^- concentration of prepared glass is as low as 3.45 ppm, which is evidently lower than that of germanate glass [20]. This indicates that the prepared fluoride glass has the potential for mid-infrared laser.

Besides the effect of OH^- groups, multiphonon decay rate is another important factor to influence mid-infrared fluorescence. It is required that multiphonon decay rate is as low as possible so as to achieve better mid-infrared emissions. Multiphonon decay rate (WMP) can be estimated by [21]

$$W_{MP} = W_0[1 - \exp\left(\frac{-h\nu}{kT}\right)]^{-(\Delta E/h\nu)} \tag{2}$$

where W_0 is the rate at 0 K, ΔE is the energy gap between the levels involved and ν is the relevant phonon's frequency. The energy gap for both Ho^{3+}: $^5I_6 \rightarrow {}^5I_7$ and Er^{3+}: $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transitions is above 6 times of the high-energy phonons ($574\,cm^{-1}$). It is reported that when ΔE is equal to or less than 4–5 times of the high-energy phonons, the multiphonon decay becomes competitive with the radiative processes [21]. It is suggested that 2.7 and 2.9 μm emissions in the prepared glass can be obtained.

Fig. 3 shows the fluorescence spectra in Er^{3+}/Ho^{3+} co-doped and $Er^{3+}/Ho^{3+}/Pr^{3+}$ tri-doped fluoride glasses in the wavelength range of 1100–3100 nm excited at 800 nm. From Fig. 3(a), it can be seen