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Broadband 2 μm fluorescence and energy transfer evaluation in Ho^{3+}/Er^{3+} codoped germanosilicate glass

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ABSTRACT

This work reports the broadband 2 μm emission from Ho^{3+}/Er^{3+} codoped germanosilicate glasses. Spectral components of the 2 μm emission band were analyzed and an equivalent model of four-level system was proposed to describe the 2 μm emission band. The results suggested that Ho^{3+}/Er^{3+} codoped germanosilicate glass has high effective emission bandwidth (172 nm), large emission cross section (5.18×10^{-21} cm^2) and gain bandwidth (891×10^{-28} cm^3), which is a promising candidate for 2 μm laser and amplifier. In addition, energy transfer mechanism between Ho^{3+} and Er^{3+} ions was investigated based on the measured fluorescence spectra and decay curves of Er^{3+}:$^4I_{11/2}$ and $^4I_{13/2}$ levels. Energy transfer efficiency and microscopic parameters were calculated to evaluate the 2 μm fluorescence. Moreover, a rate equation model between Ho^{3+} and Er^{3+} ions was developed to elucidate 2 μm fluorescence behaviors. This work might provide useful guide to investigate fluorescence behavior and energy transfer mechanism of rare earth ions.

1. Introduction

In recent years, considerable efforts have been devoted to obtain efficient and powerful mid-infrared lasers and amplifiers operating in the eye-safe 2 μm wavelength region. This is due to their potential applications, including coherent laser radar systems, laser imaging, biomedical systems, remote chemical sensing and pump sources for mid-infrared lasers as well as optical communication systems [1–3].

So far, 2 μm laser is mainly achieved from Tm^{3+} or Ho^{3+} ions. In 2009, single- frequency ~2 μm laser was demonstrated in Tm-doped silicate glass fiber with laser linewidth less than 3 kHz using a single-mode Er-doped fiber laser at 1575 nm as a core-pump source [4]. In 2013, a direct diode-pumped monolithic thulium doped fiber laser was reported [5]. It offered more than 250 nm continuous total tuning range and a 3 dB power flatness of 200 nm [5]. In addition, a multiple-watt Tm^{3+}/Ho^{3+} codoped aluminosilicate glass fiber laser operating in narrowband (<0.5 nm) and tuned across a range exceeding 280 nm was presented in 2010 [3]. Its maximum slope efficiency and average output power were 25% and 6.8 W at 2.04 μm. In 2012, a single-frequency gain-switched Ho-doped silicate fiber laser was also achieved with output wavelength at 2.05 μm [6].

Compared with Tm^{3+}, the emission cross section of Ho^{3+} ion is much larger, which makes Ho^{3+} ions more suitable for high efficient laser operation [7]. Unfortunately,

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Ho^{3+} can not be pumped directly by readily available commercial high-power 808 nm or 980 nm laser diodes owing to the lack of an appropriate absorption band [1]. Hence, Yb^{3+}, Tm^{3+}, Nd^{3+} and Er^{3+} with a strong absorption band near 808 nm or 980 nm wavelengths have been utilized as the sensitizer to solve this problem [1,8–10]. So far, Ho^{3+}/Yb^{3+} codoped [8,11,12], Ho^{3+}/Tm^{3+} codoped [13–15], and Ho^{3+}/Nd^{3+} codoped [1,16] glasses have been investigated by researchers. However, to our knowledge, Er^{3+} sensitized Ho^{3+} doped glasses are less reported for 2 μm radiations but some investigations on upconversion and energy transfer process [10,17].

On the other hand, suitable glass host is as important as the luminescent ion. Recent decades have witnessed the great development on various glasses such as fluorophosphates [12,18], tellurite [19,20], germanate [7,21] and bismuthate glass [22]. In 2009, Wang et al. reported 2 μm fluorescence properties in Ho^{3+} doped fluorophosphate glasses sensitized with Er^{3+} and Tm^{3+} under 800 nm pumping [23]. Energy transfer mechanism of Ho^{3+}-Er^{3+}-Tm^{3+} ions was discussed in detail [23]. Simultaneously, Gao et al. investigated the 2 μm emission in Tm^{3+} and Ho^{3+} codoped TeO_2–ZnO–Bi_2O_3 glasses [24,25]. High radiative transition probabilities and large emission cross sections were obtained [24]. Besides, in 2010, Xu et al. reported Yb^{3+}/Ho^{3+} codoped germanate glass with high 2 μm emission cross section of Ho^{3+} and efficient energy transfer of $Yb^{3+} \rightarrow Ho^{3+}$ [7].

Germanosilicate glass, which combines the advantages of higher index of refractionof germanate glass and low cost together with higher thermal stability of silicate glass, is a promising candidate for 2 μm laser material [26]. In our previous work, germanosilicate glass has been investigated for 1.53 μm optical amplifier and results indicate that broadband 1.53 μm emission can be achieved from Er^{3+} doped germanosilicate glass [26,27]. Therefore, it is expected that broadband 2 μm radiation can also be obtained from Ho^{3+} activated germanosilicate glass for laser and amplifier.

In this work, Ho^{3+}/Er^{3+} codoped germanosilicate glasses were prepared for 2 μm emissions. Spectroscopic properties of Ho^{3+} and energy transfer mechanism between Er^{3+} and Ho^{3+} ions were discussed in detail. Energy transfer efficiency and microscopic parameters were calculated based on absorption spectra and lifetime measurements. Moreover, a rate equation model was developed to elucidate 2 μm emission behaviors.

2. Experimental

Host glasses possessing the compositions of $30SiO_2$–$30GeO_2$–8CaO–$12Li_2O$–$5Nb_2O_5$–15BaO (in mol%) were prepared by melting-quenching technique with an analytic reagent as raw materials. External co-doping of 1 mol% Er_2O_3 (99.99%) and x mol% Ho_2O_3 (99.99%) (x=0.25; 0.5; 0.75; 1) were carried out, which is named as SGEH-x. In addition, Ho^{3+} and Er^{3+} singly doped samples were also prepared for the comparisons and denoted as SGH and SGE, respectively. Raw materials (20 g) were mixed homogeneously and melted in a platinum crucible in a SiC-resistance electric furnace at 1450 °C for 45 min. Then the melts were quenched on preheated stainless steel plate and annealed at 10 °C below the glass transition temperature (580–590 °C) for 4 h before they were cooled to room temperature. Finally, the annealed samples were fabricated and optically polished to the size of 10 mm × 10 mm × 1.5 mm for the optical property measurement.

The densities and refractive indexes of the prepared glasses were tested according to the Archimedes principle using distilled water as the immersion medium and the prism minimum deviation method, respectively. Absorption spectra were determined by means of a Perkin Elmer Lambda 900UV–vis–NIR spectrophotometer in the range of 300–2200 nm with the resolution of 1 nm. Fluorescence spectra (900–2800 nm) were measured with a computer-controlled Triax 320 type spectrometer upon excitation by 808 nm laser diode with the maximum power of 1 W. Fluorescence lifetimes of $^4I_{11/2}$ level (975 nm) and $^4I_{13/2}$ level (1.53 μm) were recorded with light pulses of the 808 nm LD and HP546800B 100-MHz oscilloscope. All the measurements were carried out at room temperature.

3. Results

3.1. Absorption spectra

Fig. 1 shows the absorption spectra of Er^{3+}, Ho^{3+} singly doped and Ho^{3+}/Er^{3+} codoped germanosilicate glasses in the spectral region of 300–2200 nm. The absorption spectra are characterized by absorption bands of Er^{3+} (from the ground level of $^4I_{15/2}$ to the excited levels of $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{7/2}$) and Ho^{3+} (from the ground state ($^5I_8$) to higher levels of $^5I_7$, $^5I_6$, $^5I_5$, $^5F_5$ and $^5F_4+^5S_2$, respectively). No shape change and peak position shift of Ho^{3+}/Er^{3+} absorption bands can be observed with increasing Ho^{3+} concentration as is shown in the inset of Fig. 1. For Ho^{3+} singly doped sample, no absorption bands match readily available 808 or 980 LDs. Ho^{3+}/Er^{3+} codoped samples show an absorption band of Er^{3+}: $^4I_{15/2} \rightarrow {}^4I_{9/2}$ around 808 nm, which matches commercialized 808 nm LD.

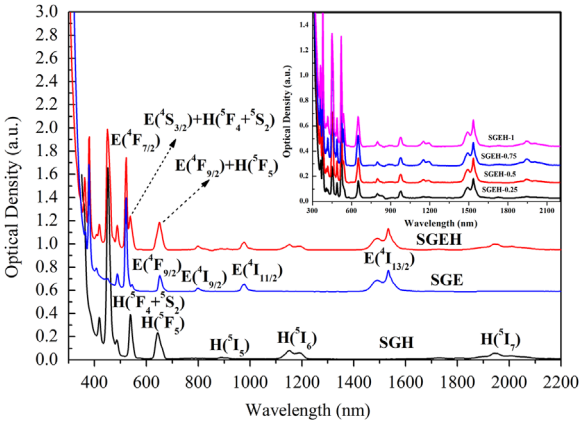

Fig. 1. Absorption spectra of Er^{3+}, Ho^{3+} singly doped and Er^{3+}/Ho^{3+} codoped germanosilicate glasses. Inset of the figure represents the peak shape and positions varied with Ho^{3+} concentrations of all prepared samples.