



Efficient 2.0 μm emission in $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped barium gallo-germanate glasses under different excitations for mid-infrared laser



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ABSTRACT

We report the visible up-conversion, near to middle infrared luminescence, and energy transfer mechanism of $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped barium gallo-germanate glasses under 980 and 1550 nm excitations, respectively. The 2.0 μm emission lifetime of the present glass is as high as 5.67 ms with the corresponding energy transfer efficiency of 70.0% from Er^{3+} : $^4\text{I}_{13/2}$ to Ho^{3+} : $^5\text{I}_7$ when pumped by 980 nm laser diode. In addition, the enhanced 2.0 μm emission is also obtained upon excitation of 1550 nm due to the efficient energy transfer from Er^{3+} to Ho^{3+} . Meanwhile, the calculated maximum gain is 2.13 cm^{-1} at 2024 nm. These results suggest that $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped barium gallo-germanate glasses is a potential material for 2.0 μm fiber laser.

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1. Introduction

Fiber laser operating at eye-safe 2.0 μm emission spectral region has been a hot research topic for its wide applications in laser imaging, biomedical systems, coherent laser radar system, and remote chemical sensing, etc [1–5]. Among the rare earth ions, Tm^{3+} : $^3\text{F}_4 \rightarrow ^3\text{H}_6$ and Ho^{3+} : $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transitions are usually utilized to generate 2.0 μm laser. Compared with Tm^{3+} , Ho^{3+} possesses higher gain cross-section, longer radiative lifetime, and longer-operating laser wavelength, which make it an efficient active ion to emit 2.0 μm laser [6,7]. However, the efficient laser emitting of Ho^{3+} was limited by the lack of an appropriate ground absorption band in commercial laser diode (LD). In order to solve this problem, other rare earth ions such as Er^{3+} , Yb^{3+} , Tm^{3+} , and Nd^{3+} with strong absorption bands in commercial LD at wavelength of 808 or 980 nm are desirable to be incorporated in the host glass and play the role of a sensitizer [8–11]. Er^{3+} and Yb^{3+} have been considered as the most suitable sensitive ions to improve the absorption band

of Ho^{3+} since Er^{3+} can absorb 808 and 980 nm while Yb^{3+} can efficiently absorb 980 nm through the transition of $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ [12]. Compared with Yb^{3+} , the Er^{3+} : $^4\text{I}_{13/2}$ level can match better with the Ho^{3+} : $^5\text{I}_7$ level, which is more beneficial for 2.0 μm emission [13]. In addition, Ho^{3+} is more effectively sensitized by Er^{3+} under 1550 nm excitation compared with 808 or 980 nm excitation, due to its strongly absorption at ~1550 nm, which corresponds to the transition of Er^{3+} : $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ [14,15]. Therefore, $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doping could be a good dopant method to realize 2.0 μm fluorescence.

As glass host material for middle infrared emissions, many kinds of glass host have been studied. To date, 2.0 μm fiber lasers have been realized in fluoride, silicate, tellurite, and germanate glass fibers [16–19]. Unfortunately, the fluoride glasses and tellurite glasses have poor chemical durability, lower damage threshold, low thermal shock resistance, which limit the stability and output power of fluoride and tellurite fiber lasers [20,21]. Silicate glasses are not the ideal host glass for mid-infrared lasers since the high phonon energy could lead to fast multiphoton relaxation which decreases the quantum efficiency and causes thermal damage of the fiber laser [22]. Germanate glasses, especially barium gallo-germanate (BGG), offer an ideal alternative to overcome the drawbacks of silicate, fluoride, and tellurite glasses [5]. They

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combine the attributes of high rare-earth solubility, comparatively low phonon energy, superior infrared transparency, high damage threshold and strong mechanical strength, which have been successfully applied in military and commercial high-energy lasers operating in middle infrared [23,24]. However, few reports have been focused on the $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped barium gallo-germanate glasses under 980 or 1550 nm excitation for 2.0 μm fluorescence.

In this work, we present a detailed investigation of the visible up-conversion, near to middle infrared luminescence, and energy transfer mechanism of $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped barium gallo-germanate glasses under 980 and 1550 nm excitations, respectively. The emission cross section and gain coefficients corresponding to the $\text{Ho}^{3+}: {}^5\text{I}_8 \rightarrow {}^5\text{I}_7$ transition in $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped sample are calculated. In addition, the energy transfer efficiency from Er^{3+} to Ho^{3+} is calculated when the sample was pumped at 980 nm. The results indicate that $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped barium gallo-germanate glasses could be potential fiber laser material for 2.0 μm laser.

2. Experimental

2.1. Samples preparation

Barium gallo-germanate (BGG) glasses with the molar composition of $20\text{BaF}_2\text{--}14\text{Ga}_2\text{O}_3\text{--}65\text{GeO}_2\text{--}1\text{La}_2\text{O}_3\text{--}1\text{Ho}_2\text{O}_3$, $20\text{BaF}_2\text{--}14\text{Ga}_2\text{O}_3\text{--}65\text{GeO}_2\text{--}1\text{La}_2\text{O}_3\text{--}1\text{Er}_2\text{O}_3\text{--}x\text{Ho}_2\text{O}_3$ ($x = 0, 0.25, 0.5, 1, 2$), which are denoted as BGGH, and BGGEH- x ($x = 0, 0.25, 0.5, 1, 2$), respectively, were prepared by the conventional melt-quenching method. High purity (99.99% minimum) raw materials (20 g) were well mixed and then placed in a covered alumina crucible and melted at 1380 $^\circ\text{C}$ for 60 min in air atmosphere. Then, the melts were quickly poured on preheated stainless steel plates and annealed at 560 $^\circ\text{C}$ for 2 h, after which they were cooled slowly inside a furnace to room temperature. The annealed samples were cut and polished to a size of 20 mm $\times$ 10 mm $\times$ 1.5 mm for optical property measurements.

2.2. Measurements and apparatus

Optical absorption spectra from 400 to 2200 nm were measured by a Perkin–Elmer Lambda 900/UV/VIS/NIR spectrophotometer. The fluorescence spectra were recorded with a computer-controlled Triax 320 type spectrofluorimeter (Jobin-Yvon Crop.) under excitations of 980 nm LD and 1550 nm fiber laser. Lifetimes were obtained from the first e-folding time of emission intensities in the decay curves recorded with a digital oscilloscope. All the measurements were done at room temperature.

3. Results and discussion

3.1. Optical absorption spectra

Fig. 1 shows the absorption spectra of the Er^{3+} singly doped, Ho^{3+} singly doped, and $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped glasses in the wavelength range from 400 to 2200 nm. The characteristic absorption bands corresponding to the transitions from ground state to excited states of Er^{3+} and Ho^{3+} are labeled in the figure. For Ho^{3+} singly doped sample, the absorption spectrum consists of five absorption bands centered at 536, 644, 889, 1155, and 1920 nm, corresponding to transitions from the ${}^5\text{I}_8$ ground state to excited states ${}^5\text{F}_4 + {}^5\text{S}_2$, ${}^5\text{F}_5$, ${}^5\text{I}_5$, ${}^5\text{I}_6$, and ${}^5\text{I}_7$, respectively. Meanwhile, the absorption bands of the Er^{3+} singly doped sample center around 488, 520, 652, 800, 980, and 1550 nm, corresponding to transitions from the ${}^4\text{I}_{15/2}$ ground state to excited states ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$, ${}^4\text{F}_{9/2}$, ${}^4\text{I}_{9/2}$, ${}^4\text{I}_{11/2}$, and ${}^4\text{I}_{13/2}$, respectively. Therefore, the $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped samples can be

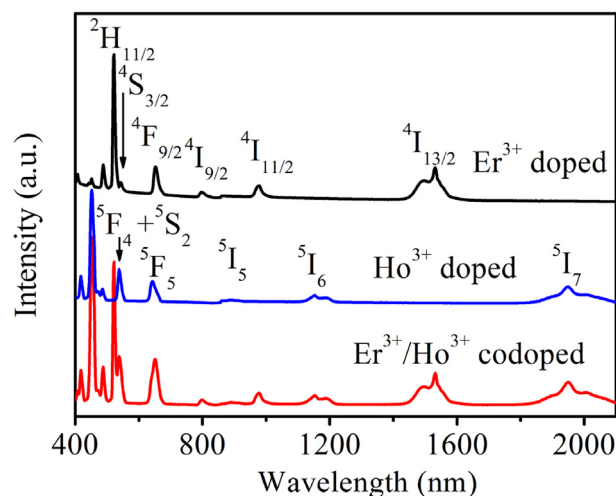


Fig. 1. Absorption spectra of BGGH, BGGEH-0, BGGEH-1 glasses.

pumped by 808, 980, and 1550 nm lasers and it is obvious that the 1550 nm absorption has the largest cross section. So the $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped samples can be pumped by 1550 nm laser efficiently. And the intense 2.0 μm fluorescence is also obtained in the $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped samples pumped at 980 nm.

3.2. Luminescent properties of $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped samples pumped at 980 nm

Fig. 2 displays the up-conversion luminescence spectra of BGGEH- x glasses pumped at 980 nm. For the Er^{3+} singly doped sample (BGGEH-0), three emission peaks at 523, 546, and 658 nm are observed, which correspond to ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transitions, respectively. It should be noted that the enhanced red light (658 nm) up-conversion emission is observed from $\text{Er}^{3+}/\text{Ho}^{3+}$ co-doped samples due to the $\text{Er}^{3+}: {}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ and $\text{Ho}^{3+}: {}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ transitions. In addition, the emission intensity of green light (523 and 546 nm) up-conversion decrease slightly with further Ho_2O_3 addition. It is well-known that the Ho^{3+} cannot be pumped by 980 nm due to its absence of an efficient absorption band. Therefore, an energy transfer process must exist between Er^{3+} and Ho^{3+} , which can be confirmed by the enhanced

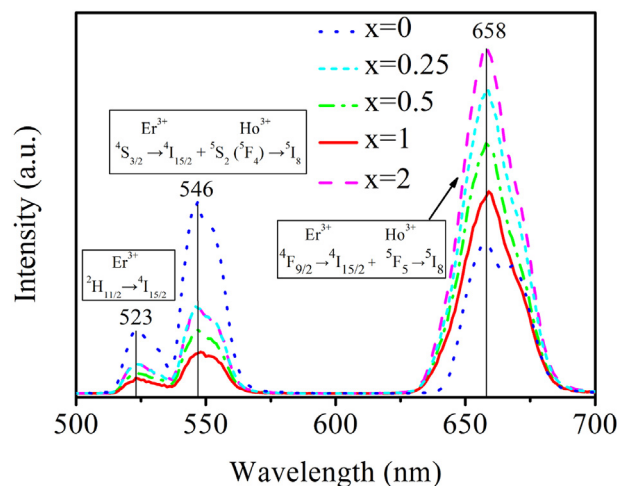


Fig. 2. Up-conversion luminescence spectra of BGGEH- x ($x = 0, 0.25, 0.5, 1, 2$) glasses pumped at 980 nm.

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