**Enhanced 3.9 μm emission from diode pumped Ho3+/Eu3+ co-doped fluoroindate glasses**

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The use of Eu3+ codoping for enhancing the Ho3+: 5I5→5I6 emission in fluoroindate glasses shows that Eu3+ could depopulate the lower laser state Ho3+: 5I6 while having little effect on the upper state Ho3+: 5I5, resulting in greater population inversion. The Ho3+/Eu3+ co-doped glass has high spontaneous transition probability (6.31 s−1) together with large emission cross section (7.68×10–21 cm2). This study indicates that codoping of Ho3+ with Eu3+ is a feasible alternative to quench the lower energy level of the 3.9 μm emission and the Ho3+/Eu3+ co-doped fluoroindate glass is a promising material for efficient 3.9 μm fiber lasers. © 2021 Optical Society of America

Mid-IR fiber lasers have drawn much attention owing to their potential applications in sensing, countermeasures, nonlinear optics and materials processing[[1-3](#_ENREF_1)]. However, it is still a challenge to extend the wavelength coverage of fiber lasers above 3 μm at high output powers[[4-9](#_ENREF_4)]. The Ho3+ transition 5I5 → 5I6, which has already been demonstrated in fluoride fibers[[10-13](#_ENREF_10)], is a well-known candidate for 3.9 μm lasers. In 1995, Schneider demonstrated 3.9 μm fiber laser with maximum output power of 1 mW from Ho3+doped ZBLAN fiber at room temperature[[14](#_ENREF_14)]. Two years later, Schneider *et al.* raised the output power to 11 mW, but this approach required liquid nitrogen cooling[[15](#_ENREF_15)]. The use of Ho3+: ZBLAN 3.9 μm for fiber lasers displayed relatively low efficiency because of the phonon-related properties of ZrF4-based glasses. The 3.9 μm emission in ZBLAN is quenched by the large multi-phonon decay, which increases exponentially with both temperature and emission wavelength[[16](#_ENREF_16)]. Therefore, different glass matrices have been investigated to provide suitable fiber for laser emission around 3.9 μm.

Compared to ZrF4-based glasses, fluoroindate glasses have lower phonon energy and broader transmission window[[17](#_ENREF_17)]. The recent availability of low-loss fluoroindate glass fibers allowed for generating broadband supercontinuum light sources and mid-IR fiber lasers[[18](#_ENREF_18)]. In 2018, Maes et al. demonstrated room-temperature 3.92 μm fiber laser operation with a record output power of 200 mW and efficiency of 10.2%, by employing Ho3+-doped fluoroindate fiber as the gain medium[[19](#_ENREF_19)]. However, the laser efficiency is still much lower than that achieved for operation at around 3 μm. One bottleneck is that the 5I5 → 5I6 transition of Ho3+ is self-terminating[[16](#_ENREF_16)]: the lifetime of the upper level (5I5) is much shorter than that of the lower one(5I6)[[11](#_ENREF_11)]. Compared to the heavy-doping method, codoping with deactivated ions is also a promising method to depopulate the lower level of the laser transition. In 2017, Zhang et al. investigated the sensitization and deactivation effects of Nd3+ on the Ho3+: 3.9 μm emission in a PbF2 crystal pumped by an 808 nm laser diode[[20](#_ENREF_20)], and results indicated that the employment of deactivated ions is a good option. Therefore, it is still needed to seek for other deactivated ions to improve the performance of 3.9 μm emission[[21-25](#_ENREF_21)]. The simplified energy level scheme illustrated in Fig. 1 shows that, under the excitation at 888 nm, Ho3+ is excited to the upper state 5I5 by ground state absorption (GSA), and subsequently decays radiatively to the ground state 5I6 with emission at 3.9 μm. After codoping with Eu3+, ET1 and ET2 processes occur and transfer energy from Ho3+ to Eu3+, which depopulates the 5I7 and 5I6 levels, respectively. The ET1 process is dominating due to the narrow energy level gap between 5I7 and 7F6. Meanwhile, CR1 process also depopulates 5I6. These processes contribute to the 3.9 μm emission enhancement.

In this letter, the spectroscopic properties of Ho3+-doped and Ho3+/Eu3+-codoped fluoroindate glasses are compared through transmission and emission spectra, metastable lifetimes, oscillator strengths and Judd-Ofelt parameters, and the suitability of this optical materials for 3.9 μm fiber-laser applications is assessed.

Glass samples with different molar compositions of 26InF3-15ZnF2-18BaF2-11.5GaF3-8SrF2-12PbF2-5LiF-1.7YF3-(1.75-x)LaF3-1.5HoF3-xEuF3 (x=0, 0.005, 0.01, 0.015, 0.02, 0.05, 0.1, named as 1.5Ho-xEu, respectively) were prepared from high-purity (99.99%) raw materials. The precursor materials were melted in a dry glove box at 850 °C for 2 h and then annealed at 240 °C for 5 h to remove residual stress and internal defects. After natural cooling to room temperature, the glass samples were cut into a size of 10 \* 10 \* 1.5 mm3 and polished for subsequent optical testing.

The experimental absorption and transmission spectra were measured using a Perkin-Elemer Lambda 750 UV-VIS-NIR spectrophotometer and a Perkin-Elmer FTIR spectrometer, respectively. An 888 nm diode laser with an output power of 2.5 W was used to excite the fluoroindate glass samples. The infrared fluorescence spectra were measured using an Edinburg FLS1000 spectrometer. Differential scanning calorimetry (DSC) was conducted using a NETZSCH DSC 204 F1 calorimeter in the temperature range 50−500°C with a heating rate of 10 K/min. The fluorescence decay lifetime of the glass samples were measured using a Surelite OPO pulsed laser, with central wavelength set at 888 nm, 5nm pulse durations and 10 Hz repetition rate. During the experiments, appropriate filters were used to block the undesired signals. All the tests were carried out at room temperature.



Fig. 1. Simplified energy level diagram of the Ho3+/Eu3+ co-doped system.

The absorption spectra of the Ho3+-, Eu3+-, and Ho3+/Eu3+-doped samples at room temperature in the wavelength region of 300–2200 nm are shown in Fig. 2. The absorption bands centered at 910, 1190, and 1900 nm of the Ho3+-doped sample correspond to transitions from the 5I8 ground state to the upper levels 5I5, 5I6, and 5I7, respectively. The presence of absorption of Ho3+: 5I5 in the wavelength region of 880–920 nm indicates that the possibility for the glass samples to be pumped by an 888 nm LD. The inset of Fig. 2 shows the infrared transmittance spectrum of the 1.5Ho sample. It is important to mention that the residual OH- groups in the glass participate in energy transfer processes and lower the luminescence efficiency of rare earth ions, which is owing to the overlap between the energy gap of Ho3+: 5I6 → 5I7 and the energy of the OH- stretching vibration[[26](#_ENREF_26)]. To minimize the residual OH- content in fluoroindate glasses, all the preparation process was conducted in a glove box filled with dry nitrogen. The H2O content in the glove box was monitored by a calibrated H2O sensor, which provided a value below 0.1 ppm. The αOH- and OH- content (in ppm, parts per million) of the fluoroindate glass with a sample thickness of 1 cm were calculated to be 0.0007 cm-1 and 0.3 ppm[[27](#_ENREF_27)], respectively, significantly small to greatly decrease the energy migration from Ho3+ to OH-. In future, we will try to further reduce the OH- content by optimizing the preparation processes of fluoride glasses. In addition, the DSC curve has been measured for characteristic temperatures, including glass transition temperature Tg and onset crystallization temperature Tx. Higher ∆T(Tx–Tg) usually indicates that the glass has better thermal stability and lower temperature sensibility. The evaluated ∆T of fluoroindate glass is 96 °C, confirming that it has good thermal properties and could be drawn into low-loss fibers[[28](#_ENREF_28)].

The Judd-Ofelt theory[[29](#_ENREF_29), [30](#_ENREF_30)] and measured absorption spectra were used to calculate the spectroscopic parameters Ωt (t=2, 4, 6) of Ho3+ ions and shown in Table 1 with other Ho3+-doped glasses for comparison. The RMS error deviation of intensity parameters for Ho3+ doped and co-doped glasses were 1.93×10-7 and 2.69×10-7, respectively, which confirms the reliability for predicting the spectral intensities. The value of Ω2, is normally related to the covalency and symmetry of the ligands around rare earth ions[[31](#_ENREF_31)]. It is clear to see that the Ω2 of Ho3+ in the Ho3+/Eu3+ co-doped fluoroindate glass is higher than that in the Ho3+ doped glass, indicating that the introduction of Eu3+ leads to a lower symmetry surrounding Ho3+. Moreover, the ratio Ω4/Ω6 of Ho3+/Eu3+ co-doped fluoroindate glass is bigger than that of Ho3+ doped glass, suggesting that the introduction of Eu3+ increased the spectroscopic quality of the host materials.



Fig. 2. Absorption spectra of samples. Insets: transmission spectra of 1.5 mol.% Ho3+-doped glass (right) and photograph of glass samples (left).

Table 1. The Calculated J-O parameters of Ho3+ in various glasses

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Glass | Ω2,4,6(10–20 cm2) | | | Ω4/Ω6 | Reference |
| Ω2 | Ω4 | Ω6 |
| 1.5Ho | 0.99 | 1.86 | 1.70 | 1.09 | Present work |
| 1.5Ho-0.02Eu | 1.07 | 2.71 | 1.97 | 1.38 |
| ISBZ | 1.00 | 2.80 | 1.90 | 1.47 | [[11](#_ENREF_11)] |
| ZBLAY | 1.70 | 1.82 | 1.52 | 1.19 | [[32](#_ENREF_32)] |

Table 2. Predicted Spontaneous Transition Probability(A), Branching Ratios (β) and Radiative Life Times (τrad) of fluoroindate glass samples for various selected excited states of Ho3+

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Transition | Wavelength(nm) | A (s-1) | β (%) | τrad (ms) |
| 5I5→ 5I6 | 3920 | 6.31 | 3.48 | 5.52 |
| → 5I7 | 1680 | 99.67 | 55.05 |  |
| → 5I8 | 889 | 75.07 | 41.46 |  |
| 5I6→ 5I7 | 2870 | 19.61 | 9.36 | 4.78 |
| → 5I8 | 1190 | 189.83 | 90.64 |  |
| 5I7→ 5I8 | 2020 | 75.96 | 100.00 | 13.16 |

The J-O intensity parameters allow for the evaluation of the spontaneous transition probability(A), branching ratios(β) and radiative lifetime(τrad) of the optical transitions for the Ho3+ doped fluoroindate glass, which are shown in Table 2. The A of the 5I5 → 5I6 transition can be calculated to be 6.31 s-1 for the Ho3+/Eu3+ co-doped glass, which is larger than that (4.31 s-1) of the Ho3+ doped fluoroindate glass, indicating that co-doping of Eu3+ has a positive influence on the Ho3+: 3.9 μm emission in this fluoroindate glasses.



Fig. 3. Emission spectra of the Ho3+-doped and Ho3+/Eu3+co-doped fluoroindate glasses in the range 3700-4200 nm. Insert: luminescence intensity at different Eu3+ doping concentrations.



Fig. 4. Luminescence spectra of the Ho3+-doped and Ho3+/Eu3+co-doped fluoroindate glasses at (a) λ ~ 2.9 μm; (b) λ ~ 2.0 μm; (c) λ ~ 1.7 μm; and (d) λ ~ 1.2 μm for 888 nm pumping.

Fig. 3. shows the emission spectra of Ho3+-doped and Ho3+/Eu3+ co-doped fluoroindate glasses. Under the excitation of an 888 nm LD, intense emissions centered at 3930 nm were observed from both the fluoroindate glasses, which are assigned to the 5I5 → 5I6 transition of Ho3+. The emission intensity of the glass co-doped with Eu3+ is significantly higher than that without. In particular, the maximum 3930 nm emission intensity of the Ho3+/Eu3+ co-doped glasses can be as high as 2.03 times that of the Ho3+-doped glass. These results confirm that Eu3+ ions can act as an efficient deactivation ion to enhance the 3.9 μm emission in fluoroindate glasses. In addition, when the concentration of Eu3+ is higher than 0.02 mol.%, concentration quenching may occur and consequently decrease the 3930 nm emission intensity, which may be attributed to feasible CR2 process (Ho3+: 5I5 + Eu3+: 7F1 → Ho3+: 5I6 + Tb3+: 7F4) shown in Fig. 1. Considering about the potential thermal effects caused by the involvement of multiphonon, we are trying to optimize the doped concentration in practical laser experiments.

To further understand the enhancement of the 3.9 μm emission, fluorescence spectra at other wavelengths were investigated. Fig. 4. shows the emission spectra of Ho3+-doped and Ho3+/Eu3+ co-doped fluoroindate glasses centered at 2.9 μm, 2.0 μm, 1.7 μm and 1.2 μm corresponding to the radiative transitions of 5I6 → 5I7, 5I7 → 5I8, 5I5 → 5I7 and 5I6→5I8, respectively. It is worth mentioning that the emission intensity at both 2.9 μm and 1.7 μm present the same luminescence enhancement and quenching trend as the 3.9 μm emission, while the fluorescence intensity at 2 μm and 1.2 μm decrease for increasing concentrations of Eu3+. A possible explanation for this is that the fluorescence decay of 5I7 is sharper than that of 5I6. When introducing Eu3+, the Ho: 5I6, 5I7 energy levels experience energy transfer to Eu3+: 7F6, depopulating the Ho3+: 5I6 and 5I7 levels and weakening the transitions 5I6 → 5I8 and 5I7 → 5I8.



Fig. 5. (a) Absorption σabs and emission σemi cross-sections of the optical transition Ho3+: 5I5 → 5I6; (b) gain coefficient of Ho3+: 5I5 → 5I6 transition.



Fig. 6. Decay lifetime of (a) 5I5 level; (b) 5I6 level; and (c) 5I7 level; (d) experimental lifetimes of 5I5, 5I6 levels for different Eu3+ concentrations; (e) experimental lifetimes of 5I7 level for different Eu3+ concentrations.

The emission cross-sections were subsequently calculated using the Fuchtbauer-Ladenburg equation[[33](#_ENREF_33)]. Since the transition Ho3+: 5I5 → 5I6 exists in two excited states, the absorption cross-sectional area *σ*abs can be calculated by *σ*emi using the McCumber theory [[34](#_ENREF_34)]. The absorption cross section (5I6 → 5I5) and emission cross section (5I5 → 5I6) of Ho3+ in fluoroindate glass at 3.9 μm are shown in Fig. 5(a). The peak emission cross-section of Ho3+/Eu3+ co-doped sample is 7.68×10–21 cm2, significantly larger than that of Ho3+ singly doped one (6.71×10–21 cm2 at 3.9 μm), indicating that codoping with Eu3+ has a positive influence on the 3.9 μm emission of Ho3+ in fluoroindate glasses. Based on the above absorption and emission cross-section spectra, the gain cross-section spectra *G*(*λ*) are calculated by the equation: *G*(*λ*)*=N*[*Pσemi*(*λ*)*-*(*1-P*)*σabs*(*λ*)][[35](#_ENREF_35)] and shown in Fig. 5(b), where population inversion *P* represents the ratio of the excited state 5I5 level to total Ho3+ population. The gain cross-section becomes positive when the population inversion level reached 50%.

The fluorescence decay curves of 5I5, 5I6 and 5I7 are shown in Fig. 6. In our work, the lifetime of Ho3+: 5I5 has not changed significantly with the introduction of Eu3+, although this may be due to the detection capabilities of our current facilities. On the other hand, Eu3+ codoping reduces the lifetime of Ho3+: 5I6 from 3.47 ms to 1.35 ms as illustrated in Fig. 6(d), which means that efficient energy transfer from Ho3+: 5I6 to Eu3+: 7F6 occurs. The diversity of lifetimes confirms that he introduced Eu3+ has the positive effects of suppressing the self-termination effect in Ho3+. Besides, the measured lifetime (τmea) is much lower than the radiative lifetime (τrad), and the energy transfer efficiency η can be calculated to be only 6.3% from the equation: η=1-τHo/Eu/τHo, where τHo and τHo/Eu are the lifetimes of 5I6 in the Ho3+-doped and Ho3+/Eu3+ co-doped fluoroindate glasses, respectively. The low quantum efficiency of Ho3+ is mainly caused by its intrinsic energy level structure, especially for glasses with high phonon energy. The results confirm that Eu3+ can be used as effective deactivation ions to depopulate Ho3+: 5I6 and enhance the 3.9 μm emission. In addition, Fig. 6(e) shows that the 5I7 lifetime decreases dramatically with increasing Eu3+ concentration owing to the occurrence of predicted ET1 process, which further demonstrates the 2.9 µm emission enhancement. Subsequently, the reinforcement of the 2.9 µm emission in turn accelerates the depopulation of Ho3+:5I6, forming a positive feedback on the 3.9 µm emission.

In conclusion, Ho3+/Eu3+ codoped fluoroindate glasses with low hydroxyl content have been prepared and their optical properties investigated. The 3.9 μm emission of Ho3+ is significantly enhanced through the energy transfer process between Ho3+ and Eu3+. The emission cross-section of Ho3+: 5I5 → 5I6 in Ho3+/Eu3+ codoped fluoroindate glass is improved to 7.68×10–21 cm2. Because of its desirable transmittance properties and fluorescence characteristics this Ho3+/Eu3+ codoped fluoroindate glass is a promising candidate for 3.9 μm fiber lasers.

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