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Full Length Article

Discrepancies between Pr^{3+} and Ho^{3+} de-sensitized Er^{3+}:2.7 μm emission

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ABSTRACT

This paper studied the de-sensitization effect of Pr^{3+} and Ho^{3+} to Er^{3+}:2.7 μm emission. Results show that both Pr^{3+} and Ho^{3+} are effective de-sensitizers, while great differences exist between them because of their non-phonon and phonon assisted energy transfer (ET) mechanisms. Ho^{3+} depresses the 2.65 μm emission while Pr^{3+} strengthens it greatly. ET coefficient indicates that Pr^{3+} performs ten times higher $^4I_{13/2}$ depletion ability than Ho^{3+}. In Er/Ho glasses, about 1/10 energy back transfers to $^4I_{13/2}$ level, which partially counterweights the depopulation of $^4I_{13/2}$ level. The high absorption cross section of Ho^{3+} is the reason for the larger $^4I_{11/2}\rightarrow{}^5I_6$ ET coefficient. Line strength and spontaneous radiation probability of $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition enhance moderately in E, E/H and E/P order, proving that the de-sensitizers promote the 2.7 μm transition positively. Long lifetime of Ho^{3+}:$^5I_6$/$^5I_7$ brings many problems, such as energy back transfer and strengthened upconversion, which also implies that the interactions of the particles obstruct the effective $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition correspondingly.

1. Introduction

Requirements for the 1.1 μm pumping source limit the application of Ho^{3+}:3 μm fiber laser [1,2]. Meanwhile, Er^{3+}:2.7 μm fiber laser is popular because it can be pumped by the commercial 790 nm or 976 nm LD. Nowadays, Er^{3+}:2.7 μm fiber lasers are very important mid-IR laser sources owing to their applications in IR countermeasures, laser surgery, high-efficiency pump sources for longer wavelength oscillators, and so on [3–5]. It is known that the output from Er^{3+} singly-doped ZBLAN fiber saturates because of ground-state bleaching and a competing laser transition which terminates in the $^4I_{13/2}$ lower laser level of the 2.7 μm transition [6], then energy-transfer-upconversion (ETU) and cross relaxation (CR) processes within Er^{3+} ions play very important role in the energy recycling of $^4I_{11/2}$ level and fast depletion of $^4I_{13/2}$ level, which enables CW operation of 2.7 μm laser [7]. For this reason, high Er^{3+} concentration is preferred to promote ETU and CR processes. Except for the highly dopant effort, other methods were used to realize quick repopulation of the ground state, including the cascade method [8,9] and co-doping with other RE^{3+} ions to balance the bottleneck problems of Er^{3+}: $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition [10,11] and avoid ground-state bleaching [2,7,12]. RE^{3+} ions, such as Pr^{3+}, Tm^{3+}, Ho^{3+} and Nd^{3+} have been proved to be efficient in enhancing Er^{3+}:2.7 μm emission in fluoride, germanate, bismuthate and chalcohalide hosts [9,10,1–17]. Energy level diagram indicates that to Er^{3+}: $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition, the de-sensitization processes by Pr^{3+} and Nd^{3+} are non-phonon-assisted [13–15] while those of Tm^{3+} and Ho^{3+} are phonon-assisted [9]. Theoretically, non-phonon-assisted ET process is more efficient than the phonon-assisted one for the population depletion of $^4I_{13/2}$ and $^4I_{11/2}$ levels, but $^4I_{11/2}$ depopulation is harmful to 2.7 μm emission. Because of the efficient depletion of $^4I_{13/2}$, Pr^{3+} is usually used in commercial Er^{3+} doped ZBLAN fiber to date, and Er^{3+}/Pr^{3+}:2.7 μm lasers have been widely achieved in ZBLAN fibers [2,7,12,18]. But as mentioned above, the undesired $^4I_{11/2}\rightarrow{}^3F_{3,4}$ process depopulates the upper level of 2.7 μm transition, and it is interesting to know whether the phonon-assisted ET process will weaken it. Further, to comprehend the differences between phonon- and non-phonon- assisted ET process, concentrating on their de-excitation effects to Er^{3+} from the point of spectroscopic and theoretical analysis. In comparison, Ho^{3+} is used for the phonon-assisted ET investigation. Fluorophosphate glass with low phosphate was used as the doping host because of its better glass forming ability than fluoride glass.

2. Experiment

Fluorophosphate glasses with the compositions of $5Al(PO_3)_3$–$50(Mg,Ca,Sr,Ba)F_2$–$37AlF_3-5YF_3$–(0.5, 2.0)Er_2O_3–(0, 0.1, 1.0)PrF_3/HoF_3 were prepared under 1050 °C. Er^{3+} concentration is about 2 and 8×10^{20} ions/cm^3 in 0.5 and 2 mol% Er_2O_3 samples,

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respectively, corresponding to the low and highly Er^{3+} doping. Er^{3+}, Pr^{3+}, Ho^{3+} singly doped, Er^{3+}/Pr^{3+} and Er^{3+}/Ho^{3+} co-doped glasses labeled as E, P, H, E/P and E/H were annealed at 450 °C, then cut and polished for further measurements. Under room temperature, fluorescence spectra and lifetime were recorded by FLSP920 fluorescence spectrometer (Edinburgh Analytical Instruments Ltd.) with 976 nm pumping. In order to keep the consistency of the results, all samples were measured under the same conditions. Absorption spectra were obtained with a JASCO V-570 UV/VIS spectrophotometer (JASCO International Co. Ltd., Tokyo, Japan) in a range of 300–2200 nm.

3. Results and discussion

3.1. 2.7 μm and 2.65 μm emission

Fig. 1 is the fluorescence spectra around 2.7 μm in Er^{3+} singly doped and Ho^{3+}/Pr^{3+} de-sensitized Er^{3+} glasses. E2.0 performs minor intensity advantage over E0.5, and both Ho^{3+} and Pr^{3+} are efficient de-sensitizers to Er:2.7 μm emission. In E0.5/H0.1 and E0.5/P0.1, although the 2.7 μm fluorescence intensity decreases compared with E0.5, co-doping with Ho^{3+} or Pr^{3+} is necessity to overcome the ground state bleaching in low Er^{3+} concentration samples. While to E2.0, the 2.7 μm intensity in co-doping samples enhances obviously. Great discrepancy is observed when Ho^{3+} or Pr^{3+} increases to 1.0 mol%:E2.0/P1.0 maintains stronger 2.7 μm intensity but that of E2.0/H1.0 declines greatly, suggesting quite different ET mechanisms in the two samples.

It can be seen that in E and E/H glasses, 2.65 μm and 2.7 μm emission exhibit the same intensity tendency. However, the spectra indicate that the 2.65 μm emissions in E/P glasses are much stronger than those of E and E/H. Fluorescence intensity ratio of 2.65 μm/2.7 μm is calculated, shown in Fig. 1. Obviously, Ho^{3+} depresses the 2.65 μm emission while Pr^{3+} strengthens it greatly. Stronger 2.65 μm emission is harmful to 2.7 μm lasing, and should be suppressed. From this point, E2.0/H0.1 is better than E2.0/P0.1. Highly doped Er^{3+}, combined with low concentration de-sensitizer, such as E2.0/H0.1 and E2.0/P0.1, can keep the correspondingly lowest 2.65 μm/2.7 μm ratio.

3.2. 1.5 μm emission and ET mechanisms

De-sensitization effect of Pr^{3+} or Ho^{3+} to Er^{3+} is depicted by the 1.5 μm fluorescence spectra in Fig. 2(a). Er^{3+}:1.5 μm emission is greatly depressed with 1.0 mol% Ho^{3+}, while only 0.1 mol% Pr^{3+} has the same effect. Table 1 is the Er^{3+}:1.5 μm and Ho^{3+}:2.0 μm lifetime of the samples. $\tau_{f1.5\ \mu m}$ of E2.0 declined greatly to 7 ms, implying the intense ETU and CR processes in Er^{3+} highly doped situation, which is benefit for the population recycling and 2.7 μm lasing. Undoubtedly, Pr^{3+} performs much efficient $^4I_{13/2}$ depleting ability than Ho^{3+}, replenishing the ground state quickly, which is the main reason that Pr^{3+} is always used as the de-sensitizer to Er^{3+}:2.7 μm emission. Variations of $\tau_{f1.5\ \mu m}$ and $\tau_{f2.0\ \mu m}$ in E/H glasses indicate the complicated but reasonable ET processes between Er^{3+} and Ho^{3+}, and the long lifetime of Ho^{3+}:$^5I_7$ level also means that intense interactions exist among the Er^{3+}–Ho^{3+}, Er^{3+}–Er^{3+} and Ho^{3+}–Ho^{3+} ions, especially in highly RE^{3+} doped samples. For instance, the 11 ms lifetime of E0.5/H0.1 at 2.0 μm declined to 5.0 ms and 2.2 ms in E2.0/H0.1 and E2.0/H1.0. Pr^{3+} related lifetime or fluorescence spectra can not be detected.

Several absorption bands that relate to the ET processes in E, P and H are illustrated in Fig. 2(b), inset is the simplified energy level diagram of Pr^{3+}, Er^{3+} and Ho^3. It can be seen that Er^{3+}:$^4I_{13/2}$ and Pr^{3+}:$^3F_{3,4}$, Er^{3+}:$^4I_{11/2}$ and Pr^{3+}:$^1G_4$ overlap totally, but Er^{3+}:$^4I_{13/2}$ and Ho^{3+}:$^5I_7$, Er^{3+}:$^4I_{11/2}$ and Ho^{3+}:$^5I_6$ are separate from each other. This means Er^{3+}:$^4I_{13/2}\rightarrow Ho^{3+}$:$^5I_7$ (ET3) and Er^{3+}:$^4I_{11/2}\rightarrow Ho^{3+}$:$^5I_6$ (ET4) are phonon-assisted processes, while Er^{3+}:$^4I_{13/2}\rightarrow Pr^{3+}$:$^3F_{3,4}$ (ET1) and Er^{3+}:$^4I_{11/2}\rightarrow Pr^{3+}$:$^1G_4$ (ET2) are not. Certainly, ET1 and ET3 are beneficial for population inversion of $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition, but ET2 and ET4 are undesired procedures for the population accumulation of $^4I_{11/2}$.

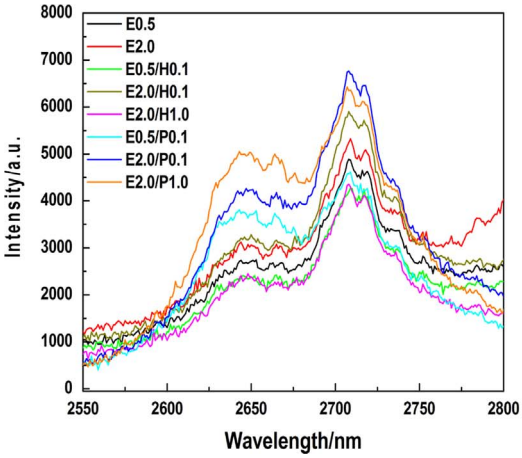
3.3. ET coefficient and spectral cross section superposition

To describe the differences between Pr^{3+} and Ho^{3+}, ET efficiency is studied by the Tarelho's method [19] together with the Förster and Dexter's investigations [20,21]. The forward ET coefficient C_{DA} from Er^{3+}(Donor) to the sensitizers Pr^{3+} or Ho^{3+} (Accepter) can be determined from the following equations:

$$C_{DA}=\frac{6cg_{low}^{D}}{(2\pi)^4 n^2 g_{up}^{D}}\sum_{m=0}^{\infty} e^{-(2\overline{n}+1)s_0}\frac{S_0^m}{m!}(\overline{n}+1)^m \times\int \sigma_{emi}^{D}(\lambda_m^+)\sigma_{abs}^{A}(\lambda)d\lambda \quad (1)$$

n is the refractive index of the glass, c is the speed of light, g_{low}^{D} and g_{up}^{D} are the degeneracy of donor and accepter states from the lower and upper levels involved in the process. σ_{emi}^{D} and σ_{abs}^{D} are the emission and absorption cross section, which can be derived from:

$$\sigma_{emi}^{D}\left(\lambda_m^+\right)\approx\frac{S_0^m e^{-S_0}}{m!}(\overline{n}+1)^m\sigma_{emi}^{D}(E-E_1) \quad (2)$$



glass	Intensity ratio 2.65μm/2.7μm
E0.5	0.5605
E2.0	0.5863
E0.5/H0.1	0.5570
E2.0/H0.1	0.5437
E2.0/H1.0	0.5540
E0.5/P0.1	0.8263
E2.0/P0.1	0.6219
E2.0/P1.0	0.7861

Fig. 1. Mid-IR fluorescence spectra in Er^{3+} singly doped glasses and Ho^{3+}/Pr^{3+} desensitized Er^{3+} glasses. Right-side is the corresponding ratio of 2.65 μm/2.7 μm emission intensity.