

Luminescent properties of $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped LiYF_4 crystals*

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Ho^{3+} with various concentrations and Tm^{3+} with molar concentration of 1.28% are co-doped in LiYF_4 (YLF) single crystals. The luminescent properties of the crystals are investigated through emission spectra, emission cross section and decay curves under the excitation of 808 nm. The energy transfer from Tm^{3+} to Ho^{3+} and the optimum fluorescence emission of Ho^{3+} around 2.05 μm are investigated. The emission intensity at 2.05 μm keeps increasing with the molar concentration of Ho^{3+} improved from 0.50% to 1.51% when the molar concentration of Tm^{3+} is kept at 1.28%. Moreover, for the co-doped crystals in which the molar concentrations of Tm^{3+} and Ho^{3+} are 1.28% and 1.51%, respectively, the maximum emission cross section reaches $0.760 \times 10^{-20} \text{ cm}^2$ and the maximum fluorescence lifetime is 21.98 ms. All the parameters suggest that these materials have more advantages in the future 2.0 μm laser applications.

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The 2 μm solid laser has attracted great interest due to its applications in optical communications, coherent laser radar, medical treatment, etc^[1-3]. The luminescent ion Ho^{3+} is important for the solid laser because of its emission at $\sim 2 \mu\text{m}$ by $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transition. There have been some researches on the lasers based on $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped LiYF_4 (YLF) crystals because of the excellent optical and physical-chemical properties. Recently, the optical bistable performance, the longwave-infrared optical parametric oscillator and the tuning upconversion luminescence in $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF crystals have also been reported^[4-6]. Although some parameters and properties of $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF crystals have been studied systematically, some aspects are not comprehensive enough. The energy transfer from $\text{Tm}^{3+} : ^3\text{F}_4$ to $\text{Ho}^{3+} : ^5\text{I}_7$ at room temperature in YLF crystals has been firstly reported by Brenier et al^[7]. However, they just discussed the characteristics of singly-doped YLF crystals. Because of the main difficulty in growing YLF single crystals, including the oxidation and the volatilization of melting, it is difficult to obtain high-quality crystal.

In this paper, YLF single crystal is obtained by Bridgman method using a sealed platinum crucible in air atmosphere, in which the crucible is completely sealed to

isolate the water and the oxygen from the atmosphere and to prevent the volatilization of the melting during crystal growth. This process is proven to improve the crystal quality of the rare earth ion doped YLF crystals. The efficient near infrared (NIR) emission spectra of YLF with optimum concentrations of Tm^{3+} and Ho^{3+} around 1.8 μm emission are obtained and investigated.

A series of $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF single crystals were grown in our laboratory using an improved Bridgman method. The molar concentration of TmF_3 in raw materials is held to be 1.3%, and that of HoF_3 is 0.5%, 1.0% and 1.5%, respectively. The detailed process of the growth and schematic diagram of the apparatus used for the experiment have been reported in our previous work^[8].

The typical single crystal with the size of $\Phi 10 \text{ mm} \times 82 \text{ mm}$ is shown in Fig.1(c). It is transparent with pale red, and the color changes gradually from light to dark along the growth direction due to the higher Ho^{3+} dopant concentration. It can be seen that they are single crystals since they are highly transparent and no grain boundary is observed. The crystals were cut into pieces and well polished to 2.3 mm thickness for optical measurements. The concentrations of Tm^{3+} and Ho^{3+} in YLF single

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crystals were obtained by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Inc., Optima 3000). The measured molar concentrations of $\text{Tm}^{3+}/\text{Ho}^{3+}$ in YLF single crystals for three samples are 1.28%/0.5%, 1.28%/1.01% and 1.28%/1.51%, respectively. The structure of the crystal was analyzed by X-ray diffraction (XRD) using an XD-98X diffractometer (XD-3, Beijing). The absorption spectra were recorded with a Cary 500 UV/VIS/NIR spectrophotometer (Agilent Co., America). The emission spectra and fluorescence decay curves were detected by an FLSP 920 type spectrometer (Edinburgh Co., England) excited by 808 nm laser diode (LD). All the measurements were carried out at room temperature.

The XRD pattern for YLF sample with Tm^{3+} (1.28%)/ Ho^{3+} (1.51%) is displayed in Fig.1(a). By comparison, the peak positions are consistent with those in JCPD 77-0816 ($a=b=0.5171$ nm, $c=1.0748$ nm) of YLF which is also listed in Fig.1(b). One can confirm that the current doping levels of Tm^{3+} and Ho^{3+} do not cause any obvious peak shift or second phase. The similar XRD patterns are obtained for YLF samples with 1.28% $\text{Tm}^{3+}/y\%$ Ho^{3+} ($y=0.50, 1.01$ and 1.51), which suggests that the samples have been crystallized into the pure orthorhombic phase.

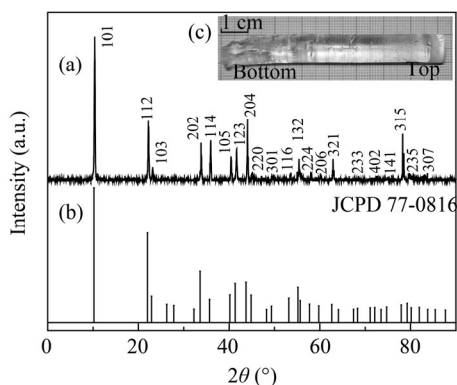


Fig.1 (a) XRD pattern of YLF: $\text{Tm}^{3+}/\text{Ho}^{3+}$; (b) Standard line pattern of the orthorhombic phase YLF (JCPD 77-0816); (c) Photograph of $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF single crystal

Fig.2 shows the absorption spectra of $\text{Ho}^{3+}/\text{Tm}^{3+}$ co-doped YLF samples with different Ho^{3+} doping concentrations. The characteristic absorption bands corresponding to the transitions of Tm^{3+} and Ho^{3+} from the ground state to the excited states are marked in the spectra. As can be seen from Fig.2, the corresponding absorption coefficient is proportional to the Ho^{3+} doping concentration, while the peaks of Tm^{3+} and the positions of all absorption peaks do not change any more.

Our previous work^[9] shows that as Tm^{3+} doping level is increased from 0.29% to 1.28%, the fluorescence intensity ratio of 1.8 μm is also increased. However, the intensity ratio is decreased rapidly, when the molar concentration is further improved to 1.75% and 3.49%. We obtain the optimal doping concentration for Tm^{3+} singly doped YLF crystal, which is 1.28%. On the basis of the

optimum doping concentration of Tm^{3+} singly doped YLF crystal, we further investigate the energy transfer of Tm^{3+} and Ho^{3+} in YLF crystals.

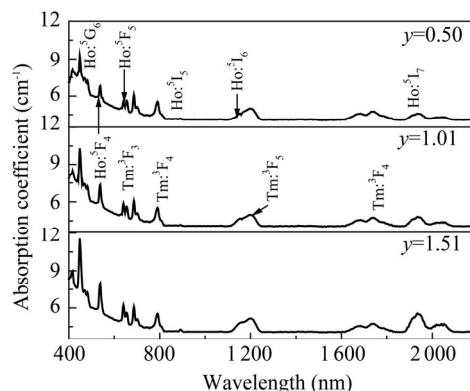


Fig.2 Absorption spectra of $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF crystals with molar concentrations of 1.28%/y% ($y=0.50, 1.01$ and 1.51)

Fig.3 illustrates the emission spectra of the $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF crystal samples under the excitation of 808 nm. As shown in Fig.3, the emission spectra are characterized by three emission bands at 1.47 μm , 1.8 μm and 2.05 μm , corresponding to ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ in Tm^{3+} and ${}^5\text{I}_7 \rightarrow {}^5\text{I}_8$ in Ho^{3+} , respectively. It is noted that the variation of the 2.05 μm fluorescence intensity with the Ho^{3+} doping level exhibits a linear trend in YLF samples, and at this doping level, there is no luminescence quenching. When Ho^{3+} molar concentration is improved from 0.50% to 1.51%, the emission intensity at 1.8 μm decreases monotonously, but that at 2.05 μm increases constantly. It can be also observed that the wavelength range of emission spectrum of Tm^{3+} is from 1.47 μm to 2.0 μm , which partly overlaps with that of Ho^{3+} in 1.88–2.11 μm . Therefore, the $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped samples may lead to a substantially larger and wider emission band than the singly doped one.

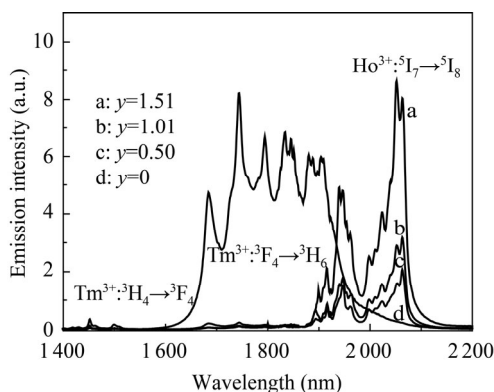


Fig.3 Infrared emission spectra of the $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF crystal samples (1.28%/y%) and Tm^{3+} singly doped YLF crystal under excitation of 808 nm

The possible energy transfer mechanism for $\text{Tm}^{3+}/\text{Ho}^{3+}$

co-doped YLF samples can be explained by the simplified energy-level diagram as shown in Fig.4. Under the excitation of 808 nm, Tm^{3+} is initially excited from 3H_6 ground state to 3H_4 level, and then it transfers to the 3F_4 manifold quickly in two ways. One is radiatively decaying to 3F_4 to emit photons at 1.47 μm , and the other is the well-known two-for-one cross-relaxation (CR) process. Therefore, a fraction of the energy stored in 3F_4 level is transferred to the adjacent Ho^{3+} , and then a strong interaction occurs between the two ions, which yields 2.05 μm emission efficiently. The energy transfer efficiency is correlated with the concentration of Ho^{3+} , and it is worthwhile to mention that the lifetime of Tm^{3+} at 1.8 μm is too weak to be detected, which means that the energy transfer efficiency is very high.

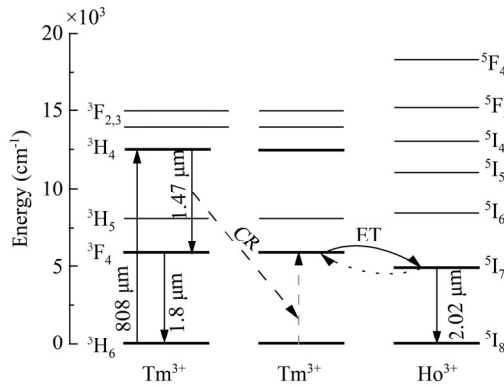


Fig.4 Simplified energy level diagrams of Tm^{3+} and Ho^{3+} under 808 nm LD excitation

According to the absorption spectra, the transition cross-sections of Tm^{3+} from 3F_4 level and Ho^{3+} from 5I_7 level can be calculated. The absorption cross-section can be determined by^[10]

$$\sigma_{abs}(\lambda) = \frac{2.303 \log(I_0 / I)}{NL} = \frac{\alpha}{N}, \quad (1)$$

where L is the thickness of the sample, $\log(I_0/I)$ is the measured optical density as a function of wavelength, N is the number of Tm^{3+} ions per volume (ions/ cm^3), and α is the absorption coefficient.

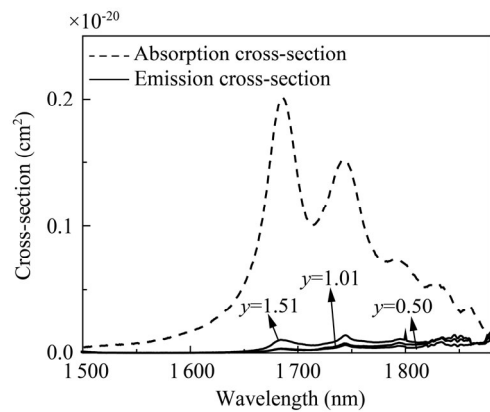
According to Futchbauer-Ladenburg theory, the stimulated emission cross-section based on fluorescence spectrum for Tm^{3+} in $^3F_4 \rightarrow ^3H_6$ transition and for Ho^{3+} in $^5I_7 \rightarrow ^5I_8$ transition is determined by^[11]

$$\sigma_{em}(\lambda) = \frac{\lambda^5 \cdot I(\lambda) \beta}{8\pi n^2 c \tau_{rad} \int \lambda I(\lambda) d\lambda}, \quad (2)$$

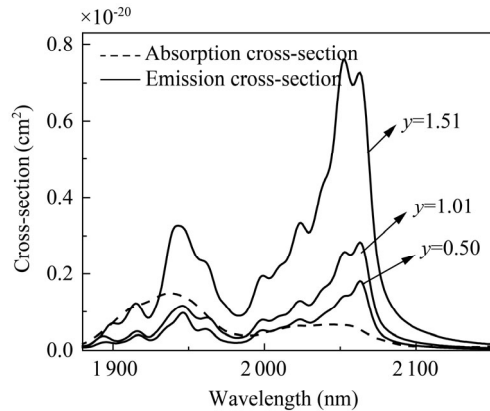
where $I(\lambda)$ represents the emission intensity, c is the light velocity, n is the refractive index of crystal, β notes the branching ratio, and τ_{rad} is the radiative lifetime obtained from Judd-Ofelt (J-O) theory.

Fig.5(a) gives the absorption cross-section and emission cross-section in the region from 1.5 μm to 1.9 μm corresponding to $Tm^{3+}: ^3F_4 \rightarrow ^3H_6$ transition. It can be

found that the largest value of σ_{abs} in this region is $0.201 \times 10^{-20} cm^2$ at the wavelength of 1.686 μm . Obviously, the emission cross-section is much smaller than the absorption cross-section. However, in the region from 1.9 μm to 2.2 μm corresponding to $Ho^{3+}: ^5I_7 \rightarrow ^5I_8$ transition shown in Fig.5(b), it can be noted that emission cross-section σ_{ems} keeps increasing with the Ho^{3+} molar concentration improved from 0.50% to 1.51% when the molar concentration of Tm^{3+} is kept constant at $\sim 1.28\%$. The maximum σ_{ems} reaches $0.760 \times 10^{-20} cm^2$ at 2.052 μm , and the maximum σ_{abs} is $0.149 \times 10^{-20} cm^2$ at 1.938 μm . Beyond the wavelength of 2.0 μm , the absorption cross-section becomes minor, even can be ignored especially for the Tm^{3+} (1.28%)/ Ho^{3+} (1.51%) co-doped sample. Under the excitation of 808 nm, the emission cross-section of Ho^{3+} keeps increasing with that of Tm^{3+} decreasing as illustrated in Fig.5(a). Comparing the results in Fig.5(a) and (b), it can be confirmed that the energy transfer efficiency between Tm^{3+} and Ho^{3+} is higher.



(a)



(b)

Fig.5 Absorption cross-sections and emission cross-sections of (a) $Tm^{3+}: ^3F_4 \rightarrow ^3H_6$ transition and (b) $Ho^{3+}: ^5I_7 \rightarrow ^5I_8$ transition in Tm^{3+}/Ho^{3+} co-doped YLF samples

Fig.6 gives the decay curves of Tm^{3+}/Ho^{3+} co-doped YLF samples observed at 2.052 μm with different Ho^{3+} molar concentrations. It is found that the decay curves can be described very well by a single exponential decay, and the fitted values are marked in Fig.6. The fluores-

cence decay increases monotonously with Ho^{3+} doping level improving. As the Ho^{3+} molar concentration is increased from 0.50% to 1.51%, the lifetime of $^5\text{I}_7$ state changes from 13.03 ms to 21.98 ms. It means that the higher the Ho^{3+} molar concentration, the larger the energy transfer efficiency, which is in good agreement with the result obtained by Walsh et al^[11]. This phenomenon can be described by the complicated energy transfer process. The energy transfer between Tm^{3+} and Ho^{3+} involves some detrimental processes, such as energy transfer upconversion (ETU) ($^3\text{F}_4+^5\text{I}_7\rightarrow^3\text{H}_6+^5\text{I}_5$), which reduces the effective lifetime of the upper level $^5\text{I}_7$, and increases the threshold pump power of 2 μm laser^[12].

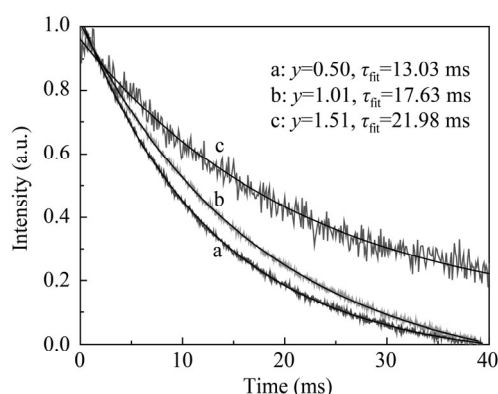


Fig.6 Decay curves of 1.28% $\text{Tm}^{3+}/y\%\text{Ho}^{3+}$ co-doped YLF crystal samples ($y=0.50, 1.01$ and 1.51) monitored at 2.052 μm under 808 nm LD excitation

$\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped YLF crystals were synthesized by the improved Bridgman method. Luminescence spectra and fluorescent decays are recorded to prove the occurrence of energy transfer from Tm^{3+} to Ho^{3+} . Under the excitation of 808 nm, the optimum fluorescence emission of Ho^{3+} around 2.05 μm is obtained when the molar concentration of Tm^{3+} is kept constant at $\sim 1.28\%$ in YLF

crystal. The maximum emission cross-section is as high as $0.760\times 10^{-20}\text{ cm}^2$, and the lifetime is 21.98 ms. Hence, due to the good optical parameters for these $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped crystals, it is expected that these materials have a potential application in mid-infrared laser devices at $\sim 2.0\ \mu\text{m}$.

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