

Enhanced emission of 2.9 μm from $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 crystal excited by 640 nm^{*}

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The use of Pr^{3+} co-doping for great enhancement of mid-infrared (mid-IR) emissions at 2.9 μm and 2.4 μm is investigated in the $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 crystals. With the introduction of Pr^{3+} ions, the fluorescence lifetime of $\text{Ho}^{3+}:^5\text{I}_7$ level is 2.15 ms for $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped crystal, and the lifetime for Ho^{3+} singly doped crystal is 17.70 ms, while the lifetime of $\text{Ho}^{3+}:^5\text{I}_6$ level decreases slightly from 2.11 ms for $\text{Ho}^{3+}:\text{LiYF}_4$ to 1.83 ms for $\text{Ho}^{3+}/\text{Pr}^{3+}:\text{LiYF}_4$. It is also demonstrated that the introduction of Pr^{3+} greatly increases the mid-infrared emission of $\text{Ho}^{3+}:^5\text{I}_6 \rightarrow ^5\text{I}_7$ which depopulates the $\text{Ho}^{3+}:^5\text{I}_7$ level, while it has little influence on the $\text{Ho}^{3+}:^5\text{I}_6$ level, which is beneficial for greater population inversion and laser operation. The analysis on the decay curves of the 2.0 μm emissions in the framework of the Inokuti-Hirayama model indicates that the energy transfer from Ho^{3+} to Pr^{3+} is mainly from electric dipole-dipole interaction. The calculated efficiency of energy transfer from $\text{Ho}^{3+}:^5\text{I}_7$ to $\text{Pr}^{3+}:^3\text{F}_2$ level is 87.53% for $\text{Ho}^{3+}/\text{Pr}^{3+}$ (1.02%/0.22%) co-doped sample. Our results suggest that the $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 single crystals may have potential applications in mid-IR lasers.

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Ho^{3+} has been considered as a suitable ion for mid-infrared (mid-IR) emission with transition $^5\text{I}_6 \rightarrow ^5\text{I}_7$ at 2.9 μm . Some Ho^{3+} doped solid state materials were investigated for mid-IR laser^[1-4]. Previous work shows that sensitizers, such as Nd^{3+} , in the Ho^{3+} -doped LiYF_4 crystals could effectively quench the excited state population in the $^5\text{I}_7$ level. However, the population of the upper $^5\text{I}_6$ laser level was reduced, and the luminescence efficiency of the 2.9 μm emission was decreased by approximately 50%^[5]. Fortunately, with the introduction of Pr^{3+} , the effective deactivation of the $^5\text{I}_7$ level of Ho^{3+} led to continuous wave (CW) output at 2.9 μm from $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped ZBLAN-based fiber laser^[6], which motivates the search of new materials for mid-IR laser.

Because of their high mechanical strength and excellent chemical durability, fluoride crystals are more favorable as the host material for practical application than fluoride glasses. Moreover, the rigid symmetric structure of single crystal is beneficial for higher luminescence efficiency from the activator centers. The LiYF_4 crystal has been proved to be a suitable laser material because of its low maximum phonon energy, long fluorescence life-

time, low thermal lens effect and laser threshold, and ability to incorporate trivalent rare-earth ions which substitute for the Y^{3+} ions^[7]. Although the 2.9 μm mid-IR emission properties of Ho^{3+} doped and $\text{Ho}^{3+}/\text{Nd}^{3+}$ co-doped LiYF_4 crystals have been investigated^[4,5,8], the growth of $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 crystals and the effect of Pr^{3+} on the 2.9 μm emission in the crystal are rarely reported due to the difficulty of crystal growth.

In this paper, the $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 single crystal is grown by a modified Bridgman method. Pr^{3+} is explored as a sensitizer to improve the luminescence. With proper Ho^{3+} and Pr^{3+} ion concentrations and Pr^{3+} as a sensitizer, an enhanced emission at 2.9 μm of Ho^{3+} is obtained under 640 nm excitation.

Ho^{3+} singly doped and $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 crystals were grown by Bridgman method in a resistively heated furnace along $\langle 001 \rangle$ direction. Starting materials were prepared from stoichiometric mixture of 99.99% pure LiF , YF_3 , HoF_3 and PrF_3 powder with the molar compositions of 51.5% LiF -47.5% YF_3 -1% HoF_3 and 51.5% LiF -47% YF_3 -1% HoF_3 -0.5% PrF_3 . Details of the growth procedure were described in Refs.[7,8]. The

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X-ray power diffraction (XRD) was carried out to determine the crystal phase. By comparing the peak positions with those in JCPD 77-0816 of LiYF₄, one can confirm that the obtained crystal is of pure orthorhombic phase. The Ho³⁺ and Pr³⁺ concentrations in the crystals were measured by inductively coupled plasma (ICP). The molar concentrations of Ho³⁺ and Pr³⁺ were 1.02% and 0.22% in Ho³⁺/Pr³⁺ co-doped LiYF₄ crystals, and 1.02% in Ho³⁺ singly doped crystal. According to the measured density of crystals, the densities are calculated to be 3.011×10²⁰ cm⁻³ for Ho³⁺ and 0.65 ×10²⁰ cm⁻³ for Pr³⁺ in Ho³⁺/Pr³⁺ co-doped LiYF₄ crystals, and 3.024× 10²⁰ cm⁻³ for Ho³⁺ in Ho³⁺ singly doped crystal. The samples for spectroscopic measurements were cut from the grown LiYF₄ crystals along <001> direction and polished to the thickness of 2.20 mm. The absorption spectra in the range from 200 nm to 2500 nm were measured using a U-4100 spectrophotometer. The emission spectra and fluorescence decay curves were tested with a Traix 320 type spectrometer (Jobin-Yvon Co., France) in the ranges of 1.0–1.8 μm and 1.8–3.02 μm excited by a 640 nm light. All measurements were carried out at room temperature.

As shown in Fig.1, nine absorption bands located at 358 nm, 416 nm, 448 nm, 472 nm, 482 nm, 536 nm, 638 nm, 1150 nm and 1932 nm can be seen in Ho³⁺ singly doped LiYF₄ crystal. These bands are ascribed to the transitions from the ground state ⁵I₈ to ³H₆, ³G₅, ⁵G₆+⁵F₁, ⁵F₂+³K₈, ⁵F₃, ⁵F₄+⁵S₂, ⁵F₅, ⁵I₆, ⁵I₇ levels of Ho³⁺ ions, respectively. Four new bands appear at 2300 nm, 1530 nm, 1443 nm and 592 nm in the Ho³⁺/Pr³⁺ co-doped LiYF₄ crystal. They are corresponding to the transitions from the ground state ³H₄ to ³H₆, ³F₃, ³F₄ and ¹D₂ levels of Pr³⁺ ion, respectively.

Based on the measured absorption spectra shown in Fig.1, the absorption and emission cross sections for Ho³⁺ emissions at 1.2 μm and 2.05 μm are calculated by using Beer-Lambert equation and McCumber theory^[9]. The emission cross section σ_{em} can be calculated by:

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_l}{Z_u} \exp[(E_{zl} - hc/\lambda)/kT], \quad (1)$$

where σ_{abs}(λ)=α(λ)/N represents the absorption cross section, α(λ) is absorption coefficient and N is the number of ions in the unit volume. Z_l and Z_u are the partition functions of the lower and upper manifolds, respectively. Values of 0.8567 and 0.8052 for Z_l/Z_u can be used for the transitions of ⁵I₆→⁵I₈ (1.2 μm) and ⁵I₇→⁵I₈ (2.05 μm), respectively, as reported in Ref.[10]. E_{zl} is the zero-line energy, and is defined as the energy difference between the lowest Stark level of the upper manifold and the lowest Stark level of the lower manifold. The energy level reported for Ho³⁺:LiYF₄^[10] is used to calculate the zero-line energy for the manifolds studied. k is the Boltzmann's constant, and T is the absolute temperature (room temperature). The derived absorption and emission cross sections of 1.2 μm and 2.05 μm emissions for Ho³⁺:LiYF₄ crystal are calculated and shown in Fig.2.

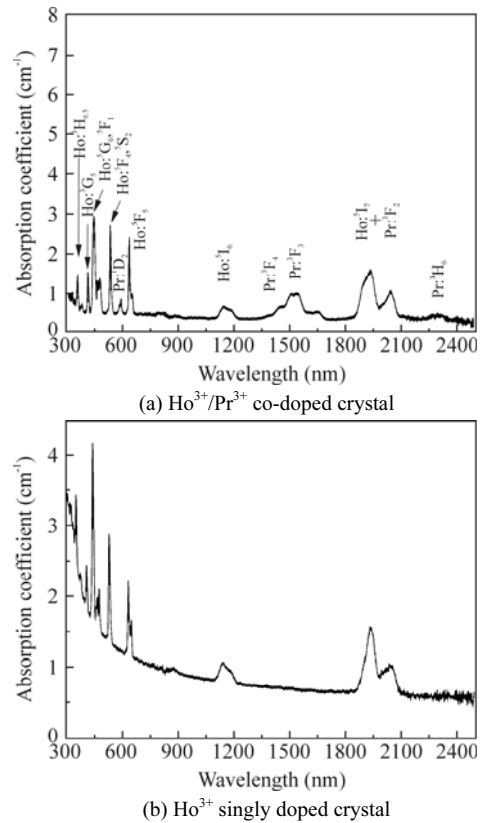


Fig.1 Absorption spectra of Ho³⁺/Pr³⁺ co-doped and Ho³⁺ singly doped LiYF₄ crystals

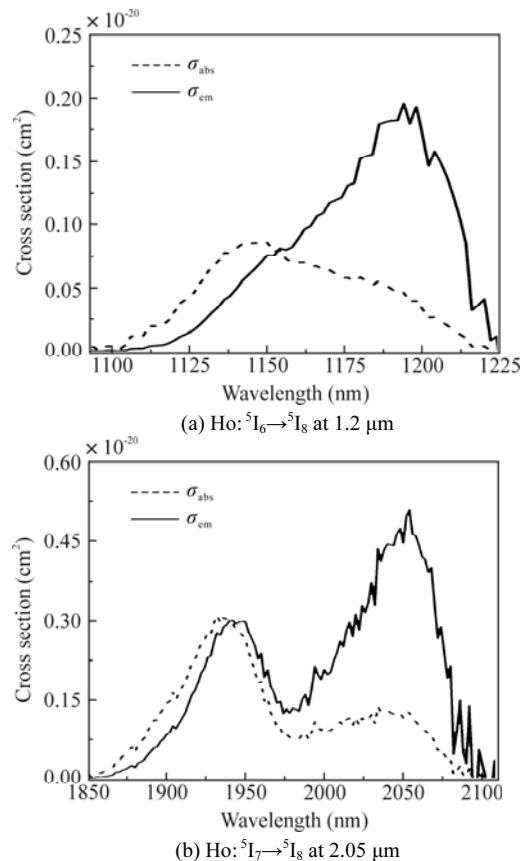


Fig.2 Absorption and emission cross sections for Ho³⁺ emissions at (a) 1.2 μm and (b) 2.05 μm for Ho³⁺:LiYF₄ crystal

The maximum emission cross sections of $\text{Ho}^{3+}:\text{LiYF}_4$ crystal located at 1.2 μm and 2.05 μm are $0.20 \times 10^{-20} \text{ cm}^2$ and $0.51 \times 10^{-20} \text{ cm}^2$, respectively. The value at 2.05 μm can be compared with that of $\text{Ho}^{3+}:\text{SrMoO}_4$ ($0.271 \times 10^{-20} \text{ cm}^2$)^[11], $\text{Ho}^{3+}:\text{SrWO}_4$ ($1.05 \times 10^{-20} \text{ cm}^2$)^[12] and $\text{Ho}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ ($0.45 \times 10^{-20} \text{ cm}^2$)^[13].

The two emission bands at 1.2 μm and 2.05 μm , which are attributed to $^5\text{I}_6 \rightarrow ^5\text{I}_8$ and $^5\text{I}_7 \rightarrow ^5\text{I}_8$ transitions, respectively, can be observed in Fig.3(a). Compared with Ho^{3+} singly doped LiYF_4 crystal, two new strong emission bands at 2.4 μm and 2.9 μm corresponding to $\text{Pr}^{3+}:\text{H}_6 \rightarrow \text{H}_4$ and $\text{Ho}^{3+}:\text{I}_7 \rightarrow ^5\text{I}_8$ transitions appear in the $\text{Pr}^{3+}/\text{Ho}^{3+}$ co-doped sample. Evident emission enhancement at 1.2 μm and a significant emission suppression at 2.05 μm are also observed from the $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 under excitation of 640 nm. Generally, the 1.2 μm emission corresponding to the transition $^5\text{I}_6 \rightarrow ^5\text{I}_8$ is only observed in low phonon energy host, such as fluoride^[10], chalcogenide^[14] and oxyfluoride glass ceramics^[15]. On the other hand, the broad emission at 2.0 μm usually results from the transition of $\text{Ho}^{3+}:\text{I}_7 \rightarrow ^5\text{I}_8$, and was observed in many types of hosts including glasses^[2] and crystals^[10,16]. Its peak wavelength depends on the host material.

The possible mechanisms of the energy transfer processes between Ho^{3+} and Pr^{3+} have been reported in previous work^[17]. The energy level diagram for the $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 crystal is illustrated in Fig.3(c). Under 640 nm excitation, in Ho^{3+} singly doped LiYF_4 crystal, 2.9 μm emission from the transition of $^5\text{I}_6 \rightarrow ^5\text{I}_7$ for Ho^{3+} ions is almost absent, whereas the intense fluorescences at 2.0 μm from the transition of $^5\text{I}_7 \rightarrow ^5\text{I}_8$ for Ho^{3+} ions and at 1.2 μm ascribed to the $\text{Ho}^{3+}:\text{I}_6 \rightarrow ^5\text{I}_8$ transition are observed. However, 2.9 μm fluorescence is much more efficient in $\text{Ho}^{3+}/\text{Pr}^{3+}:\text{LiYF}_4$ with the introduction of Pr^{3+} ions. Moreover, a significant reduction in the emission intensity of the $^5\text{I}_7$ level at 2.0 μm is observed in the Ho^{3+} and Pr^{3+} co-doped sample, which justifies that Pr^{3+} ions can be used effectively to depopulate the $\text{Ho}^{3+}:\text{I}_7$ level. In $\text{Ho}^{3+}/\text{Pr}^{3+}:\text{LiYF}_4$ crystal, it is noted that there is an increase of 1.2 μm emission corresponding to transition $^5\text{I}_6 \rightarrow ^5\text{I}_8$, which is not beneficial for making the population inversion of the upper 2.9 μm laser level ($\text{Ho}^{3+}:\text{I}_6$). It has been revealed that the Pr^{3+} ions can efficiently deactivate the first excited ($^5\text{I}_7$) state of Ho^{3+} in $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped glass, and the net effect introduced by the Pr^{3+} ion deactivation of the Ho^{3+} ion supports the fast recovery of the ground state of Ho^{3+} . It may be the reason for the increase of 1.2 μm emission.

Since the energy levels of $^3\text{F}_2$ of Pr^{3+} and $^5\text{I}_7$ of Ho^{3+} match very well as shown in Fig.3, the energy transfer ($\text{Ho}^{3+}:\text{I}_7, \text{Pr}^{3+}:\text{H}_4 \rightarrow \text{Ho}^{3+}:\text{I}_8, \text{Pr}^{3+}:\text{F}_2$) can take place. The ions in $\text{Pr}^{3+}:\text{F}_2$ level nonradiatively decay to the lower $\text{Pr}^{3+}:\text{H}_6$ level, then radiatively decay to the $\text{Pr}^{3+}:\text{H}_4$ level, and emit a broadband emission around 2.4 μm as observed in Fig.3(a). It further demonstrates the existence of the energy transfer process from Ho^{3+} to Pr^{3+} ions.

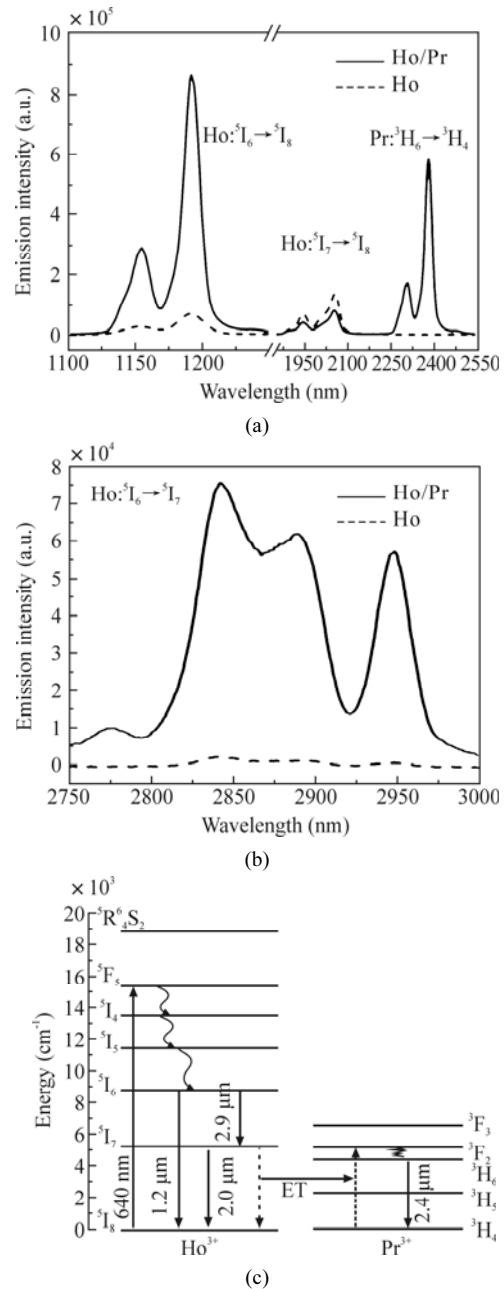


Fig.3 Infrared fluorescence spectra of $\text{Ho}^{3+}:\text{LiYF}_4$ and $\text{Ho}^{3+}/\text{Pr}^{3+}:\text{LiYF}_4$ crystals around (a) 1.2 μm , 2.05 μm , 2.4 μm and (b) 2.9 μm under excitation at 640 nm; (c) The energy level and energy transfer diagram when pumped at 640 nm

Under excitation at 640 nm, the measured decay curves for $\text{Ho}^{3+}:\text{I}_7 \rightarrow ^5\text{I}_8$ transition at 2059 nm and $^5\text{I}_6 \rightarrow ^5\text{I}_8$ transition at 1191 nm in $\text{Ho}^{3+}:\text{LiYF}_4$ and $\text{Ho}^{3+}/\text{Pr}^{3+}:\text{LiYF}_4$ samples are shown in Fig.4 and Fig.5, respectively.

In the Ho^{3+} singly doped LiYF_4 crystal, the fluorescent decays for $\text{Ho}^{3+}:\text{I}_7 \rightarrow ^5\text{I}_8$ and $^5\text{I}_6 \rightarrow ^5\text{I}_8$ transitions are well fitted into single-exponential decays. The fitting curves are shown in Fig.4(a) and Fig.5(a), and the fitted lifetime values of the $^5\text{I}_7$ and $^5\text{I}_6$ are 17.70 ms and 2.11 ms, respectively. The fluorescent decay of $\text{Ho}^{3+}:\text{I}_6 \rightarrow ^5\text{I}_8$ in $\text{Ho}^{3+}/\text{Pr}^{3+}:\text{LiYF}_4$ can also be fitted into single-exponential de-

cay shown in Fig.5(b), and the lifetime of the 5I_6 is 1.83 ms. When Pr^{3+} and Ho^{3+} are co-doped, energy transfer from $Ho^{3+}:^5I_7$ to $Pr^{3+}:^3F_2$ level takes place, and the decay curve of the $Ho^{3+}/Pr^{3+}:LiYF_4$ is non-exponential. The average experimental lifetime is given by^[18]

$$\tau_{avg} = \frac{\int I(t)tdt}{\int I(t)dt}, \quad (2)$$

where $I(t)$ is the luminescence intensity as a function of elapsed time t . With the introduction of Pr^{3+} , the measured lifetime of $Ho^{3+}:^5I_7$ manifold is 2.15 ms in the $Ho^{3+}/Pr^{3+}:LiYF_4$ crystal, which is 87.85% shorter compared with that for the $Ho^{3+}:LiYF_4$ crystal (17.70 ms). The measured lifetime of $Ho^{3+}:^5I_6$ level is 1.83 ms in the $Ho^{3+}/Pr^{3+}:LiYF_4$ crystal, which is 13.27% shorter than that for the $Ho^{3+}:LiYF_4$ crystal (2.11 ms). It confirms that the co-doping of Pr^{3+} ions has little influence on the higher laser level 5I_6 of Ho^{3+} , and depopulates the lower laser level $Ho^{3+}:^5I_7$ for 2.9 μm emission in $LiYF_4$ crystal, which are beneficial for the population inversion and laser operation.

The decay curve in Fig.4(b) is best described by the Inokuti-Hirayama (I-H) model^[19], which can be expressed as:

$$I_t = I_0 \exp\left[-\frac{t}{\tau_0} - \frac{4}{3}\pi\Gamma\left(1-\frac{3}{s}\right)R_0^3N\left(\frac{t}{\tau_0}\right)^{\frac{3}{s}}\right], \quad (3)$$

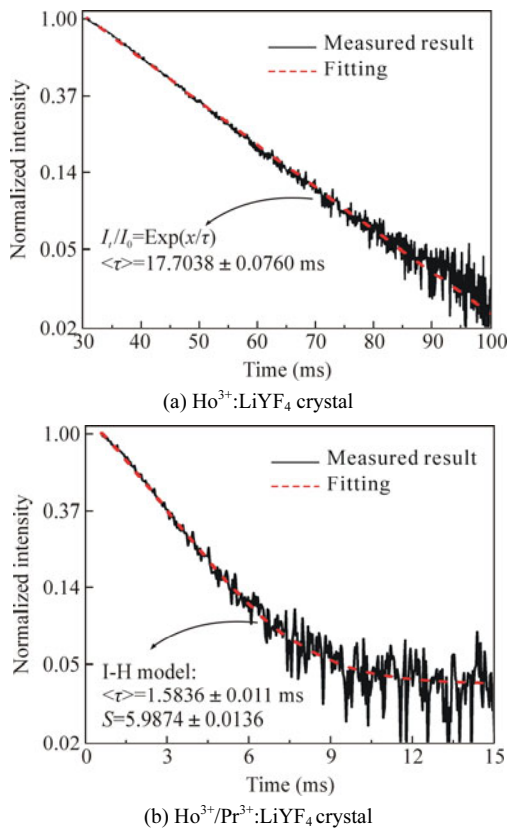


Fig.4 Fluorescence decay curves of (a) $Ho^{3+}:LiYF_4$ and (b) $Ho^{3+}/Pr^{3+}:LiYF_4$ crystals at 2059 nm under excitation at 640 nm

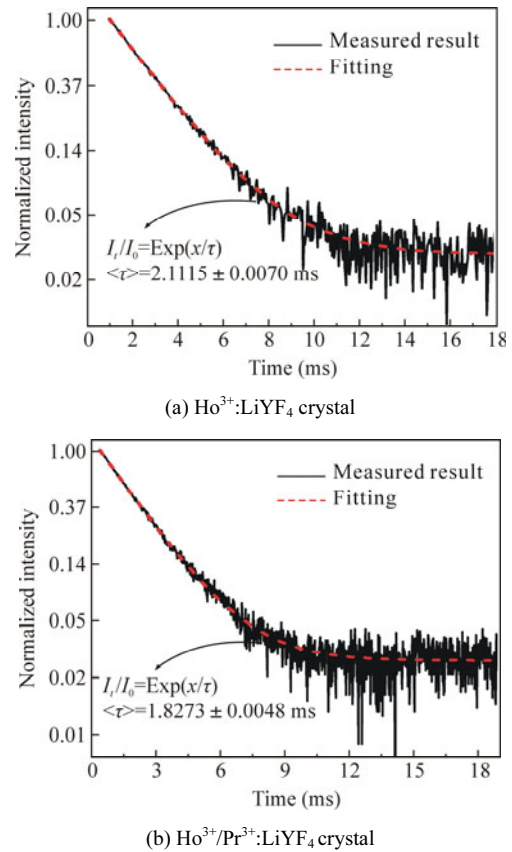


Fig.5 Fluorescence decay curves of (a) $Ho^{3+}:LiYF_4$ and (b) $Ho^{3+}/Pr^{3+}:LiYF_4$ crystals at 1191 nm under excitation at 640 nm

where I_t and I_0 represent the luminescence intensities during decay and when time is 0, respectively, τ_0 is the intrinsic radiative transition lifetime, $\Gamma(1-3/s)$ is a Gamma function, which denotes the electric dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions between luminescent centers when $s=6, 8$ and 10 , respectively, R_0 is the critical transfer distance, and N is the doping concentration. The fitting curve is shown in Fig.4(b). In the fitting processes, the value of s is assigned to about 5.9874, and it is very close to 6. It indicates that the energy transfer of electric dipole-dipole interaction is dominant in the Ho^{3+}/Pr^{3+} co-doped samples.

As discussed above, the energy transfer from the $Ho^{3+}:^5I_7$ level to the $Pr^{3+}:^3F_2$ level can depopulate the lower laser level $Ho^{3+}:^5I_7$ and make the 2.9 μm emission occur. The energy transfer efficiency can be estimated from the lifetime by^[20]

$$\eta_{ET} = 1 - \frac{\tau_{Ho/Pr}}{\tau_{Ho}}, \quad (4)$$

where $\tau_{Ho/Pr}$ and τ_{Ho} are the lifetime values monitored at 2059 nm in the Ho^{3+}/Pr^{3+} co-doped and Ho^{3+} singly doped samples, respectively. So the derived energy transfer efficiency is found to be 87.53%, indicating a quenching effect of $Pr^{3+}:^3F_2$ level on $Ho^{3+}:^5I_7$ level. It is favorable for obtaining 2.9 μm emission from $Ho^{3+}/Pr^{3+}:LiYF_4$ crystal.

In conclusion, $\text{Ho}^{3+}:\text{LiYF}_4$ and $\text{Ho}^{3+}/\text{Pr}^{3+}:\text{LiYF}_4$ single crystals are grown by a modified Bridgman method. The IR emission spectra and fluorescence decay curves are obtained under excitation at 640 nm. The energy transfer from $\text{Ho}^{3+}{}^5\text{I}_7$ level to $\text{Pr}^{3+}{}^3\text{F}_2$ level takes place in $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-existing crystal, which results in the depopulation of ${}^5\text{I}_7$ level and increases the emission at 2.9 μm . The fluorescence lifetime values of the higher and lower laser levels $\text{Ho}^{3+}{}^5\text{I}_6$, ${}^5\text{I}_7$ for Ho^{3+} singly doped and $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 crystals are investigated by using single exponential functions and the I-H model, and the transfer efficiency from Ho^{3+} to Pr^{3+} in $\text{Ho}^{3+}(1.02\%)/\text{Pr}^{3+}(0.22\%)$ co-doped LiYF_4 crystal is calculated. It is demonstrated that Pr^{3+} depopulates the $\text{Ho}^{3+}{}^5\text{I}_7$ level, and has little influence on the $\text{Ho}^{3+}{}^5\text{I}_6$ at the same time, which are both beneficial for the emission at 2.9 μm . It is suggested that the $\text{Ho}^{3+}/\text{Pr}^{3+}$ co-doped LiYF_4 crystal may be a good candidate for 2.9 μm IR laser media.

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