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# Ho<sup>3+</sup> / Tm<sup>3+</sup> 共掺 α-NaYF<sub>4</sub> 单晶体的光谱特性

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**摘 要:** 采用坩埚下降法生长出 Ho<sup>3+</sup> 离子掺杂浓度 ~ 1.90 mol%、Tm<sup>3+</sup> 不同掺杂离子浓度 (0.99 mol%, 1.58 mol%, 2.37 mol%, 3.16 mol%, 3.99 mol%, 7.19 mol%) 的双掺杂立方晶相 NaYF<sub>4</sub> 单晶体. 根据测定的吸收光谱以及 800 nm LD 波长激发下的发射光谱、发射截面和衰减曲线, 研究从 Tm<sup>3+</sup> 离子到 Ho<sup>3+</sup> 离子的能量传递机制、Tm<sup>3+</sup> 离子的浓度猝灭效应和 Ho<sup>3+</sup> 离子在 2.04 μm 波段的优化发光效应. 当 Ho<sup>3+</sup> 离子浓度保持为 ~ 1.90 mol% 不变, Tm<sup>3+</sup> 离子浓度从 0.99 mol% 增加到 1.59 mol% 时, 2.04 μm 波段的发射强度逐步增强; 当浓度从 1.59 mol% 增加到 7.19 mol% 时, 发射强度逐步减弱. Ho<sup>3+</sup> (1.90 mol%) / Tm<sup>3+</sup> (1.59 mol%) 共掺的单晶体的发射截面最大, 达到 2.17 × 10<sup>-20</sup> cm<sup>2</sup>, 其荧光寿命最长, 为 21.72 ms; 同时, 根据 Ho<sup>3+</sup> 离子的吸收截面和 Tm<sup>3+</sup> 离子的发射截面, 计算得到该样品从 Tm<sup>3+</sup> : <sup>3</sup>F<sub>4</sub> → Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> 稀土离子能量传递系数和 Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> → Tm<sup>3+</sup> : <sup>3</sup>F<sub>4</sub> 反传递系数分别为 C<sub>Tm-Ho</sub> = 24.14 × 10<sup>-40</sup> cm<sup>6</sup>/s, C<sub>Ho-Tm</sub> = 2.05 × 10<sup>-40</sup> cm<sup>6</sup>/s.

**关键词:** 光学材料; 光谱; α-NaYF<sub>4</sub> 单晶晶体; 浓度猝灭; 能量传递系数

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## Spectral Properties of Ho<sup>3+</sup> / Tm<sup>3+</sup> Co-doped α-NaYF<sub>4</sub> Single Crystals

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**Abstract:** Cubic NaYF<sub>4</sub> single crystals co-doped with ~ 1.90 mol% Ho<sup>3+</sup> and various Tm<sup>3+</sup> concentrations (0.99 mol%, 1.58 mol%, 2.37 mol%, 3.16 mol%, 3.99 mol%, 7.19 mol%) were grown by using the Bridgman method. The energy transfer from Tm<sup>3+</sup> to Ho<sup>3+</sup>, concentration quenching of Tm<sup>3+</sup> and the optimum fluorescence emission around 2.04 μm of Ho<sup>3+</sup> ion were investigated based on the measured absorption spectra, emission spectra, emission cross section and decay curves under excitation of 800 nm LD. The emission intensity at 2.04 μm increased with the increasing of Tm<sup>3+</sup> concentration from 0.99 mol% to 1.59 mol%, and decreased with the increasing of Tm<sup>3+</sup> concentration

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from 1.59 mol% to 7.19 mol% when the concentration of  $\text{Ho}^{3+}$  was held constantly at  $\sim 1.90$  mol%. Moreover, the maximum emission cross section reached to  $2.17 \times 10^{-20}$   $\text{cm}^2$  and the maximum fluorescence lifetime was 21.72 ms for  $\text{Ho}^{3+}$  (1.90 mol%)/ $\text{Tm}^{3+}$  (1.59 mol%) co-doped one. At the same time, the energy transfer coefficients of this sample were calculated based on the absorption cross-section of  $\text{Ho}^{3+}$  and the emission cross-section of  $\text{Tm}^{3+}$ , which is  $C_{\text{Tm-Ho}} = 21.14 \times 10^{-40}$   $\text{cm}^6/\text{s}$  and  $C_{\text{Ho-Tm}} = 2.05 \times 10^{-40}$   $\text{cm}^6/\text{s}$  respectively.

**Key words:** Optical material; Optical spectrum;  $\alpha$ - $\text{NaYF}_4$  single crystals; Concentration quenching; Energy transfer coefficients

**OCIS Codes:** 160.4760; 260.1180; 260.2160; 260.2510; 300.6340

## 0 Introduction

Recent years, the development of 2  $\mu\text{m}$  solid state lasers has attracted much attention due to their extensive applications including remote sensing, environment monitoring, military weapons, eye-safe laser radars et al.<sup>[1-3]</sup>. The rare earth doped crystals have been practically applied in fiber lasers and optical amplifiers because of its excellent properties<sup>[4-5]</sup>. Among rare earth ions, the transition  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  of  $\text{Tm}^{3+}$  ion is well known for generating lasers with  $\sim 2.0$   $\mu\text{m}$  radiation, which have been reported in  $\text{LiYF}_4$  and  $\text{LiLuF}_4$  crystals<sup>[6]</sup>. The transition  ${}^5\text{I}_7 \rightarrow {}^5\text{I}_8$  of  $\text{Ho}^{3+}$  ion has a markedly higher emission cross section than the transition  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  of  $\text{Tm}^{3+}$  ion<sup>[7]</sup>. The lifetime of  ${}^5\text{I}_7$  of  $\text{Ho}^{3+}$  ion is  $\sim 3.5$  ms<sup>[8]</sup>, which is beneficial to store the energy to transfer. Due to the near energy levels between  $\text{Tm}^{3+} : {}^3\text{F}_4$  and  $\text{Ho}^{3+} : {}^5\text{I}_7$ , the  $\text{Ho}^{3+}$  ion got energy through energy transfer from  $\text{Tm}^{3+}$  to  $\text{Ho}^{3+}$  under pumping of 800nm LD by the way of co-doped  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  ion. Compared with those oxide hosts, the fluoride hosts have the advantages of a lower phonon energy and reduced thermal lens effect<sup>[9]</sup>.

In order to gain highly efficient laser operation with a low phonon energy, most previous researches were investigated in many host materials. It is well known that the  $\text{NaYF}_4$  with a lower phonon energy ( $\sim 360$   $\text{cm}^{-1}$ )<sup>[10]</sup> and a good optical performance in the investigative host materials. The synthesis and application of doped  $\alpha$ - $\text{NaYF}_4$  has attracted much attention, especially the up-conversion of  $\alpha$ - $\text{NaYF}_4$  with a relatively high luminous efficiency<sup>[11-12]</sup>. This host material plays an important role for the doped trivalent rare-earth ions take the place of the  $\text{Y}^{3+}$  ion, and it can be used for the mid-IR solid state lasers because of a lower phonon energy and a higher optical transparency with a wide wavelength region from infrared to ultraviolet. By comparing the fluorides with the traditional oxides, the fluorides host crystal have a longer lifetime with the excited electronic states.

In this work,  $\text{Tm}^{3+}/\text{Ho}^{3+}$  co-doped  $\alpha$ - $\text{NaYF}_4$  crystal was grown by an improved Bridgman method.

The concentration of  $\text{Ho}^{3+}$  was constant, while that of  $\text{Tm}^{3+}$  was various to study the effect of concentration quenching. The optical spectra were tested and the rate of Tm-Ho transfer coefficient and back-transfer  $f$  coefficient or  $\alpha$ - $\text{NaYF}_4$  were calculated.

## 1 Experimental procedures

The preparation of the material was from commercially available  $\text{NaF}$ ,  $\text{YF}_3$  and  $\text{KF}$  (as a flux) powders of high purity (99.99%). The molar compositions of the raw materials were  $\text{NaF} : \text{KF} : \text{YF}_3 : \text{HoF}_3 : \text{TmF}_3 = 30 : 18 : 51 - \chi : 1 : \chi$  ( $\chi = 0.5, 0.8, 1.2, 1.6, 2.0, 3.6$ ) and  $\text{NaF} : \text{KF} : \text{YF}_3 : \text{HoF}_3 = 30 : 18 : 51 : 1$ . The obtained samples were named, respectively, as Sample 1 to Sample 7. The detailed process of growth and schematic of apparatus used for the experiment have been reported before<sup>[13]</sup>.

The grown crystal with about  $\phi 10$  mm  $\times$  71 mm is shown in Fig. 1(a). The crystals were sliced into pieces and polished to be about 2.0 mm-thickness for the optical measurements. The crystal structure was performed by X-Ray Diffraction (XRD) pattern, with XD-98X diffractometer (XD-3, Beijing). The concentrations of  $\text{Ho}^{3+}$  and  $\text{Tm}^{3+}$  in these samples were confirmed severally with an Inductively Coupled Plasma (ICP) atomic emission spectroscopy (ICP-AES, PerkinElmer Inc., Optima 3000). The measured concentrations are listed in Table 1. The absorption spectra were measured with a Cary 5000 UV/VIS/NIR spectrophotometer in the wavelength region from 200 nm to 2500 nm. The emission spectra were recorded under the excitation of 800 nm LD by a Triax 320 spectrometer in the wavelength range of 1000-2200 nm. The fluorescence lifetimes were obtained with the FLSP920 fluorescence spectrophotometer. All the measurements were carried out at a room temperature under the room temperature.

**Table 1** Concentration of  $\text{Ho}^{3+}$  ions and  $\text{Tm}^{3+}$  ions in these samples (mol%)

Ions (at%)	Samples						
	1	2	3	4	5	6	7
$\text{Ho}^{3+}$	1.99	1.99	1.99	1.99	1.99	1.99	1.99
$\text{Tm}^{3+}$	0.99	1.58	2.37	3.16	3.99	7.19	0

## 2 Results and discussion

### 2.1 X-ray diffraction

The measured XRD pattern for Tm<sup>3+</sup>/Ho<sup>3+</sup> co-doped α-NaYF<sub>4</sub> crystal (Sample 2) is presented in Fig. 1(b). The pattern appearing in JCPDS card No. 77-2042 for α-NaYF<sub>4</sub> is also shown in Fig. 1(c) for comparison. By comparing the patterns in Fig. 1, it is believed that all the diffraction peak positions of the obtained sample doped with Tm<sup>3+</sup>/Ho<sup>3+</sup> ions are matched perfectly with those in standard α-NaYF<sub>4</sub>, and there are no any other peaks belong to impurity phase, which indicates that the obtained transparent crystals are cubic phase α-NaYF<sub>4</sub>.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

According to Eq. (1)<sup>[14]</sup>, the cell parameters of Sample 5 were calculated to be  $a=b=c=0.5457$  nm.

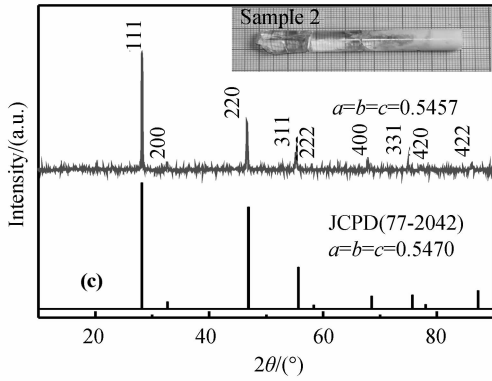


Fig. 1 XRD pattern of the α-NaYF<sub>4</sub> : Tm<sup>3+</sup>/Ho<sup>3+</sup> and the standard line pattern of the cubic phase NaYF<sub>4</sub>

### 2.2 Absorption spectra

Fig. 2 shows the absorption spectra of Tm<sup>3+</sup>/Ho<sup>3+</sup> co-doped α-NaYF<sub>4</sub> samples as a function of Tm<sup>3+</sup> concentration. The characteristic absorption bands corresponding to the transition of Tm<sup>3+</sup> and Ho<sup>3+</sup> from the ground state to the excited ones are marked in spectra. As we can see from the Fig. 2, the corresponding absorption coefficient is proportional to the Tm<sup>3+</sup> doping concentration. The absorption coefficient of samples get stronger and stronger with the increasing of Tm<sup>3+</sup> doping concentration. Compared with the absorption spectra of Ho<sup>3+</sup> and Tm<sup>3+</sup> single doped α-NaYF<sub>4</sub> crystals<sup>[15-16]</sup>, the Fig. 2 shows that the peaks of Ho<sup>3+</sup> and Tm<sup>3+</sup>, and the position of all absorption peaks do not change any more, which means that the absorption spectra of Tm<sup>3+</sup>/Ho<sup>3+</sup> co-doped α-NaYF<sub>4</sub> crystals is the superposition of Ho<sup>3+</sup> and Tm<sup>3+</sup> single doped α-NaYF<sub>4</sub> crystals.

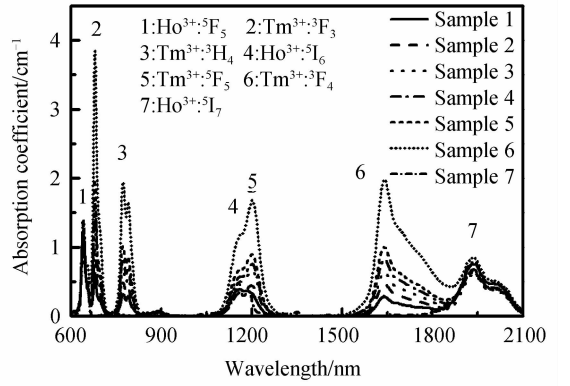


Fig. 2 Absorption spectra of Ho<sup>3+</sup> single doped and Tm<sup>3+</sup>/Ho<sup>3+</sup> co-doped α-NaYF<sub>4</sub> single crystals

### 2.3 Emission spectra and concentration quenching

The energy transfer process between Tm<sup>3+</sup> and Ho<sup>3+</sup> and cross-relaxation of Tm<sup>3+</sup> ions LiYF<sub>4</sub> is reported by some studies<sup>[17]</sup>. From these studies, we know that Ho<sup>3+</sup> ions get energy from Tm<sup>3+</sup> ions. The two emission bands at 1 948 and 2 052 nm are corresponded to the transition of splitting of the energy level Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> ground state. Fig. 3 illustrates the emission spectra of the Ho<sup>3+</sup> ions single doped and Tm<sup>3+</sup>/Ho<sup>3+</sup> ions co-doped α-NaYF<sub>4</sub> crystal samples excited by 808 nm LD. The intensity of Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> at 2 052 nm and 1 948 nm increases with the Tm<sup>3+</sup> doping concentration from 0.99 mol% (Sample 1) to 1.59 mol% (Sample 2), but it is obviously found that the intensity decreases quickly with the increasing of Tm<sup>3+</sup> doping concentration from 1.59 mol% (Sample 2) to 7.19 mol% (Sample 6), which means that the energy from Tm<sup>3+</sup> to Ho<sup>3+</sup> ions get less and less. All of these changes of emission spectra are exactly caused by the concentration quenching of Tm<sup>3+</sup> ions. With the increasing of Tm<sup>3+</sup> doping concentration from 1.59 mol% to 7.19 mol%, the effect of concentration quenching become stronger at Tm<sup>3+</sup> : <sup>3</sup>F<sub>4</sub> level. With the constant doping concentration of

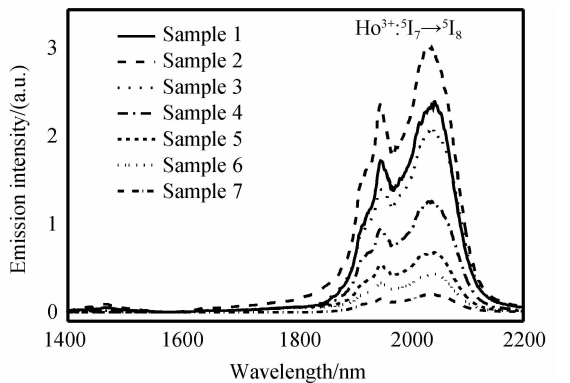


Fig. 3 Emission spectra of Ho<sup>3+</sup> single doped and Tm<sup>3+</sup>/Ho<sup>3+</sup> co-doped α-NaYF<sub>4</sub> single crystals upon excitation of 808 nm LD

Ho<sup>3+</sup> ions, the best doping concentration of Tm<sup>3+</sup> ions is 1.59mol% from the Fig. 3, in which of the situations the emission intensity of Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> at 2.052 nm and 1.948 nm shows the best performance in all samples.

### 2.4 Stimulated absorption and emission cross section

According to the absorption spectra, the transition cross-section of Tm<sup>3+</sup> ion from <sup>3</sup>F<sub>4</sub> level and Ho<sup>3+</sup> from <sup>5</sup>I<sub>7</sub> can be calculated. The absorption cross-section ( $\sigma_{\text{abs}}$ ) can be determined by<sup>[18]</sup>

$$\sigma_{\text{abs}}(\lambda) = \frac{2.303 \log(I_0/D)}{NL} = \frac{\alpha}{N} \quad (2)$$

where  $\log(I_0/D)$  is the optical density as a function of wavelength,  $N$  is the Tm<sup>3+</sup> ions concentration of sample, and  $L$  is the thickness of the polished sample, and  $\alpha$  is the absorption coefficient.

According to the Futchbauer-Ladenburg theory<sup>[19]</sup>, the simulated emission cross-section based on fluorescence spectrum for Tm<sup>3+</sup> from <sup>3</sup>F<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transition and for Ho<sup>3+</sup> from <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> transition is determined by the following formula<sup>[19]</sup>

$$\sigma_{\text{em}}(\lambda) = \frac{\lambda^5 I(\lambda) \beta}{8\pi n^2 c \tau_{\text{rad}} \int \lambda I(\lambda) d\lambda} \quad (3)$$

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

Fig. 4 gives the emission cross-section from 1.4 μm to 2.2 μm corresponding to the transition Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub>. One can be sure is that the maximum absorption cross-section  $\sigma_{\text{abs}}$  is got from the Sample 6 from the absorption spectra, which means that the higher concentration of Tm<sup>3+</sup> is benefit for the absorption. The maximum value of  $\sigma_{\text{abs}}$  is  $0.82 \times 10^{-20} \text{ cm}^2$  lying at the wavelength of 1.642 μm. From the emission cross-section, we can find that, the value  $\sigma_{\text{em}}$  gets larger with the increasing of concentration of the Tm<sup>3+</sup> from Sample 1 to Sample 2, and gradually become smaller with the continuous increasing of concentration of the Tm<sup>3+</sup> from Sample 2 to Sample 6. The result perfectly shows the concentration quenching of Tm<sup>3+</sup> ions. With the concentration of Tm<sup>3+</sup> increasing, the effect of the concentration quenching

becomes greater, resulting in the energy from Tm<sup>3+</sup> to Ho<sup>3+</sup> smaller and smaller. The maximum emission cross-section is got from the sample 2, and value is  $2.17 \times 10^{-20} \text{ cm}^2$  lying at the wavelength of 2.044 μm. From the result we discuss above, we can find that an appropriate co-doping concentration of Tm<sup>3+</sup>/Ho<sup>3+</sup> is vital to get more suitable materials for 2.0 μm laser application.

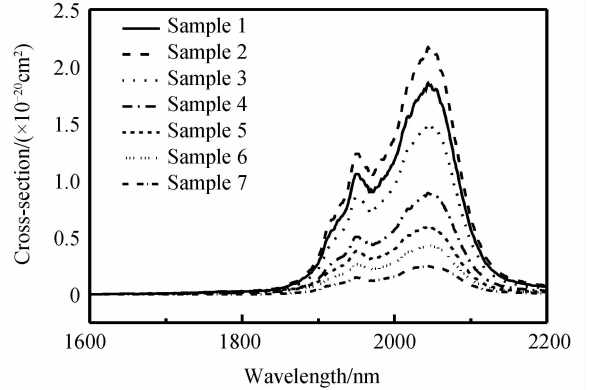


Fig. 4 Emission cross-section of Tm<sup>3+</sup>/Ho<sup>3+</sup> co-doped  $\alpha$ -NaYF<sub>4</sub> samples of Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> transition

### 2.5 Coefficients of the energy transfer

Efficiency of energy transfer from Tm<sup>3+</sup> : <sup>3</sup>F<sub>4</sub> level to Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> level and its back process deeply affects the performance of Tm-Ho laser. These transfer coefficients can be calculated from the emission and absorption cross sections with the following formulas<sup>[20]</sup>

$$C_{\text{Tm} \rightarrow \text{Ho}} = \frac{9x^2 c}{16\pi^4 n^2} \int \sigma_{\text{abs, Ho}}(\lambda) \sigma_{\text{em, Tm}}(\lambda) d\lambda \quad (4)$$

$$C_{\text{Ho} \rightarrow \text{Tm}} = C_{\text{Tm} \rightarrow \text{Ho}} \exp\left(\frac{E_{\text{ZL}, x} - E_{\text{ZL}, x}}{kT}\right) \quad (5)$$

where  $x^2$  is a quantity that includes the orientational average and is usually taken to be 2/3,  $c$  is the speed of light,  $n$  is the refraction index,  $\sigma_{\text{abs, Ho}}$  is the absorption cross-section of Ho<sup>3+</sup> : <sup>5</sup>I<sub>7</sub> level and  $\sigma_{\text{em, Tm}}$  is the emission cross-section of Tm<sup>3+</sup> : <sup>3</sup>F<sub>4</sub> level, and  $E_{\text{ZL}, x}$  is the zero phonon line of Tm or Ho ion. The values of Sample 2 obtained for the Tm-Ho and Ho-Tm transfer coefficients are  $C_{\text{Tm} \rightarrow \text{Ho}} = 24.14 \times 10^{-40} \text{ cm}^6/\text{s}$  and  $C_{\text{Ho} \rightarrow \text{Tm}} = 2.05 \times 10^{-40} \text{ cm}^6/\text{s}$ , and these values are the best of all that of the samples.

Table 2 Tm-Ho energy transfer coefficients for  $\alpha$ -NaYF<sub>4</sub> and other laser crystals

Crystals	$C_{\text{Tm} \rightarrow \text{Ho}} / (\times 10^{-40} \text{ cm}^6 \cdot \text{s}^{-1})$	$C_{\text{Ho} \rightarrow \text{Tm}} / (\times 10^{-40} \text{ cm}^6 \cdot \text{s}^{-1})$	$C_{\text{Tm} \rightarrow \text{Ho}} / C_{\text{Ho} \rightarrow \text{Tm}}$	Refs.
YSGG	17	0.7	24.3	[21]
YLF	16.9	1.2	13.6	[22]
YAG	10.9	1.1	9.5	[22]
Gd <sub>3</sub> Ga <sub>5</sub> O <sub>12</sub>	10.5	0.3	35	[23]
LYF	14.9	1.4	10.6	[14]
$\alpha$ -NaYF <sub>4</sub>	24.14	2.05	11.8	This work

In the Table 2, the Tm-Ho and Ho-Tm energy transfer coefficients in different hosts are compared. The table reveals that the energy transfer coefficient  $C_{\text{Tm-Ho}}$  of  $\alpha\text{-NaYF}_4$  is higher than YSGG, LYF, YLF, YAG and  $\text{Gd}_3\text{Ga}_5\text{O}_{12}(\text{Ca}, \text{Zr})$ . The ratio between the back-transfer Ho-Tm coefficient and that of the direct Tm-Ho energy transfer process is about 11.8.

A high value of this ratio is an important condition for an efficient  $2\ \mu\text{m}$  laser of  $\text{Ho}^{3+}$  ions. It is worth noting that Tm/Ho:  $\alpha\text{-NaYF}_4$  shows a value of this ratio that is comparable with that of LYF and YLF, but lower than that observed in YSGG, and YLF. However, in these later hosts, the value of the direct energy transfer process is much smaller than that of Tm/Ho:  $\alpha\text{-NaYF}_4$ . Therefore, Tm/Ho:  $\alpha\text{-NaYF}_4$  is a promising material for the realization of efficient diode pumped laser devices.

## 2.6 Fluorescence decay curves

Fig. 5 gives the decay curves and the fitted values of  $\text{Tm}^{3+}/\text{Ho}^{3+}$  co-doped  $\alpha\text{-NaYF}_4$  samples observed at  $1.8\ \mu\text{m}$  with  $\text{Tm}^{3+}$  variation. And Fig. 6 shows the decay curves and the fitted values of  $\text{Tm}^{3+}/\text{Ho}^{3+}$  co-doped  $\alpha\text{-NaYF}_4$  samples observed at  $2.052\ \mu\text{m}$  with  $\text{Tm}^{3+}$  variation. We found that both the decay curves can be described by a single exponential decay by fitting. As the  $\text{Tm}^{3+}$  concentration increased from 1.59 mol% (Sample 2) to 7.19 mol% (Sample 6), the lifetime of  $\text{Tm}^{3+} : ^3\text{F}_4$  state decreased from 21.40 ms to 16.02 ms in Fig. 5, and the lifetime of  $\text{Ho}^{3+} : ^5\text{I}_7$  state decreased from 21.72 ms to 15.47 ms in Fig. 6. It means that the higher the  $\text{Tm}^{3+}$  concentration, the smaller the lifetime of  $\text{Tm}^{3+} : ^3\text{F}_4$  state from Sample 2 to Sample 6. This phenomenon can be explained by two ways. One is the complicated energy transfer process, and the other is the concentration quenching. While in Fig. 6, the lifetime of  $\text{Ho}^{3+} : ^5\text{I}_7$  state doesn't increase

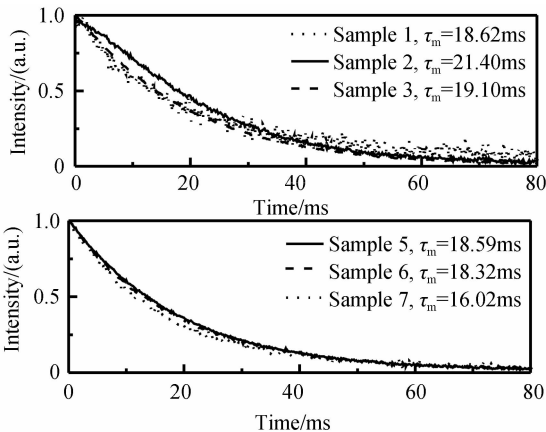


Fig. 5 Decay curves of 1.99 mol%  $\text{Ho}^{3+}/x$  mol%  $\text{Tm}^{3+}$  ( $x=0.99, 1.58, 2.37, 3.16, 3.99, 7.19$ ) co-doped  $\alpha\text{-NaYF}_4$  crystal samples monitored at  $1.8\ \mu\text{m}$  under 800nm LD excitation

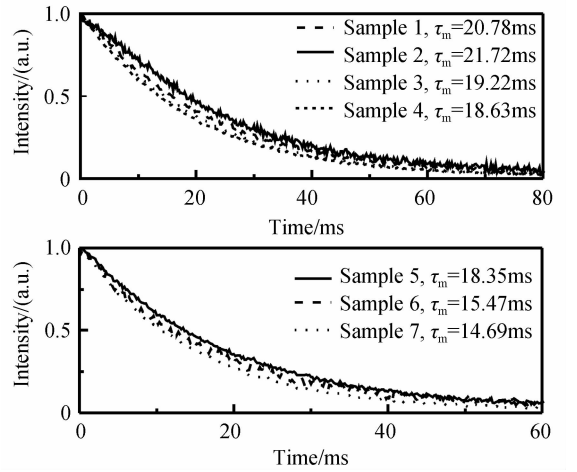


Fig. 6 Decay curves of 1.99 mol%  $\text{Ho}^{3+}/x$  mol%  $\text{Tm}^{3+}$  ( $x=0.99, 1.58, 2.37, 3.16, 3.99, 7.19$ ) co-doped  $\alpha\text{-NaYF}_4$  crystal samples monitored at  $2.052\ \mu\text{m}$  under 800nm LD excitation

monotonously with the  $\text{Tm}^{3+}$  doping level rising. On the contrary, the lifetime decreases, which means that the higher  $\text{Tm}^{3+}$  doping level doesn't lead to the higher energy transfer efficiency from  $\text{Tm}^{3+}$  to  $\text{Ho}^{3+}$ . On the other hand, the effect of concentration quenching gets greater with the  $\text{Tm}^{3+}$  doping level increasing. The largest life time of  $\text{Tm}^{3+} : ^3\text{F}_4$  state and  $\text{Ho}^{3+} : ^5\text{I}_7$  are 20.40ms and 21.72ms, both of them coming from the Sample 2, 0.99 mol%  $\text{Ho}^{3+}/1.59$  mol%  $\text{Tm}^{3+}$ .

## 3 Conclusions

The  $\text{Tm}^{3+}/\text{Ho}^{3+}$  co-doped  $\alpha\text{-NaYF}_4$  crystals were grown by the improved Bridgman methods. Luminescence spectra and fluorescent decays have been recorded to prove the effect of concentration quenching of  $\text{Tm}^{3+}$ . Under excitation of 800 nm LD, we obtained the best optimum fluorescence emission of  $\text{Ho}^{3+}$  around  $2.052\ \mu\text{m}$  when the concentration of  $\text{Ho}^{3+}$  ions is 1.99 mol% and concentration of  $\text{Tm}^{3+}$  is 1.59 mol% in all  $\alpha\text{-NaYF}_4$  crystal samples, in which case the maximum emission cross-section of is as high as  $2.17 \times 10^{-20}\ \text{cm}^2$  and the lifetime of  $\text{Ho}^{3+} : ^5\text{I}_7$  state is 21.72ms, and the energy transfer coefficients is  $C_{\text{Tm-Ho}} = 24.14 \times 10^{-40}\ \text{cm}^6/\text{s}$  and  $C_{\text{Ho-Tm}} = 2.05 \times 10^{-40}\ \text{cm}^6/\text{s}$  respectively. Hence, due to the great optical parameters for these  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  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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