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SPECTROSCOPIC INVESTIGATION ON THE PROPERTIES OF VISIBLE AND NEAR INFRARED EMISSIONS IN Tm^{3+}, Ho^{3+} Co-DOPED YVO_4 CRYSTALS

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With the help of absorption and fluorescence spectra, the spectroscopic properties of Tm^{3+}, Ho^{3+}:YVO_4 crystals have been investigated under different dopant concentrations. The absorption results show that the maximum absorption in the spectral range of currently available powerful laser diodes (LD) is at 796 nm, corresponding to the transition $^3H_6 \rightarrow {}^3H_4$ of Tm^{3+} in the crystals. Upon the excitation with a LD at 808 nm, we have detected ten fluorescence bands in the spectral range spanning from visible to infrared. In visible region 4 upconversion bands have been observed centered at 475, 547, 660, and 701 nm. Discussions of the energy transfer processes suggest that cross relaxations and excited absorptions with the involvement of Tm^{3+} $^3F_4$, $^3H_5$ and Ho^{3+} $^7I_5$ states are responsible for the four upconversion emissions. Comprising the relative integrated intersities of 2 μm (Ho^{3+}: $^5I_7 \rightarrow {}^5I_8$) and 1.8 μm (Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$) bands we have observed an efficient energy transfer from Tm^{3+} ($^3F_4$) to Ho^{3+} ($^5I_7$). Examination of the ratios of the intensity of 2 μm band to that of 1.8 μm band as a function of the ratios of Tm^{3+} concentration (c_{Tm}) to Ho^{3+} concentration (c_{Ho}) indicates that small concentration ratios (c_{Tm}/c_{Ho}) lead to high efficient energy transfers of $Tm^{3+}(^3F_4) \rightarrow Ho^{3+}(^5I_7)$.

PACC: 7820; 7860

I. INTRODUCTION

The increasing demands for high power lasers operating in eye-safe spectral regions have fostered renewed interest in crystals co-doped with Tm and Ho to be used as active media in laser diodes (LD) pumped solid-state lasers.[1,2] With these crystals, 2 μm lasers can be realized through the transition from the first excited state $^5I_7$ to the ground state $^5I_8$ of Ho^{3+} ions. Sensitization of these ions occurs via energy transfer from Tm^{3+} ions, which can be efficiently optically pumped with commercially available high power LD in 800 nm spectral region. Up to present, yttrium aluminum garnet (YAG) and yttrium lithium fluoride (YLF) have been recognized as two of the most interesting crystals for efficient laser operation.[3,4] Most recently, Elder *et al.*[5] have also demonstrated a 2 μm laser operation in a Tm, Ho: YAP crystal.

Yttrium vanadate (YVO_4) has been proved to be an interesting host for LD pumping when doped with Nd^{3+}.[6,7] In 1992, Saito *et al.*[8] have also obtained a better 2 μm laser activity in Tm^{3+}: YVO_4 over that in Tm: YAG. However, to our best knowledge, investigations on the spectroscopic and lasing properties of Tm^{3+}, Ho^{3+} co-doped YVO_4 crystals have not been published in literatures so far. We report here an experimental investigation on the spectroscopic properties of Tm^{3+}, Ho^{3+}: YVO_4 crystals. Especially, we have emphasized on the influence of doping concentrations on the fluorescent emissions, particularly the 2 μm band. The energy transfer processes involved in the emissions have also been discussed.

II. EXPERIMENTAL

In our experiment, four crystals with different concentrations have been investigated. The samples were numbered as in Table 1, within which the concentrations, thicknesses (along *a*-axis of the crystals) and the peak absorption coefficients at 796 nm are listed. Absorption spectra have been performed using a Cary 2390 spectrophotometer. The fluorescence measurements have been carried out with a 25 cm monochromator mounted with proper gratings corresponding to different spectral range. Luminescences were excited by a LD at 808 nm with its polarization parallel to the c-axis of the crystals. The emissions from the crystals were collected perpendicular to the laser beam and

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detected with an R943-02 photomultiplier and a PbS detector for visible and infrared spectral regions respectively. The fluorescent signals were then fed to a SR 510 lock-in amplifier that was interfaced with a computer. The luminescence data were corrected for the different grating and detector responses with a tungsten calibration lamp. All the measurements were carried out at room temperature.

Table 1. The parameters of the four samples and their peak absorption coefficients at 796 nm.

Serial number of the samples	1#		2#		3#		4#	
	Tm^{3+}	Ho^{3+}	Tm^{3+}	Ho^{3+}	Tm^{3+}	Ho^{3+}	Tm^{3+}	Ho^{3+}
Dopant concentrations (at%)	1.53	2.70	3.16	2.85	4.76	2.97	7.49	5.15
Tickness of the samples/cm	0.206		0.204		0.202		0.202	
Absorption coefficients of the transition Tm^{3+}: $^3H_4 \leftarrow {}^3H_6$(796 nm) /(cm^{-1})	2.87		5.06		7.25		11.06	

Ⅲ. RESULTS AND DISCUSSIONS

A. The absorption band near 800 nm

In order to facilitate comprehension, an indicative energy level diagram for Tm^{3+} and Ho^{3+} ions in YVO_4, with positions for the multiplets, is depicted in Fig.1. The spectroscopic features reported in Fig.1 will be discussed afterwards.

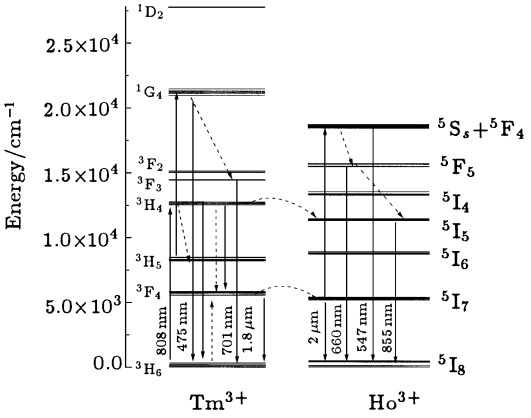


Fig.1. Indicative energy levels of Tm^{3+}, and Ho^{3+} in YVO_4 crystal showing the fundamental spectroscopic features discussed in the text.

In near infrared region, the absorption band corresponding to the transition Tm^{3+}: $^3H_6 \rightarrow {}^3H_4$ near 800 nm is of interest for optical pumping with currently available powerful laser diode. Figure 2 shows the absorption spectra of this band for the four samples with different dopant concentrations. The peak absorption coefficients are summarized in Table 1. It can be seen that in YVO_4 crystal the maximum absorption is at 796 nm, compared with those in YLF and YAG as 780 nm and 785.5 nm[9] for the Tm^{3+}, Ho^{3+} Co-doping crystals. According to Falconieri's results,[9] the peak coefficients of $^3H_6 \rightarrow {}^3H_4$ transition in YLF and YAG are 6.64 and 6.3 cm^{-1}, at the Tm^{3+} concentrations of 5.4 at% and 5.75 at%, respectively. In YVO_4, an absorption coefficient of 7.25 cm^{-1} was obtained at Tm^{3+} concentration of 4.76 at% in our measurement. This result probably implies that a relatively more efficient LD pumping can be expected in Tm^{3+}, Ho^{3+}: YVO_4 crystals.

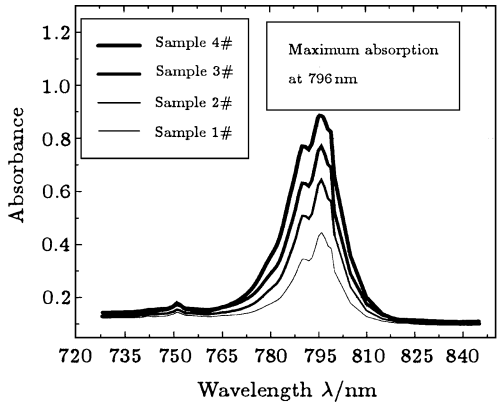


Fig.2. The absorption band corresponding to the transition $^3H_6 \rightarrow {}^3H_4$ of Tm^{3+} in Tm^{3+}, Ho^{3+}: YVO_4 for the samples with different combinations of Tm^{3+}- and Ho^{3+}-concentrations.

B. Fluorescence spectra

In the spectral range of 400–2300 nm, we have observed up to ten emission bands from the crystals under the excitation of a LD at 808 nm. The emission spectrum of sample 4# is displayed in Fig.3 with its emission bands identified as in Table 2.

Table 2. Observed emission bands and the corresponding transitions in Tm^{3+}, Ho^{3+}: YVO_4 alter excitation with a 808 nm LD.

Spectral range of the emission band/nm	Peak emission intensity wavelength/nm	Relative Intensities (Normalized to that of 701 nm band for visible range, and to that of 2 μm band for infrared range)	Transitions	
			Tm^{3+}	Ho^{3+}
467–484	475	0.05	$^1G_4 \rightarrow ^3H_6$	
533–558	547	0.15		$^5S_2+^5F_4 \rightarrow ^5I_8$
641–667	660	0.07		$^5F_5 \rightarrow ^5I_8$
677–728	701	1	$^3F_3 \rightarrow ^3H_6$	
776–831	799	–	$^3H_4 \rightarrow ^3H_6$	
876–882	879	–		$^5I_5 \rightarrow ^5I_8$
1146–1224	1192	0.002	$^5H_5 \rightarrow ^3H_6$	$^5I_6 \rightarrow ^5I_8$
1370–1550	1482	0.05	$^3H_4 \rightarrow ^3F_4$	
1690–1890	1820	0.22	$^3F_4 \rightarrow ^3H_6$	
1890–2210	2020	1		$^5I_7 \rightarrow ^5I_8$

1. *Visible emissions.* As shown in Fig.3 and Table 2, 4 emission bands have been observed in visible region. With a consideration of the spectral data summarized in Kaminskii's book,[10] similarly as in YLF and YAG,[9] the transition of Tm^{3+}: $^1G_4 \rightarrow ^3H_6$ is identified as responsible for the blue emision band near 475 nm. To excite $^1G_4$ state, the most resonant of possible processes includes interaction of $^3H_5$ states with either ions in $^3H_4$ state or the pump photons. From the concentration-dependent fluorescence spectra (Fig.4) it can be seen that the intensities of the 475 nm band decrease as Tm^{3+} concentration increases, especially severely at higher concentrations. This clearly suggests that there exists a competition between radiative or nonradiative decays from $^4H_3$ to $^3H_5$ and cross-relaxations of Tm^{3+} ions in $^3H_4$ manifold, which become dominant at high Tm^{3+} concentrations.

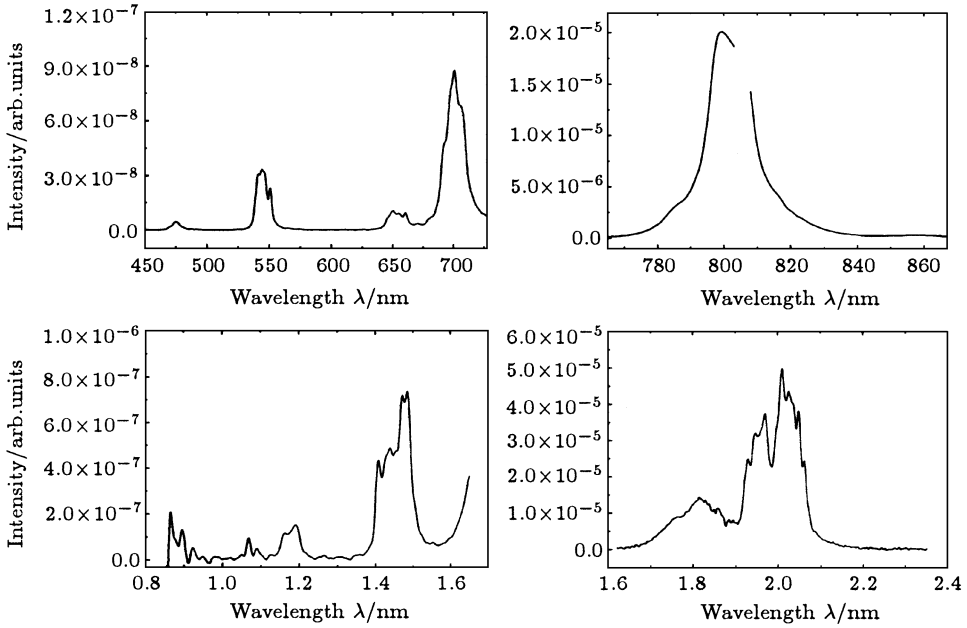


Fig.3. Emission spectrum of Tm^{3+}, Ho^{3+}: YVO_4 crystal at concentrations of 7.49 at% for Tm^{3+} and 5.15 at% for Ho^{3+} under the excitation of a 808 nm LD.

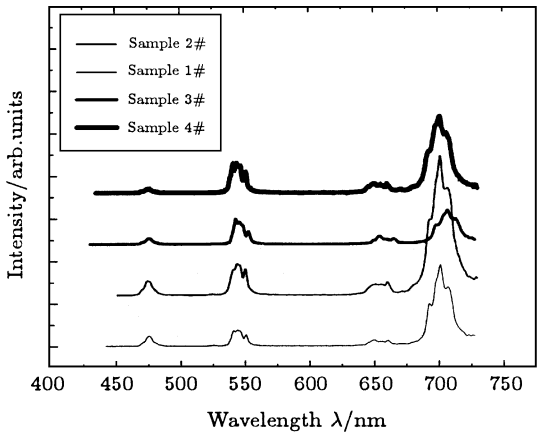


Fig.4. The concentration dependent emissions in visible range of Tm^{3+}, Ho^{3+}: YVO_4 crystals.

Also from Fig.4, we can see that the green band in the range of 533–558 nm does not change its intensity more obviously as the dopant concentration changes. Referring to the spectral data of Ho^{3+} ion and its concentration-dependent feature we identify this band as contributed by the transition of Ho^{3+}: $^5S_2$+$^5F_4$ $\rightarrow$$^5I_8$. There are two possible ways to populate the mixture state $^5S_2$+$^5F_4$ of Ho^{3+}.[9,11,12] The first one is a so-called co-operative energy transfer (COE). A Tm^{3+} ion in $^3H_4$ state interacting with one in ground state $^3H_6$ allows the latter to rise to $^3F_4$ state and the former itself descends to $^3F_4$ state. Thus, two Tm^{3+} ions on $^3F_4$ have been obtained for one absorbed pump photon. Ho^{3+} $^5I_7$ state gets populated through nearly resonant energy transfer between it and Tm^{3+} $^3F_4$ state. Ho^{3+} ions on $^5I_7$ state will then interact with Tm^{3+} ions on $^3H_4$ state, which leads Ho^{3+} ions to be further excited to the mixture state $^5S_2$+$^5F_4$ so that the green upconversion band is emitted as a result of transition $^5S_2$+$^5F_4$ $\rightarrow$$^5I_8$. The $^5I_7$ state is a metastable state of Ho^{3+} with a lifetime in the order of ms (e.g., 6 ms in YAG[12]) and a well energy match between the transition $^5I_7$ $\rightarrow$$^5S_2$+$^5F_4$ and the pump photons exists, therefore excited state absorption (ESA) can also occur. Thus Ho^{3+} ion on $^5I_7$ directly absorbs a pump photon and is excited to $^5S_2$+$^5F_4$ state. It should be noted that COE processes should have a concentration dependence, but this has not been apparently reflected by Fig.4. This result probably implies that the green band should be contributed by COE and ESA simultaneously and a backtransfer from Ho^{3+} $^5I_7$ state to Tm^{3+} $^3F_4$ may come out at higher doping concentrations.

In the visible range we have observed two red bands centered at 660 and 701 nm, respectively (see Figs.3 and 4). As shown in Fig.4, the 660 nm band has relatively weak intensity for the four samples investigated. According to its spectral range, transitions possibly contributing to it should include Ho^{3+}: $^5F_5$$\rightarrow$$^5I_8$, Tm^{3+}: $^1G_4$$\rightarrow$$^3F_4$ and Tm^{3+}: $^3F_2$$\rightarrow$$^3H_6$. If it stemmed from the two transitions of Tm^{3+}, it would have a similar concentration dependence as the blue band. But its concentration dependence is much different from the blue band's and similar to the green band's, as shown in Fig.4. This result suggests that the 660 nm band is mainly contributed by the transition of Ho^{3+}: $^5F_5$ $\rightarrow$$^5I_8$. The Ho^{3+} $^5F_5$ state can be excited with the help of relaxation from $^5S_2$+$^5F_4$. The 701 nm band is identified as the contribution of transition Tm^{3+}: $^3F_3$ $\rightarrow$$^3H_6$. It can be seen from Fig.4 that this band fluoresces relatively weak at high concentrations (Sample $3^{\#}$ and $4^{\#}$) and intensively at low concentrations (Sample $1^{\#}$ and $2^{\#}$). This probably means that a competition comes out between the cross-relaxation $^3H_4$+$^3H_6$ $\rightarrow$ 2^3F_4+phonons and the downward relaxation from $^3H_4$ to $^3H_5$.

2. *Infrared emissions* In the infrared region we have observed six emission bands (see Fig.3 and Table 2). As shown in Fig.3, the fluorescence from the same upper state $^3H_4$ as the pump transition centers at 799 nm. The gap near 808 nm in the profile of the band is brought by the deleted pump laser line. The intensity of this band has a strong concentration dependence as presented in Fig.5. From Fig.5, a considerable decrease of the emission intensity can be found

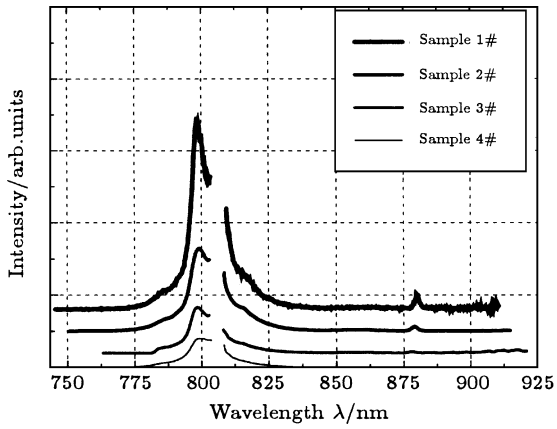


Fig.5. The concentration dependent spectra of 799 nm emission band. The doping concentration increases with the increasing sample number from $1^{\#}$ to $4^{\#}$. The concentrations of the four samples can be found in Table 1.

with increasing doping concentration. This further confirms that a serious cross relaxation depopulates $^3H_4$ state. It is also observed that the 879 nm band resulted from Ho^{3+}: $^5I_5$ $\rightarrow$$^5I_8$ transition. Obviously this band has a similar concentration dependence as the

799 nm band. Therefore, this feature probably means that the Ho^{3+} $^5I_5$ state is populated dominantly by a direct cross relaxation from Tm^{3+} $^3H_4$ to Ho^{3+} $^5I_5$ state for the closeness of the two states.

The most interesting band in the infrared region is the 2 μm band corresponding to the transition of Ho^{3+}: $^5I_7 \rightarrow {}^5I_8$. It is with this transition that 2 μm lasers have been realized in some Tm^{3+}, Ho^{3+} Co-doped crystals.[5,12] Referred to the results presented in Table 2 and Fig.3, it can be readily seen that this band fluoresces most intensively among the infrared bands. Within Fig.3, it is also clearly seen that a band centered at 1.82 μm accompanied the 2 μm band on its short wave side. This band results from the transition of Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$. It can be expected that the efficiency of the cross-relaxation $Tm^{3+}(^3F_4) \rightarrow Ho^{3+}(^5I_7)$, a dominant energy transfer channel in the pumping mechanism of 2 μm lasers, can be examined at different combination of Tm^{3+}-(c_{Tm}) and Ho^{3+}-concentrations (c_{Ho}). Figure 6 displays the ratios of the integrated intensity of the 2 μm band to

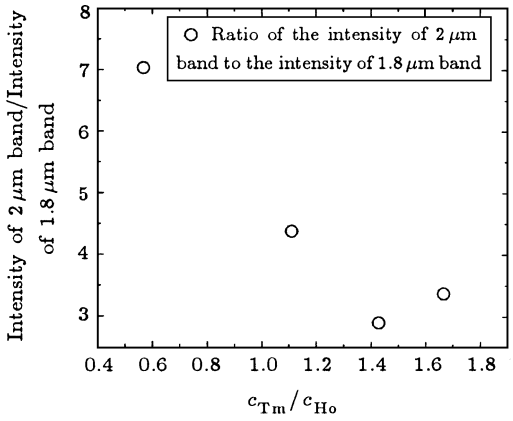


Fig.6. Ratios of the integrated intensity of 2 μm band to that of 1.82 μm band as the function of ratios of Tm^{3+}-concentration (c_{Tm}) to Ho^{3+}- concentration (c_{Ho}).

that of 1.82 μm band at different values of c_{Tm}/c_{Ho}. This result indicates that the intensity ratios decline as the value of c_{Tm}/c_{Ho} increases. We have obtained a maximum intensity ratio at the minimum c_{Tm}/c_{Ho} value corresponding to the concentrations as 1.53 at% for Tm^{3+} and 2.70 at% for Ho^{3+} (Sample 1#). Therefore, it can be concluded that a high efficient energy transfer of Tm^{3+} $(^3F_4) \rightarrow Ho^{3+}(^5I_7)$ requires a small concentration ratio of c_{Tm}/c_{Ho}. However, this will contradict the fact that an efficient optical pumping in laser experiment demands a high Tm^{3+} concentration. It is therefore necessary to adjust the concentrations of the two ions for getting an optimum combination. For comparison, in Table 3 we have summarized the concentrations and concentration ratios used by other authors in some other crystals. It can be seen that in the three crystals listed the c_{Tm}/c_{Ho} values are generally over 10 and therefore the Tm^{3+} concentrations are always one order higher than that of Ho^{3+}. As for YVO_4, investigations are still needed to get an optimum combination of the two concentrations for both efficient optical pumping and energy transfer.

Table 3. Ion concentrations and the values of c_{Tm}/c_{Ho} in some other crystals used in some of the papers.

Crystals	Concentrations/(at%)		c_{Tm}/c_{Ho}	References
	Tm^{3+}	Ho^{3+}		
Tm, Ho: YAP	4.2	0.28	14.6	[5]
	6	0.4	15.0	[5]
Tm, Ho: YLF	5	0.5	10.0	[3]
	5.4	0.36	15.0	[9]
Tm, Ho: YAG	5.75	0.3	19.2	[3]

Near 1.19 μm, we have also observed a weak infrared band (as seen in Fig.2). Its spectral range covers the wavelengths of two transitions, Tm^{3+}: $^3H_5 \rightarrow {}^3H_6$ and Ho^{3+}: $^5I_6 \rightarrow {}^5I_8$. In addition, it should noted that in Fig.2 there is also a much weak band near 1.06 μm, which is attributed to the undesired impurity ion of Nd^{3+}.

IV. CONCLUSION

In conclusion, spectroscopic properties of Tm^{3+}, Ho^{3+}: YVO_4, especially the dopant concentration effects on them, have been investigated through absorption spectra and fluorescence spectra under excitation of a LD at 808 nm. The wavelength of the transition Tm^{3+}: $^3H_6 \rightarrow {}^3H_4$, a promising wavelength of optical pumping, has been measured as 799 nm in the crystals. Examinations of the excitation processes involved in the upconversion emissions suggest that both the cross relaxations between dopant ions and excited state absorptions contribute to the visible emissions. The concentration-dependent spectra of the 800 nm band present an efficient energy transfer from Tm^{3+} to Ho^{3+} ions in Tm^{3+}, Ho^{3+}: YVO_4 crystals, especially at high dopant concentrations. This is desired for the optical pumping with a LD near 800 nm. To further exploit the effects of the combination of the dopant concentrations on the Tm-to-Ho energy transfer the intensity ratios between the 2 μm and 1.82 μm bands have been examined as a function of the ratios of Tm^{3+}- to Ho^{3+}- concentrations (c_{Tm}/c_{Ho}). It is shown that lower values favor the 2 μm emission and therefore the Tm-to-Ho energy transfer. With this result a careful adjustment of the concentrations of the two ions must be made for getting an efficient energy transfer as well as an efficient optical pumping.

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