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# Judd–Ofelt analysis of spectroscopic properties of $Tm^{3+}$ , Ho<sup>3+</sup> doped GdVO<sub>4</sub> crystals

Yanmin Yang <sup>a</sup>, Baoquan Yao <sup>b</sup>, Baojiu Chen <sup>a,c,\*</sup>, Cheng Wang <sup>a</sup>, Guozhong Ren <sup>a</sup>, Xiaojun Wang <sup>a</sup>

<sup>a</sup> Lab of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China <sup>b</sup> National Key Laboratory of Tunable Laser Technology, Harbin Institute of Technology, Harbin 150001, China <sup>c</sup> Optoelectronic Technology Institute, Department of Physics, Dalian Maritime University, Dalian 116026, China

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## Abstract

Tm<sup>3+</sup>: GdVO<sub>4</sub> and Ho<sup>3+</sup>: GdVO<sub>4</sub> crystals with good optical quality were grown by Czochralski technique. Polarized absorption and unpolarized fluorescence spectra of Tm<sup>3+</sup> and Ho<sup>3+</sup> in GdVO<sub>4</sub> crystals were measured. The Judd–Ofelt (JO) model was applied to obtain the three phenomenological intensity parameters. For Tm<sup>3+</sup>,  $\Omega_2 = 8.16 \times 10^{-20}$ ,  $\Omega_4 = 2.45 \times 10^{-20}$ ,  $\Omega_6 = 0.98 \times 10^{-20}$  (with dimension of cm<sup>2</sup>). For Ho<sup>3+</sup> $\Omega_2 = 1.51 \times 10^{-20}$ ,  $\Omega_4 = 1.61 \times 10^{-20}$ ,  $\Omega_6 = 1.22 \times 10^{-20}$  (with dimension of cm<sup>2</sup>). The radiative probabilities, radiative lifetimes, and branch ratios of Tm<sup>3+</sup> and Ho<sup>3+</sup> in GdVO<sub>4</sub> crystals were then determined. Using the reciprocity method and Fuch-tbauer–Ladenberg formula, the stimulated emission cross-sections for some interested transitions, such as ( ${}^{5}F_{4}$ ,  ${}^{5}S_{2}$ )  $\rightarrow {}^{5}I_{8}$  of Ho<sup>3+</sup> and  ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ ,  ${}^{3}H_{4} \rightarrow {}^{3}F_{4}$  of Tm<sup>3+</sup> in GdVO<sub>4</sub>, were determined and discussed. © 2006 Elsevier B.V. All rights reserved.

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## 1. Introduction

In recent years, most of the interest in luminescent rareearth ions have concentrated on trivalent thulium and holmium and in particular the emission bands around  $2 \mu m$  (Tm:  ${}^{3}F_{4} - {}^{3}H_{6}$ , Ho:  ${}^{5}I_{7} - {}^{5}I_{8}$ ) [1–3]. The 2  $\mu m$  laser emission operates in the eye-safe spectral region and generates a great interest in many fields like optical communications, coherent laser radar, and medical instrumentation. Among the laser sources, those based on solid-state materials now represent the main area of development because of their reliability and compactness. Despite of the success however, key problems still remain. These include severe dependence on pump diode temperature control due to the relatively narrow Tm absorption bands in YAG and YLF. Therefore, cooling to sub-zero temperatures is often required. The use of  $GdVO_4$  as host crystal offers possible solutions to these problems, since the absorption cross-section of thulium in  $GdVO_4$  is considerably stronger and broader than in YAG. Thus, the spectrum is shifted closer to the emission wavelength of commercially available AlGaAs laser diodes.

Several articles have recently appeared on growth and characterization of  $\text{Tm}^{3+}$ :GdVO<sub>4</sub> crystal [4,5]. However, no detailed analysis of Judd–Ofelt theory has been performed on  $\text{Tm}^{3+}$  or Ho<sup>3+</sup> doped GdVO<sub>4</sub> crystals. In this paper, we reported the spectroscopic properties of  $\text{Tm}^{3+}$  and Ho<sup>3+</sup> in GdVO<sub>4</sub> crystals. In order to give a reliable optical transition intensity parameters, the polarized absorption spectra data are needed. We have measured the polarized absorption spectra of  $\text{Tm}^{3+}$  and Ho<sup>3+</sup> doped GdVO<sub>4</sub>. By using the polarized absorption spectra the Judd–Ofelt parameters were obtained. Consequently, the optical transition properties such as oscillator strengths,

<sup>&</sup>lt;sup>\*</sup> Corresponding author. Tel./fax: +86 431 6176338. *E-mail address:* chenmbj@sohu.com (B. Chen).

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radiative transition probabilities and radiative lifetime as well as branch ratios were estimated. Finally, the stimulated emission cross-sections for some transitions of  $Tm^{3+}$  and  $Ho^{3+}$  in GdVO<sub>4</sub> were derived.

# 2. Experimental

 $\text{Tm}^{3+}$ : GdVO<sub>4</sub> and Ho<sup>3+</sup>: GdVO<sub>4</sub> crystals with good optical quality were grown by Czochralski technique method. Some preparative details of these crystals have been reported in Refs. [6–9]. The samples were cut along perpendicular or parallel crystal axis directions and well polished for the convenience of spectral measurements. Based on the distribution coefficient and the dopant concentration in the melt, the samples contained approximately 2 wt.% Tm<sup>3+</sup> or Ho<sup>3+</sup>. The corresponding ion

concentration of  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  were determined to be Ho:  $3.887 \times 10^{20} \text{ ions/cm}^3$ , Tm:  $3.804 \times 10^{20} \text{ ions/cm}^3$ .

The absorption spectra for both  $\pi$  and  $\sigma$  polarization were measured at room temperature with a Shumandzu UV\3101PC double beam spectrophotometer in the range 345–2500 nm. The unpolarized fluorescence spectra of Tm<sup>3+</sup> and Ho<sup>3+</sup> were obtained under excitation at 808 nm (AlGaAs laser-diode) and 488 nm (argon laser), respectively.

#### 3. Results and discussion

#### 3.1. Absorption spectra

The polarized absorption spectra of  $\text{Tm}^{3+}$  (Ho<sup>3+</sup>) in GdVO<sub>4</sub> crystals measured at room temperature are shown in Fig. 1, where the absorption bands are attributed to the



Fig. 1. The polarized absorption spectra for (a) Ho<sup>3+</sup>: GdVO<sub>4</sub> crystal and (b) Tm<sup>3+</sup>: GdVO<sub>4</sub> crystal.

Table 1

transitions from the ground state  ${}^{3}\text{H}_{6}$  of Tm<sup>3+</sup> and  ${}^{5}\text{I}_{8}$  of Ho<sup>3+</sup> to the corresponding excited states of Tm<sup>3+</sup> and Ho<sup>3+</sup>. The polarization spectrum of Tm<sup>3+</sup> at 0.8 µm shows the most highest absorption cross-section and the Full Width and Half Maximum (FWHM) of  $1.8 \times 10^{-20}$  cm<sup>2</sup> and 14 nm, respectively (for  $\sigma$  polarization spectrum) and of  $1.8 \times 10^{-20}$  cm<sup>2</sup> and 15 nm (for  $\pi$  polarization spectrum, respectively). Tm<sup>3+</sup> doped GdVO<sub>4</sub> crystals has larger FWHM and moderate absorption cross-section as compared to other Tm<sup>3+</sup> doped crystals [10–13] and is suitable for AlGaAs laser pumping.

### 3.2. Judd–Ofelt calculation and optical transition

Nowadays the Judd–Ofelt theory in its formulation uses three host dependent parameters  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  per rare earth ion/host combination to predict the electric dipole oscillator strengths of all radiative transitions. In this theory, the electric dipole line strengths  $S_{ed}$  are given by

$$S_{\rm ed} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle f^N \psi J | U^{(\lambda)} | f^N \Psi' J' \rangle|^2, \tag{1}$$

where  $\langle f^N \psi J | U^{(\lambda)} | f^N \Psi' J' \rangle$  are the reduced matrix elements of the unit tensor operator U of  $\lambda$  which are calculated from the tables of Nielson and Koster [14].

The line strength for magnetic dipole (md) transitions between J and J' manifolds is given by

$$S_{\rm md} = \frac{h^2}{16\pi^2 m^2 c^2} |\langle f^N \ \psi J \| L + 2S \| f^N \ \Psi' J' \rangle|^2 \tag{2}$$

Eqs. (1) and (2) are used to calculate the oscillator strength  $f_{calc}$  by following equation:

$$f_{\rm calc} = \frac{8\pi^2 mcv}{3h(2J+1)} (x_{\rm ed} S_{\rm ed} + x_{\rm md} S_{\rm md}), \tag{3}$$

where v is the frequency of the transition, J is the total angular momentum of the ground state.  $x_{ed} = (n^2 + 2)^2/9n$  and  $x_{md} = n$ , the electric and magnetic local field correction factors with the index of refraction n.

From the absorption spectra the integral over each absorption band can give the experimental oscillator strength of the appropriate absorption transition.

$$f_{\rm exp} = \frac{mc^2}{\pi e^2 N} \Gamma, \tag{4}$$

where N is the  $\text{Tm}^{3+}$  or  $\text{Ho}^{3+}$  concentration,  $\Gamma$  is the integrated absorbance for each absorption band.

Because GdVO<sub>4</sub> crystal belongs to anisotropy uniaxial crystals, it has two polarized absorption spectra,  $\sigma$  spectrum and  $\pi$  spectrum. According to the equation,  $f_{exp}^{\pi} + 2f_{exp}^{\sigma} = f_{calc}^{\pi} + 2f_{calc}^{\sigma}$  the experimental line strength can be expressed in the following term [15].

$$S_{\rm exp} = \frac{3h(2J+1)c}{8\pi^3 N v e^2} \frac{\Gamma_{\pi} + 2\Gamma_{\sigma}}{x_{\rm ed}^{\pi} + 2x_{\rm ed}^{\sigma}} - \frac{x_{\rm md}^{\pi} + 2x_{\rm md}^{\sigma}}{x_{\rm ed}^{\pi} + 2x_{\rm ed}^{\sigma}} S_{\rm md},$$
(5)

where  $x_{\rm ed}^{\pi,\sigma} = (n_{\pi,\sigma}^2 + 2)/9n_{\pi,\sigma}$ ,  $x_{\rm md}^{\pi,\sigma} = n_{\pi,\sigma}$  is the Lorentz local-field correction for  $\pi$  spectrum ( $\sigma$  spectrum), and  $\Gamma_{\pi,\sigma}$ is the integrated absorbance for  $\pi$  spectrum ( $\sigma$  spectrum). By a least-square fitting, the Judd–Ofelt parameters for  $\text{Ho}^{3+}$  and  $\text{Tm}^{3+}$  in GdVO<sub>4</sub> crystals were calculated to be  $\Omega_2 = 8.16 \times 10^{-20}$ ,  $\Omega_4 = 2.45 \times 10^{-20}$ ,  $\Omega_6 = 0.98 \times 10^{-20}$  for  $\text{Tm}^{3+}$  and  $\Omega_2 = 1.51 \times 10^{-20}$ ,  $\Omega_4 = 1.61 \times 10^{-20}$ ,  $\Omega_6 = 1.22 \times 10^{-20}$  for  $\text{Ho}^{3+}$  (all with dimension of cm<sup>2</sup>).

Tm<sup>3+</sup>:GdVO<sub>4</sub> crystal has larger J–O parameters  $\Omega_{\lambda}(\lambda = 2,4,6)$  as compared to other doped crystals (see Table 1). As known that  $\Omega_2$  is very sensitive to the structure and it is associated with the asymmetry and covalency of the lanthanide sites. The larger  $\Omega_2$  value indicates the stronger covalence characteristics of this crystal. The values of the J–O parameters are useful to calculate the spectroscopic quality factor  $X = \Omega_4/\Omega_6$  which is critically important in predicting the stimulated emission for the laser active medium. The spectroscopic quality factor of Tm<sup>3+</sup>:GdVO<sub>4</sub> crystal is 2.5 which is close to that of LiTaO<sub>3</sub>, KYb(WO<sub>4</sub>)<sub>2</sub>, YAG, and larger than of other crystals listed in Table 1. This relatively high X value indicates that Tm:GdVO<sub>4</sub> is a promising material for efficient laser action.

The experimental and theoretical oscillator strengths for the  $Ho^{3+}$ ,  $Tm^{3+}$  doped GdVO<sub>4</sub> crystals were calculated

The Judd–Ofelt parameters and the spectroscopic quality factors for Tm<sup>3+</sup> doped various crystals

Crystal	$\Omega_2$ (x10 <sup>-20</sup> cm <sup>2</sup> )	$\Omega_4$ (x10 <sup>-20</sup> cm <sup>2</sup> )	$\frac{\Omega_6}{(\times 10^{-20} \mathrm{cm}^2)}$	X	Refs.
				• • •	
LiTaO <sub>3</sub>	2.1	1.5	0.72	2.08	[10]
$SrWO_4$	7.41	0.25	1.71	0.15	[11]
$KYb(WO_4)_2$	0.14	0.21	0.10	2.1	[13]
YLF	1.67	1.93	1.10	1.75	[16]
KLa(MoO <sub>4</sub> ) <sub>2</sub>	8.29	5.01	7.51	0.67	[17]
YAG	0.7	1.2	0.5	2.4	[18]
$KGd(WO_4)_2$	2.64	5.84	14	0.42	[19]
LiLuF <sub>4</sub>	2.12	1.17	1.11	1.05	[20]
GdVO <sub>4</sub>	8.16	2.45	0.98	2.5	This
					work

Table 2 The experimental and theoretical oscillator strengths for (a)  $\text{Tm}^{3+}$ : GdVO<sub>4</sub> crystal and (b) Ho<sup>3+</sup>: GdVO<sub>4</sub> crystal

Absorption	Wavenumber (cm <sup>-1</sup> )	Oscillator strengths ( $\times 10^{-6}$ )		
		Experimental	Theoretical	
(a) $rms = 0.8$	$30 \times 10^{-6}$			
${}^{3}F_{4}$	5715.9	6.76	6.29	
$^{3}H_{5}$	8295.3	3.8	3.56(ed) + 0.47(md)	
$^{3}H_{4}$	12500	6.1	6.17	
${}^{3}F_{3}$	14342	4.57	3.99	
${}^{3}F_{2}$	14842.5	0.78	0.65	
${}^{1}G_{4}$	21130.5	3.00	2.21	
$^{1}D_{2}$	27643.4	2.91	4.06	
(b) $rms = 0.3$	$33 \times 10^{-6}$			
<sup>5</sup> I <sub>7</sub>	5027.05	2.46	2.19(ed) + 0.51(md)	
<sup>5</sup> I <sub>6</sub>	8523.42	1.24	1.36	
<sup>5</sup> I <sub>5</sub>	11088.02	0.25	0.25	
<sup>5</sup> F <sub>5</sub>	15371.8	3.94	3.66	
${}^{5}F_{4} - {}^{5}S_{2}$	18424.72	4.59	4.84	
${}^{5}G_{5}$	23749.5	3.85	3.47	
${}^{3}\text{H}_{6} - {}^{5}\text{G}_{5}$	27567.31	4.82	4.58	

Table 3

The oscillator strengths, radiative probabilities, the branching ratios and the radiative lifetimes for partial transitions of (a)  $Ho^{3+}$  and (b)  $Tm^{3+}$  in  $GdVO_4$  crystal

Start levels	Terminal levels	Wavelength (nm)	Oscillator strength		Radiative probabilities		Branch ratio	Lifetime (ms)
			Electric	Magnetic	Electric	Magnetic		
(a)								
<sup>5</sup> F <sub>3</sub>	${}^{5}F_{4}$	2057	0.20	0.63	2.47	7.469	0.00145	0.146
	${}^{5}S_{2}$	2214	0.00		0.09		0.00001	
	<sup>5</sup> F <sub>5</sub>	5138	0.48		36.44		0.00530	
	${}^{5}I_{4}$	7383	1.52		234.69		0.03415	
	<sup>5</sup> I <sub>5</sub>	9449	1.13		285.27		0.04151	
	<sup>5</sup> I <sub>6</sub>	12016	1.58		647.03		0.09414	
	<sup>5</sup> I <sub>7</sub>	15530	3.38		2301.7		0.33490	
	<sup>5</sup> I <sub>8</sub>	20586	2.80		3358.57		0.48867	
${}^{5}F_{4}$	${}^{5}S_{2}$	157	0.00	0.61	0.00	16.13	0.00000	0.144
	<sup>5</sup> F <sub>5</sub>	3081	0.35		9.44		0.00367	
	<sup>5</sup> I <sub>4</sub>	5326	0.47		37.82		0.00543	
	<sup>5</sup> I <sub>5</sub>	7392	1.46		225.06		0.03230	
	<sup>5</sup> I6	9959	1.56		436.67		0.06266	
	5I <sub>2</sub>	13473	1.20		615.84		0.08837	
	<sup>5</sup> I <sub>8</sub>	18529	5.81		5629.4		0.80782	
<sup>5</sup> S <sub>2</sub>	<sup>5</sup> F5	2924	0.03		0.82		0.00020	0.250
2	<sup>5</sup> L	5169	0.92		69 94		0.01749	
	5 1	7235	0.41		61.08		0.01527	
	5 <sup>1</sup>	9802	0.95		260.05		0.06501	
	<sup>5</sup> I <sub>2</sub>	13316	3.08		1541 13		0.38528	
	<sup>5</sup> I <sub>8</sub>	18372	2.17		2069.59		0.51740	
<sup>5</sup> F.	<sup>5</sup> L	2245	0.00		0.09		0.00002	0.265
- 5	<sup>5</sup> L	4311	0.22		11.83		0.00311	0.205
	<sup>15</sup>	6878	1.16		155 35		0.04083	
	51 51	10302	2 32		706 79		0.18574	
	<sup>17</sup> <sup>5</sup> I <sub>8</sub>	15448	4.35		2931.83		0.77048	
<sup>5</sup> L.	<sup>5</sup> T-	2066	0.70	0.79	8 47	9.476	0 10624	5.02
14	15 51	2000	0.70	0.79	60.51	9.470	0.10024	5.92
	1 <sub>6</sub> 51	4033 9147	0.99		75.29		0.33622	
	<sup>1</sup> 7 <sup>5</sup> I.	13203	0.40		15 11		0.08945	
5 <sub>T</sub>	5 <sub>1</sub>	2567	0.54	1.04	10.17	10.10	0.10492	2 57
15	16 51	2307	0.34	1.04	10.17	19.19	0.10462	5.57
	51 51	0081	1.40		140.//		0.32397	
-	18	11157	0.29		104.00		0.3/128	
°I <sub>6</sub>	<sup>5</sup> I <sub>7</sub>	3514	0.85	1.21	29.68	42.01	0.20145	2.81
	<sup>5</sup> I <sub>8</sub>	8570	1.37		284.04		0.79815	
<sup>5</sup> I <sub>7</sub>	<sup>5</sup> I <sub>8</sub>	5056	1.60	1.18	116.05	85.04	1.00000	4.97
(b)								
$^{1}D_{2}$	${}^{1}G_{4}$	6687	6.00		756.94		0.00757	0.01
-	$^{3}F_{2}$	12820	7.35		3410.75		0.03411	
	${}^{3}F_{2}$	13404	8.93		4529.96		0.04530	
	<sup>3</sup> H <sub>4</sub>	15280	8.99		5921.63		0.05922	
	<sup>3</sup> H <sub>5</sub>	19610	0.18		203 78		0.00204	
	<sup>3</sup> F4	22183	48.05		66706.96		0.66707	
	${}^{3}H_{6}$	27826	10.62		23212.62		0.23213	
$^{1}G_{4}$	$^{3}$ F <sub>2</sub>	6133	0.40		42.46		0 00599	0.14
04	<sup>3</sup> F-	6717	0.92		117.81		0.01661	0.14
	3 1 3	8502	3.55		720.76		0.10421	
	<sup>3</sup> L	12022	2.55		1720 16		0.10451	
	п5 <sup>3</sup> Б	12923	5.08		1/38.10		0.24308	
	<sup>-</sup> F <sub>4</sub> 311	15496	0.58		398.40		0.0561/	
	H <sub>6</sub>	21139	5.20		4036.17		0.56910	
<sup>3</sup> F <sub>2</sub>	${}^{3}F_{3}$	584	0.05	0.06	0.05	0.06	0.00000	0.22
	<sup>3</sup> H <sub>4</sub>	2460	3.20		54.72		0.01226	
	<sup>2</sup> H <sub>5</sub>	6790	3.94		513.56		0.11504	
	°F <sub>4</sub>	9363	11.35		2808.45		0.62909	
	°Н <sub>6</sub>	15006	1.71		1089.70		0.24409	

Start levels	Terminal levels	Wavelength (nm)	Oscillator strength		Radiative probabilities		Branch ratio	Lifetime (ms)
			Electric	Magnetic	Electric	Magnetic		
<sup>3</sup> F <sub>3</sub>	$^{3}H_{4}$	1876	1.10		10.94		0.00188	0.17
	${}^{3}H_{5}$	6206	11.98		1302.06		0.22395	
	${}^{3}F_{4}$	8779	0.53		116.81		0.02009	
	${}^{3}H_{6}$	14422	7.46		4378.68		0.75313	
<sup>3</sup> H <sub>4</sub>	$^{3}H_{5}$	4330	1.40	0.43	74.47	22.65	0.02185	0.23
	${}^{3}F_{4}$	6903	2.74		369.30		0.08309	
	${}^{3}H_{6}$	12546	8.95		3973.79		0.89410	
<sup>3</sup> H <sub>5</sub>	${}^{3}F_{4}$	2573	1.03		19.37		0.02305	1.19
	$^{3}H_{6}$	8216	3.49	0.82	666.10	154.73	0.97679	
${}^{3}F_{4}$	$^{3}H_{6}$	5643	8.97		806.05		1.00000	1.24



Fig. 2. The unpolarized room temperature emission spectra of Ho<sup>3+</sup> excited at 488 nm, the insert depicts the emission cross-section in green region.

and listed in order to check the correctness in the J–O calculations (see Table 2). It can be seen that the experimental and theoretical oscillator strengths are each other in a reasonable agreement. The calculated values of the rms deviations are  $8 \times 10^{-7}$ ,  $3.3 \times 10^{-7}$  for Tm<sup>3+</sup> and Ho<sup>3+</sup> doped crystal, respectively. These rms are smaller than the oscillator strengths listed in Table 2 and comparable with the values for other calculations [8,11], Thus, we are able to assert that the calculations are reliable.

The radiative transition probabilities, lifetime, and transition branch ratios are important dynamic parameters for trivalent rare earth ions and could be expressed by the formulas:  $A_{JJ'} = \frac{64\pi^4 e^2 v^3}{3\hbar(2J+1)} (x'_{ed}S_{ed} + x'_{md}S_{md}), \ \tau = \frac{1}{\sum_{J'}A_{JJ'}}$  and  $\beta_{JJ'} = A_{JJ'}\tau$ , where  $A_{JJ'}$  is the radiative transition probability from level J to level J',  $\tau$  is the lifetime of level J, and  $\beta_{JJ'}$  is the branch ratios for the transitions originating from level J. Based on these formulas, the calculated values of partial transitions for Tm<sup>3+</sup> and Ho<sup>3+</sup> in GdVO<sub>4</sub> are listed in Table 3(a) and (b). The corresponding Judd–Ofelt parameters and reduced matrix were involved in the calculations.

# 3.3. Emission cross-section

The emission cross-section is a very important parameter for measuring laser materials. The emission cross-section can be obtained from the spectroscopic data by two commonly applied methods, i.e., by the reciprocity method and by Fuchtbauer–Ladenburg (FL) formula. Using the FL formula, the emission cross-section can be expressed in the following terms

$$\sigma_{\rm em} = \frac{\lambda_0^4 A I(\lambda_0)}{8\pi c n^2 \int I(\lambda) d\lambda},\tag{6}$$

where A is the spontaneous radiative emission probabilities,  $\lambda_0$  is the peak wavelength, n is the refractive index of the host material. Another approach for determining the emission cross section is the reciprocity method in which the ground state absorption cross-section  $\sigma_{abs}$  is associated and can be functionally expressed as below, while assuming that the Stark level positions of both multiplets are known,



Fig. 3. Absorption and emission cross-sections associated with the transition between  ${}^{1}G_{4}$  and  ${}^{3}H_{6}$  levels (a) stimulated emission cross-section gotten from emission spectra data; (b) stimulated emission cross-section gotten from absorption spectra data; (c) absorption cross-section.

$$\sigma_{\rm em}(\lambda) = \sigma_{\rm abs}(\lambda) \frac{Z_{\rm l}}{Z_{\rm u}} \exp\left[\frac{E_{\rm ZL} - hc/\lambda}{k_{\rm B}T}\right],\tag{7}$$

where  $\sigma_{abs} = a/N$  is the absorption cross-section N is the dopant concentration,  $Z_1$  and  $Z_u$  are the partition function of lower and upper levels, respectively,  $E_{ZL}$  is the energy between the lowest Stark levels of the multiplets involved.

Fig. 2 shows the unpolarized room temperature emission spectra of Ho<sup>3+</sup> excited at 488 nm. It consists of four emission peaks corresponding to the  ${}^5F_3 \rightarrow {}^5I_8$ ,  $({}^5F_4, {}^5S_2) \rightarrow {}^5I_8$ ,  ${}^5F_5 \rightarrow {}^5I_8$ ,  $({}^5F_4, {}^5S_2) \rightarrow {}^5I_7$  transitions, which are in agreement with the reports [21,22]. In this figure the NIR emission  $({}^5F_4, {}^5S_2) \rightarrow {}^5I_7$  is stronger than that of the yellow-green  $({}^5F_4, {}^5S_2) \rightarrow {}^5I_8$ . The green emission has been considered to be a laser operating level and its cross-section is obtained by FL method (see the insert in the Fig. 2). The emission cross-section value is  $1.83 \times 10^{-20}$  cm<sup>2</sup> at 545 nm, which is larger. This may make the Ho<sup>3+</sup> doped GdVO<sub>4</sub> to be a suitable host material for green laser operation under upconversion or downcoversion pump.

The blue emission of  $\text{Tm}^{3+}$ :  $^{1}\text{G}_{4} \rightarrow {}^{3}\text{H}_{6}$  was measured by using an upconversion technique upon 808 nm excitation. The luminescent intensity was too weak for the used collection and detection system in our lab when excited at higher level than  ${}^{1}G_{4}$ . Probably it is due to the pumping wavelength which is unmatched and the intrinsic concentration quenching of Tm<sup>3+</sup>. However, when we used 808 nm LD excitation (laser diode, with watt level output), the emission from the upper level is strong enough. Based on the upconversion emission spectra data and the FL formula, the stimulated emission cross section was estimated and plotted in Fig. 3 as curve (a). On the aim at a comparison the stimulated emission cross-section was derived also from the absorption cross-section (curve (c)) and shown as curve (b). Obviously, the emission cross-sections obtained from various routes are very similar. The difference between line

shape is due to the deviation of the spectra measurement system. The emission cross-section at highest intensity is around  $0.4 \times 10^{-20}$  cm<sup>2</sup>.

 ${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{F}_{4}$  transition of Tm<sup>3+</sup> at around 1500 nm has been widely considered to be a useful wavelength for the applications in biomedicine and optical communication. The stimulated emission cross-section corresponding to the  ${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{F}_{4}$  transitions of Tm<sup>3+</sup> was estimated by FL method in order to evaluate the spectral performance of the Tm<sup>3+</sup> doped GdVO<sub>4</sub> as a laser material (see Fig. 4). Nine distinct emission peaks belonging to the transitions between  ${}^{3}\text{H}_{4}$  and  ${}^{3}\text{F}_{4}$  Stack splits are observed. The emission cross-section  $\sigma_{\rm em}$  at 1484 nm and 1472 nm is  $0.85 \times 10^{-20}$  cm<sup>2</sup> and  $0.79 \times 10^{-20}$  cm<sup>2</sup>, respectively.



Fig. 4. The stimulated emission cross-section of  $Tm^{3+}\!\!:\ ^3\!H_4\to {}^3\!F_4$  transition.

#### 4. Conclusion

Tm<sup>3+</sup>-, Ho<sup>3+</sup>-doped GdVO<sub>4</sub> crystals with good optical properties were grown successfully by Czochralski method. The polarized absorption spectra were measured and the standard Judd–Ofelt procedure was accomplished for these crystals. To our best knowledge, we obtained the Tm<sup>3+</sup>-, Ho<sup>3+</sup>-doped GdVO<sub>4</sub> by using the polarized absorption spectra for the first time. The J–O parameters for Ho<sup>3+</sup> are  $\Omega_2 = 1.51 \times 10^{-20}$ ,  $\Omega_4 = 1.61 \times 10^{-20}$ ,  $\Omega_6 = 1.22 \times 10^{-20}$ and for Tm<sup>3+</sup> are  $\Omega_2 = 8.16 \times 10^{-20}$ ,  $\Omega_4 = 2.45 \times 10^{-20}$ ,  $\Omega_6 = 0.98 \times 10^{-20}$  (with dimension of cm<sup>2</sup>). Consequently, the oscillator strengths, transition probabilities, branch ratios, and radiative lifetimes were estimated for both Tm<sup>3+</sup> and Ho<sup>3+</sup> doped GdVO<sub>4</sub>. The stimulated emission cross-section were derived and compared from different routes. These data would be helpful for further study on the Tm<sup>3+</sup> and Ho<sup>3+</sup> doped GdVO<sub>4</sub> crystals.

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