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Intense 3.9 μm emission of Ho^{3+} doped $YAlO_3$ single crystal

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HIGHLIGHTS

- An intense 3.9 μm emission in Ho:YAP crystal was observed for the first time.
- The spectral parameters of Ho:YAP crystal were calculated.
- Optical properties of Ho:YAP as 3.9 μm laser crystal were evaluated.

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ABSTRACT

The Ho^{3+}-doped $YAlO_3$ (YAP) crystal was successfully grown using the Czochralski technique. An intense 3.9 μm emission in Ho:YAP crystal was observed for the first time. The spectroscopic parameters were determined by Judd-Ofelt theory based on the measured polarized absorption spectra. The intensity parameters $\Omega_{2,4,6}$, exited state lifetimes, branching ratios, and emission cross-sections were calculated. Under optical pumping at 890 nm, an intense 3.9 μm emission with a bandwidth of 190 nm at full width half maximum was observed. The maximum emission cross section of Ho:YAP crystal is estimated to be 0.302×10^{-20} cm^2 at 4096 nm. The decay lifetime of the level was measured to be 0.103 ms. We propose that the Ho:YAP crystal may be a promising material for 3.9 μm laser applications.

1. Introduction

3–5 μm mid infrared (MIR) laser are useful a variety of scientific and technical applications, include in atmospheric monitoring, medical surgery and scientific research [1–3]. Furthermore, it can applications in high-quality pump sources for longer wavelength MIR lasers and optical parametric oscillators [4,5]. It is well known that Ho^{3+} is an efficient ion for obtaining 3.9 μm laser emissions due to Stark levels of the $^5I_5 \rightarrow {}^5I_6$ states transition [6]. As can be seen from the energy level diagram of trivalent holmium [7]. This ion has also several high lying metastable levels giving rise to transitions at various wavelengths from infrared (IR) to ultraviolet (UV) region [8]. The possibility of obtaining laser emission from Ho^{3+} at ~3.9 μm mainly depends on the choice of host crystals. The host material for MIR lasers is expected to possess low phonon energy, because which can decrease the non-radiative losses efficiently and thus increasing the quantum efficiency of $^5I_5 \rightarrow {}^5I_6$ transition. To date, Ho^{3+} lasing $^5I_5 \rightarrow {}^5I_6$ transition has been demonstrated in fluoride compounds such as PbF_2 crystals (257 cm^{-1}) [9], YLF crystals (442 cm^{-1}) [10], BYF crystals (420 cm^{-1}) [11]. However, up to now, there is no research about Ho^{3+} ions doped oxide crystal with 3.9 μm laser emission. Fortunately, the maximum phonon energy of Yttrium Aluminum Perovskite (YAP) is only ~570 cm^{-1} [12], such low phonon vibrational frequency leads to a reduced non-radiative decay rates between excited states of Ho^{3+} with small energy separation, and finally ensures 3.9 μm laser emission. Moreover, fluoride crystals must be grown in an inert atmosphere to avoid contamination from outside environment, and also their poor mechanical properties seriously limit the enhancement of MIR laser output power and efficiency [13]. Compared with fluoride crystals, oxide crystals are much easier to grow with higher optical quality, and they possess much better physical properties [14].

YAP crystal is a biaxial crystal with the orthorhombic system, the yttrium ions in sites of Cs (monoclinic) symmetry [11]. The

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general structure of perovskite crystals can be expressed as ABX_3, where elements A and B occupy, respectively. The vertexes and the central site of the body-centered tetrahedron, while X anions, situated on the six faces of the tetrahedron, form an octahedron around the central site B [13]. The cell parameters are a = 5.330 Å, b = 7.375 Å, and c = 5.180 Å, Its density is 5.35 g/cm^3 [15]. Compared to the original YAG, YAP is also derived from the binary Y_2O_3-Al_2O_3 system and they have similar physical characteristics such as high mechanical strength, sufficient hardness and significant thermo-conduction [16]. In addition to these advantages, it has the advantage of low phonon energy compared to YAG (800 cm^{-1}) [17]. In this work, an intense 3.9 μm emission in a Ho:YAP crystal under a 890 nm pump is reported for the first time, to the best of our knowledge. The spectroscopic investigations of ~3.9 μm emission in a Ho:YAP crystal were investigated to demonstrate its future applications in MIR lasers.

2. Experimental

Large size single crystals can be obtained by the Czochralski (CZ) method with an intermediate frequency induction heating system. Oxide powders of Ho_2O_3 (4N), Y_2O_3 (4N) and Al_2O_3 (4N) were used as starting materials. The concentrations of Ho introduced in the raw materials were 1 at.% which were mixed adequately for 20 h and pressed into disks, followed by heating in air for 15 h at 1200 °C. The bulks were loaded into an iridium crucible for crystal growth, the growth atmosphere was N_2, and temperature was set to 1900 °C. The crystal growth was carried out with a *a*-cut YAP seed. A pulling rate of 1.2 mm/h and rotation rate of 15–20 rpm were adopted during the growth. To prevent the crystal from cracking, it was cooled to room temperature very slowly with a rate of 30–40 °C/h, after its growth size Φ28 × 40 mm^2 was obtained. The real dopant of Ho^{3+} ions in YAP crystal (N_{Ho}) was calculated to be 1.335 × 10^{20} ions/cm^3. The concentrations of Ho ions were detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis. The effective segregation coefficient K for the Ho^{3+} is calculated to be 0.785.

3. Spectral analyses

The sample was cut along the as-grown Ho:YAP crystal into 10 mm × 10 mm × 5 mm and each face of the sample is perpendicular to one of the three principal crystallographic directions a, b, c, respectively. The six faces of sample were mechanically polished for absorption spectra measurements, fluorescence spectrum and the fluorescence decay lifetime measurements. The absorption spectrum of a Ho^{3+} YAP crystal in the range of 300–2300 nm was measured by Perkin–Elmer UV–VIS-NIR Spectrometer (Lambda 900). The fluorescence spectra in the wavelength of 3700–4300 nm and the fluorescence decay curves were recorded by Edinburg Instruments FLS920 and FSP920 spectrophotometers. All measurements were done at room temperature.

The polarization absorption spectra in the range from 300 to 2300 nm are shown in Fig. 1. The absorption peaks in the three directions are similar and the positions of absorption peaks are slightly different. The characteristic absorption bands corresponding to transitions from the ground state to the excited states of Ho^{3+} are marked. It is obvious to see there are six main absorption bands of Ho^{3+} ions, which corresponded to the electronic transitions from ground $^5I_8$ level to $^5I_7$, $^5I_6$, $^5F_5$, $^5F_4 + {}^5S_2$, $^5G_6$ and $^5G_5$ levels. Fig. 2 shows the simplified energy level diagram of Ho^{3+} doped YAP crystal. Under the excitation of 890 nm laser pump, the Ho^{3+} ion is excited to the state $^5I_5$, ions in the $^5I_5$ level decay radiatively to $^5I_6$ with ~3.9 μm emission.

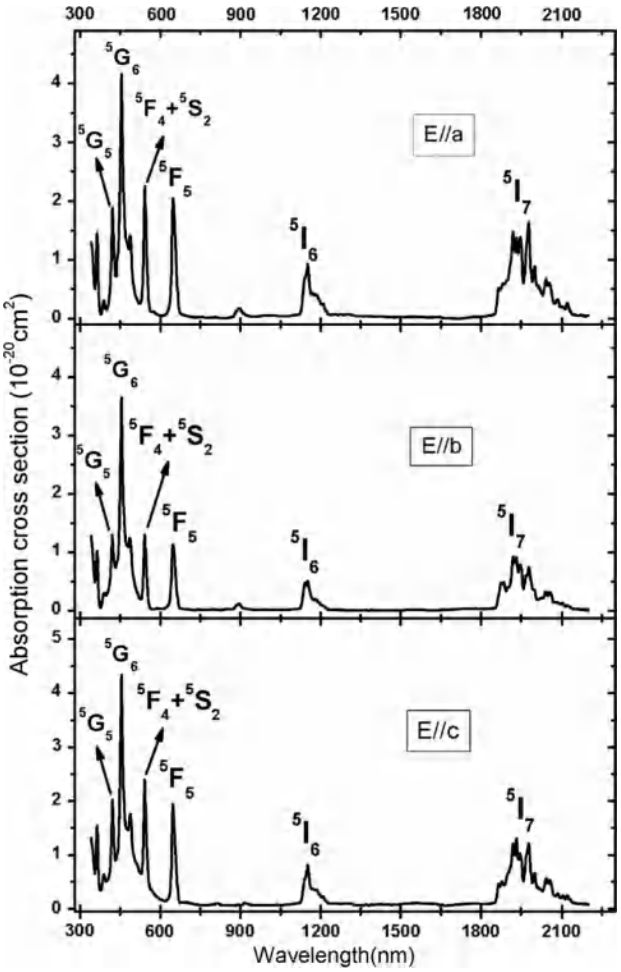

Fig. 1. Polarized absorption spectra of Ho:YAP crystal at room temperature.

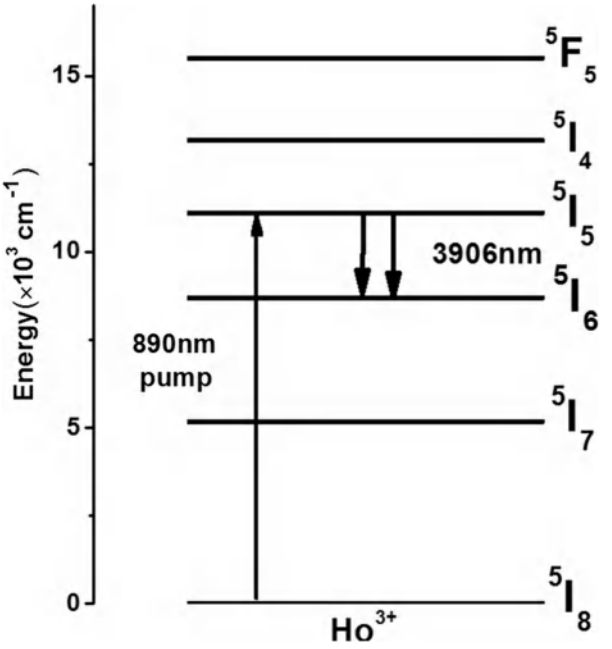

Fig. 2. The simplified energy level diagram of Ho^{3+} doped YAP crystal.

The J–O theory has become a standard tool for evaluating the spectroscopic parameters of rare-earth ions in crystals [18,19]. The calculated average wavelength and the experimental and calculated line strengths (S) are presented in Table 1. A lower root-mean-square RMS confirms a better consistency of our fitting, the root-mean-square (RMS) error deviation of intensity parameters was 0.493×10^{-20} cm^2 for a polarization, 0.456×10^{-20} cm^2 for b polarization, 0.537×10^{-20} cm^2 for c polarization. Which indicates a good result between the experimental and calculated spectral intensities. The calculated radiative transition rates, branching ratios and radiative lifetimes for different transition levels of Ho: YAP crystal are listed in Table 2.

And then, Table 3 provides spectroscopic parameters $\Omega_{2,4,6}$ of Ho^{3+} ion for each polarization, and shown in with other Ho^{3+} doped crystals for comparison. For the Ho:YAP crystal, the effective intensity parameters $\Omega_{t,eff}$ should be $\Omega_{t,eff} = (\Omega_{t,a} + \Omega_{t,b} + \Omega_{t,c})/3$ [20]. Ω_2 parameter is dependent on the local environments and the covalent chemical bonding, the high value of Ω_2 means that this crystal has the low asymmetry and the strong covalence characteristics. The value of Ω_4/Ω_6 determines the spectroscopy quality of the materials, The Ω_4/Ω_6 of Ho:YAP is higher than YLF and YAG, which were indicated to be prospective Ho^{3+} doped laser media.

The fluorescence spectra of the Ho: YAP crystals are shown in Fig. 3. A broad emission band from 3700 nm to 4300 nm was observed corresponding to $^5I_5 \rightarrow {}^5I_6$ transition. It is obvious to see that there are two emission bands around 3950 nm and 4096 nm, which are assigned to the Ho^{3+} transition of $^5I_5 \rightarrow {}^5I_6$. The emission cross sections are calculated by the F-L equation [24]:

$$\sigma_e(\lambda) = \frac{\beta\lambda^5 I(\lambda)}{8\pi c n^2 \tau_{rad} \int \lambda I(\lambda) \mathrm{d}\lambda}$$

where β is the branching ratio, $I(\lambda)$ is the emission intensity at wavelength λ, c is the vacuum speed of light, n is the refractive index and τ_r is the radiative lifetime. The maximum emission cross

Table 1
The average wavelength (λ), Polarized experimental and calculated line strengths (S) of Ho:YAP crystal.

Excited states	E//a			E//b			E//c		
Ground state $^5I_8$	Peak (λ)	*Scal* (10^{-20})	*Sexp* (10^{-20})	Peak (λ)	*Scal* (10^{-20})	*Sexp* (10^{-20})	Peak (λ)	*Scal* (10^{-20})	*Sexp* (10^{-20})
$^5I_7$	1933	3.314	3.275	1933	2.934	2.735	1931	3.573	3.506
$^5I_6$	1153	1.431	1.163	1151	1.269	1.227	1152	1.541	1.615
$^5F_5$	649	2.429	2.299	647	2.097	1.839	650	2.644	2.701
$^5F_4 + {}^5S_2$	542	2.094	2.061	541	1.828	2.061	543	2.269	1.786
$^5F_3$	487	0.651	1.223	487	0.579	1.07	486	0.699	1.223
$^5G_6$	455	4.581	4.583	454	4.252	4.256	456	5.237	5.238
$^5G_5$	421	0.574	1.327	520	0.498	1.238	422	0.624	1.592
$^5G_4, {}^2K_7$	388	0.175	0.557	386	0.151	0.633	389	0.191	0.612
$^5H_5 + {}^3H_6 + {}^5G_2$	363	0.007	0.103	363	0.007	0.072	365	0.008	0.059

Table 2
Calculated radiative transition rates, branching ratios and radiative lifetimes for different transition levels of Ho:YAP crystal.

Start levels	Terminal levels	λ (nm)	A_{ed} (S^{-1})	β (%)	τ_{rad}(ms)
$^5F_5$	$^5I_8$	645	3668	77.7	0.211
	$^5I_7$	960	862.908	18.3	
	$^5I_6$	1447	178.644	3.8	
	$^5I_5$	2298	13.471	0.28	
	$^5I_4$	4347	0.13	0.002	
$^5I_4$	$^5I_8$	760	16.325	9.5	5.84
	$^5I_7$	1233	80.624	47.1	
	$^5I_6$	2169	65.017	38	
	$^5I_5$	4854	9.257	5.4	
$^5I_5$	$^5I_8$	900	115.264	40.6	3.521
	$^5I_7$	1650	157.389	55.4	
	$^5I_6$	3906	11.331	4.0	
$^5I_6$	$^5I_8$	1150	322.564	90.1	2.817
	$^5I_7$	2857	32.475	9.1	
$^5I_7$	$^5I_8$	1933	136.354	100	7.334

Table 3
The J–O intensity parameters of Ho^{3+}-doped crystals.

Crystals	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)	Ω_4/Ω_6	Ref.
Ho:YVO_4	7.5	4.0	1.9	2.1	[21]
Ho:BaY_2F_8	6.74	1.20	0.66	1.818	[11]
Ho:PbF_2	0.41	1.50	0.86	1.744	[22]
Ho:YAG	0.101	2.086	1.724	1.209	[23]
Ho:YLF	1.161	2.224	2.079	1.069	[14]
Ho:YAP $\Omega_{t,a}$	1.087	3.18	1.879	1.692	This work
$\Omega_{t,b}$	1.166	2.68	1.672	1.603	
$\Omega_{t,c}$	1.33	3.5	2.017	1.735	
$\Omega_{t,eff}$	1.194	3.12	1.856	1.681	

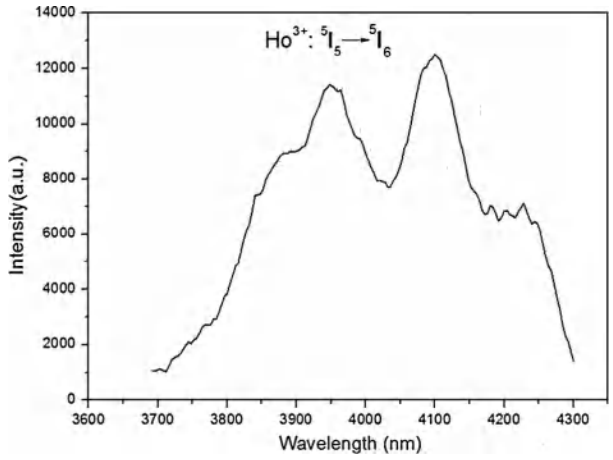

Fig. 3. Fluorescence spectrum of Ho:YAP crystal in the wavelength of 3700–4300 m.

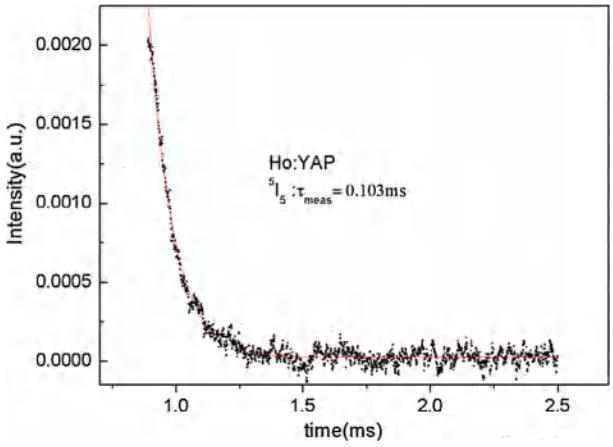

Fig. 4. The fluorescence decay curve of the $^5I_5$ level in Ho:YAP crystal at room temperature.

Table 4
Comparison of the optical spectroscopic parameters of some Ho^{3+}-doped laser crystals.

Crystals	The emission cross section (σ_e)	$^5I_5 \rightarrow {}^5I_6$ β (%)	τ_{meas} (ms) $^5I_5$	Ref.
Ho:YLF	$\sim 0.40 \times 10^{-20}$ cm^2	3.48	0.018	[25]
Ho:BYF	0.437×10^{-20} cm^2	5.7	0.052	[11]
Ho:YAP	0.302×10^{-20} cm^2	4.0	0.103	This work

section of Ho:YAP crystal is estimated to be 0.302×10^{-20} cm^2 at 4096 nm, the FWHM of this emission band is 190 nm around 4096 nm spectral region. This broad and smooth emission spectra indicates a potential for a wide tuning range and short pulse generation for the crystal.

To further explore the energy interaction mechanism, the fluorescence decay time of the $^5I_5 \rightarrow {}^5I_6$ transition has been measured by exciting the sample with 890 nm and emission at 4096 nm and is shown in Fig. 4. The experiment curve can be well fitted to single exponential functions. The measured lifetime of the $^5I_5$ manifold in the Ho:YAP crystal is 0.103 ms. Table 4 presents the comparison of several important spectroscopic parameters of several Ho^{3+}-doped laser crystals, it is clear to see that the branching ratios, emission cross-section and fluorescence lifetime of Ho:YAP crystal are comparable with other Ho^{3+} doped crystals, such as Ho:YLF and Ho:BYF, which have been demonstrated as effective laser hosts for Ho^{3+} lasing $^5I_5 \rightarrow {}^5I_6$ transition. Moreover, the measured lifetime of Ho:YAP crystal are higher than those of Ho:YLF and Ho:BYF, which indicates the YAP crystal can be used as a good host candidate material for ~3.9 μm laser applications.

4. Conclusion

In conclusion, high-quality Ho:YAP crystals were successfully grown using Czochralski method. The polarized absorption spectra, unpolarized fluorescence spectrum as well as decay curves are measured at room temperature. Under the excitation of 890 nm laser pump, one intense 3.9 μm laser emission from 3700 to 4300 nm on the phonon terminated transition $^5I_5 \rightarrow {}^5I_6$ of Ho:YAP was demonstrated for the first time. The J-O intensity parameters $\Omega_{2,eff}$, $\Omega_{4,eff}$ and $\Omega_{6,eff}$ are calculated to be 1.194×10^{-20} cm^2, 3.12×10^{-20} cm^2 and 1.856×10^{-20} cm^2, respectively. The maximum emission cross-section is 0.302×10^{-20} cm^2 at 4096 nm, and the FWHM of this emission band is 190 nm. The fluorescence lifetime of the $^5I_5 \rightarrow {}^5I_6$ transition of Ho^{3+} was determined to be 0.103 ms. With these favorable properties, the Ho:YAP crystal is a promising material for ~3.9 μm laser applications under the excitation of 890 nm laser pump.

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