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Growth, spectroscopy and CW laser operation of Ho³⁺ doped CaY_{0.9}Gd_{0.1}AlO₄ single crystal

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Abstract

Ho³⁺-doped CaY_{0.9}Gd_{0.1}AlO₄ single crystal was successfully grown by the Czochralski technique for the first time. The polarized absorption spectra, polarized emission spectra and fluorescence decay curve of the crystal were investigated at room temperature. The spectroscopic parameters are calculated based on Judd–Ofelt theory, the values of $\Omega_{2,4,6}$ were calculated to be $3.16 \times 10^{-20} \text{ cm}^2$, $3.93 \times 10^{-20} \text{ cm}^2$, $0.91 \times 10^{-20} \text{ cm}^2$, respectively. The Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal exhibits strong emission at 2013 nm for π - and 2032 nm for σ -polarizations with stimulated emission cross section of $6.64 \times 10^{-20} \text{ cm}^2$ and $1.90 \times 10^{-20} \text{ cm}^2$, respectively. The fluorescence lifetime of the ⁵I₇ level was measured to be 6.60 ms. The continuous-wave (CW) laser operation of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal around 2 μm was demonstrated.

Key words: Ho:CaY_{0.9}Gd_{0.1}AlO₄, Crystal growth, Spectral property, Laser operation

1. Introduction

Solid-state lasers operating in the two microns spectral range are extensively investigated due to widespread applications in plenty of fields such as monitoring of atmospheric pollutants, coherent laser radar, medical surgery (strongly absorbed by biological tissues), pumping sources for mid-infrared optical parametric oscillators (OPOs) and optical parametric amplifiers (OPAs) [1-5]. Such lasers can be achieved by doping Tm^{3+} ($^3\text{F}_4 \rightarrow ^3\text{H}_6$) or Ho^{3+} ($^5\text{I}_7 \rightarrow ^5\text{I}_8$) as activator ions [6-10]. Compared with Tm^{3+} -doped materials, Ho^{3+} -doped materials have advantages of wider and red-shifted emission band that is more attractive for mode-locked lasers. Additionally, the larger emission cross sections and the longer fluorescence lifetimes are beneficial to continuous-wave laser operation. In the past few years, laser operations have been realized in $\text{Ho}:\text{Lu}_2\text{O}_3$ [11], $\text{Ho}:\text{CYAlO}_4$ [12], $\text{Ho}:\text{Sc}_2\text{SiO}_5$ [13], $\text{Ho}:\text{YAG}$ [14], $\text{Ho}:\text{CNGG}$ [15]. With the development of powerful Tm^{3+} fiber lasers and GaSb laser diodes, exciting directly to the $\text{Ho}^{3+} \ ^5\text{I}_7$ state has attracted much attention.

As a promising laser host material, $\text{CaY}_{0.9}\text{Gd}_{0.1}\text{AlO}_4$ is complex oxides belonging to the tetragonal ABCD_4 compounds with the K_2NiF_4 structure. **In this crystal, the AlO_6 octahedrons formed perovskite-type structure, and Ca^{2+} and Y^{3+} ions distribute randomly in the nine coordinated sites with disordered microstructure.** Compare with CaYAlO_4 crystal, the $\text{CaY}_{0.9}\text{Gd}_{0.1}\text{AlO}_4$ has the same advantages of good mechanical properties, high thermal conductivity, chemical stability, high infrared transmittance and lower phonon energy. Furthermore, the smaller Al^{3+} ions occupy the position with octahedral symmetry, the Ca^{2+} and Y^{3+} ions are distributed statistically in the nine coordinated sites [16, 17], Y^{3+} and Gd^{3+} ions are randomly distributed on the same sites, which leads to a considerable inhomogeneous broadening of the optical spectra. So far, rare earth ions doped CaYAlO_4 disordered crystals have been widely investigated by various groups [18-22]. Recently, Ma et al. demonstrated generation 17 fs pulses with 4.68 optical cycles directly from a Kerr-lens mode-locked $\text{Yb}:\text{CaYAlO}_4$ laser [23]. Unfortunately, there have been no reports on spectral properties and laser operation of Ho^{3+} doped $\text{CaY}_{0.9}\text{Gd}_{0.1}\text{AlO}_4$ crystal.

In this letter, a promising $\text{Ho}:\text{CaY}_{0.9}\text{Gd}_{0.1}\text{AlO}_4$ crystal was grown by the conventional Czochralski method. The polarized absorption spectra, emission spectra and fluorescence lifetime were investigated at room temperature. In addition, the laser operation of $\text{Ho}:\text{CaY}_{0.9}\text{Gd}_{0.1}\text{AlO}_4$ has been investigated for the first time to the best of our knowledge.

2. Experimental

2.1 Crystal growth

$\text{Ho}:\text{CaY}_{0.9}\text{Gd}_{0.1}\text{AlO}_4$ crystal was grown by using the Czochralski method [24] with the following composition: $\text{CaHo}_{0.005}\text{Y}_{0.8975}\text{Gd}_{0.0975}\text{AlO}_4$. Ho_2O_3 , Y_2O_3 , Gd_2O_3 , CaCO_3 and Al_2O_3 powders with 5N purity were used as raw materials for crystal growth. The crystal was pulled employing seeds along a **[add orientation]** direction with dimensions of 3 mm×3 mm×35 mm cut out from pure CaYAlO_4 crystal. The growth process was carried in nitrogen atmosphere to prevent oxidation of the iridium crucible. **The low** pulling rate varied from 0.5 to 1.0 mm/h to **prevent inclusions and thermal stress propagation** and the rotation speed was 15 rpm. Finally **as shown in Fig.1, transparent Ho^{3+} -doped $\text{CaY}_{0.9}\text{Gd}_{0.1}\text{AlO}_4$ crystal of diameter 25mm and length of 60 mm was obtained,** The as-grown crystal was dark brown in color due to the interstitial oxygen atoms. The coloration was removed to a great extent by annealing under

reducing atmosphere.

2.2 Spectroscopic measurement

The Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal was cut and polished to dimension of 9 × 9 × 1 mm for spectral measurements. The absorption spectra from 350 to 2120 nm were measured by a spectrophotometer (Lambda 900, Perkin-Elmer UV-VIS-NIR). The fluorescence spectra, as well as the fluorescence lifetime were measured by Edinburgh Instruments FLS1000 spectrophotometer under the excitation 640 nm. All the measurements were performed at room temperature.



Figure. 1. Photograph of the as-grown 0.5 at.% Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal.

3. Optical spectroscopy

The room temperature absorption spectra of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal in the wavelength region of 350-2120 nm are shown in Fig. 2. It is clear to see that there are nine typical absorption bands centered at approximately 362, 388, 420, 456, 488, 540, 644, 1144, 1922 nm for σ - polarization and 362, 388, 420, 454, 487, 540, 646, 1145, 1952 nm for π - polarization, which correspond to the transitions from the ground state 5I_8 to $^5G_5+^3H_5+^3H_6$, $^3K_7+^5G_4$, $^5G_5+^3G_5$, $^5F_1+^5G_6$, $^5F_2+^5F_3$, $^5S_2+^5F_4$, 5F_5 , 5I_6 and 5I_7 , respectively. The absorption cross-section of peak at 644 nm of σ - and 646 nm of π - polarizations was calculated to be $2.80 \times 10^{-20} \text{ cm}^2$ and $1.65 \times 10^{-20} \text{ cm}^2$, which match well to the commercially available red laser diode (LD) lasers. The absorption cross-section of peak at 1922 nm of σ - and 1952 nm of π - polarizations was calculated to be $0.80 \times 10^{-20} \text{ cm}^2$ and $0.75 \times 10^{-20} \text{ cm}^2$, and full width at half maximum (FWHM) was calculated to be 15.5 nm and 11.2 nm, respectively. The broad bandwidth means that Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal is suitable for pumping.

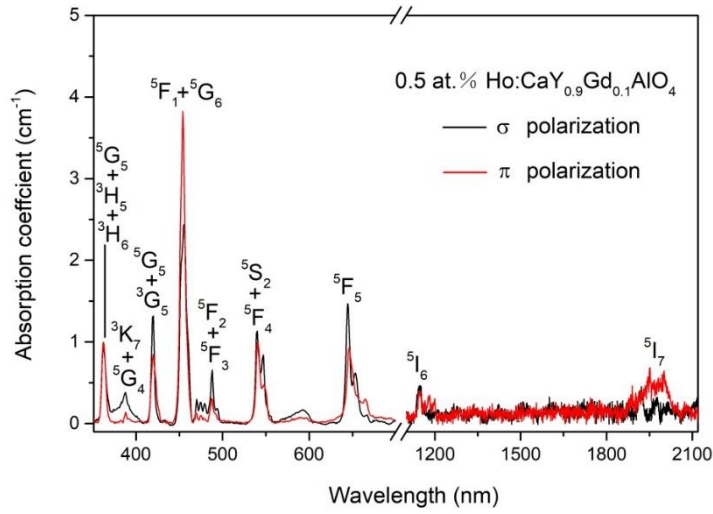


Figure. 2. The polarized absorption spectra of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal.

Table 1 The calculated absorption cross-section, FWHM, peak wavelength, measured and calculated line strength of Ho³⁺ in CaY_{0.9}Gd_{0.1}AlO₄

⁵ I ₈ →	Peak λ (nm)		α (cm ⁻¹)		σ _{abs} (10 ⁻²⁰ cm ²)		FWHM (nm)		Scal (10 ⁻²⁰ cm ²)		Sexp (10 ⁻²⁰ cm ²)	
	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π
⁵ G ₅ + ³ H ₅ + ³ H ₆	362	362	0.86	0.97	1.65	1.86	5.35	5.13	1.23	2.36	3.33	2.80
³ K ₇ + ⁵ G ₄	388	388	0.28	0.13	0.54	0.25	8.67	3.04	0.14	0.40	2.64	0.49
⁵ G ₅ + ³ G ₅	420	420	1.30	0.78	2.49	1.49	3.79	5.86	1.71	2.88	2.64	2.43
⁵ F ₁ + ⁵ G ₆	456	454	2.47	3.79	4.73	7.26	8.93	6.64	6.83	11.05	8.73	10.74
⁵ F ₂ + ⁵ F ₃	488	487	0.56	0.28	1.07	0.54	3.07	4.34	0.05	1.38	1.43	0.70
⁵ S ₂ + ⁵ F ₄	540	540	1.10	0.97	2.11	1.86	11.41	10.46	0.85	3.69	3.79	3.11
⁵ F ₅	644	646	1.46	0.86	2.80	1.65	5.58	8.56	1.41	3.76	4.10	3.81
⁵ I ₆	1144	1145	0.39	0.31	0.75	1.44	18.04	12.01	0.20	2.01	1.64	1.28
⁵ I ₇	1922	1952	0.42	0.39	0.80	0.75	15.45	11.17	0.63	4.74	2.94	5.92

Table 2 The Judd–Ofelt intensity parameters of Ho³⁺-doped different crystals.

Crystals	Ω ₂ (10 ⁻²⁰ cm ²)	Ω ₄ (10 ⁻²⁰ cm ²)	Ω ₆ (10 ⁻²⁰ cm ²)	Ω ₄ /Ω ₆	References
Ho:CaY _{0.9} Gd _{0.1} AlO ₄	3.16	3.93	0.91	4.32	This work
Ho:YAlO ₃	2.89	2.92	1.32	2.21	[25]
Ho:Sc ₂ SiO ₅	4.44	3.48	6.82	0.51	[13]
Ho: MgWO ₄	17.57	3.90	1.69	2.31	[26]
Ho:NaYF ₄	1.65	0.84	1.61	0.52	[27]
Ho:CeF ₃	0.28	0.58	0.40	1.45	[28]
Ho: LuLiF ₄	2.44	2.31	1.44	1.60	[29]
Ho:LaF ₃	1.03	0.98	0.31	3.16	[31]

Table 3 Spontaneous transition rate, branching ratios and radiative lifetimes of

Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal.

${}^5I_7 \rightarrow$	$\lambda(\text{nm})$		FWHM (nm)		A (J \rightarrow J') (s ⁻¹)		$\beta(\%)$		τ_{rad} (ms)
	σ	π	σ	π	σ	π	σ	π	
5I_8	2032	2013	173.04	189.92	54.41	221.49	100	100	13.76

For the Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal, the values of $\Omega_{2,4,6}$ were calculated to be 3.16×10^{-20} cm², 3.93×10^{-20} cm², 0.91×10^{-20} cm², respectively. The J-O intensity parameters of Ho³⁺ ions doped different crystals are listed in Table 2. From the Judd-Oflet theory, the larger value of Ω_2 indicates the lower asymmetry as well as the stronger covalent bonding, the parameter of Ω_4/Ω_6 determines the spectroscopy quality of the materials. The value of Ω_4/Ω_6 of Ho:CaY_{0.9}Gd_{0.1}AlO₄ was calculated to be 4.32, which higher than that of Ho:YAlO₃ [25], Ho:Sc₂SiO₅ [13], Ho:MgWO₄ [26], Ho:NaYF₄ [27], Ho:CeF₃ [28], Ho:LuLiF₄ [29]. The relatively higher Ω_4/Ω_6 value indicates that Ho:CaY_{0.9}Gd_{0.1}AlO₄ is an excellent material for laser operation.

The Judd-Ofelt theory can be successfully applied to evaluate the optical characteristics of lanthanide ions doped host materials, expressing the probability of any transition between two fⁿ states with three parameters (Ω_2 , Ω_4 , Ω_6) based on absorption spectra. From the absorption transitions in Fig. 2, merely the ${}^5I_8 \rightarrow {}^5I_7$ transition of Ho³⁺ ions is attributed to the ED and MD transitions. So the value of S_{md} of the ${}^5I_8 \rightarrow {}^5I_7$ transition was calculated to be 1.10×10^{-20} cm² for π - and σ - polarizations, The line strengths of ED transitions S_{ed} can be obtained by $S_{\text{ed}} = S_{\text{mea}} - S_{\text{md}}$. The polarized experimental oscillator strengths, calculated oscillator strengths and the J-O intensity parameters (Ω_2 , Ω_4 , Ω_6) are listed Tables 1 and 2. Based on the J-O intensity parameters, the calculated values of radiative transition rates, fluorescence branching ration β and radiative lifetime τ_{rad} are listed in Table 3. The value of τ_{rad} is larger than that of Ho:YAlO₃ ($\tau_{\text{rad}}=6.3$) [25], Ho: MgWO₄ ($\tau_{\text{rad}}=6.18$) [26], but is smaller than of Ho:NaYF₄ ($\tau_{\text{rad}}=19.67$) [27], Ho:CeF₃ ($\tau_{\text{rad}}=26.88$) [28], Ho:LuLiF₄ ($\tau_{\text{rad}}=15.2$) [29].

The emission spectra ranging from 1700 to 2400 nm of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal were measured under the excitation of 640 nm are shown in Fig. 3. The emission cross-section can be obtained according to the Fuchtbauer-Ladenburg formula [30]:

$$\sigma_{em}(\lambda)_{J'J''} = \frac{\lambda^5 A(J'' \rightarrow J')}{8\pi c n^2} \frac{I(\lambda)}{\int \lambda I(\lambda) d\lambda}$$

Where A(J, J') is the spontaneous transition rate, I(λ) is the experimental fluorescent intensity at the wavelength λ , c is the speed of light and n is the refraction index. The Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal exhibits a wide emission band around 2 μ m, corresponding to ${}^5I_7 \rightarrow {}^5I_8$ transition which centered at 2013 nm, 2032 nm with the FWHM of 189.9 nm, 173.0 nm for π - and σ - polarizations, respectively. In additional, the emission cross-sections at 2013 nm and 2032 nm are 6.64×10^{-20} cm² and 1.90×10^{-20} cm² for π - and σ - polarizations, respectively, the value of maximum emission cross section (6.64×10^{-20} cm² at 2013 nm) is larger than that of Ho:MgWO₄ (1.82×10^{-20} cm²) [26], Ho:NaYF₄ (0.69×10^{-20} cm²) [27], Ho:CeF₃ (0.24×10^{-20} cm²) [28], Ho:LuLiF₄ (1.30×10^{-20} cm²) [29], Ho:LaF₃ (0.39×10^{-20} cm²) [31]. The results indicate the Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal possesses a bigger emission cross section, which is beneficial to realize high efficiency laser output.

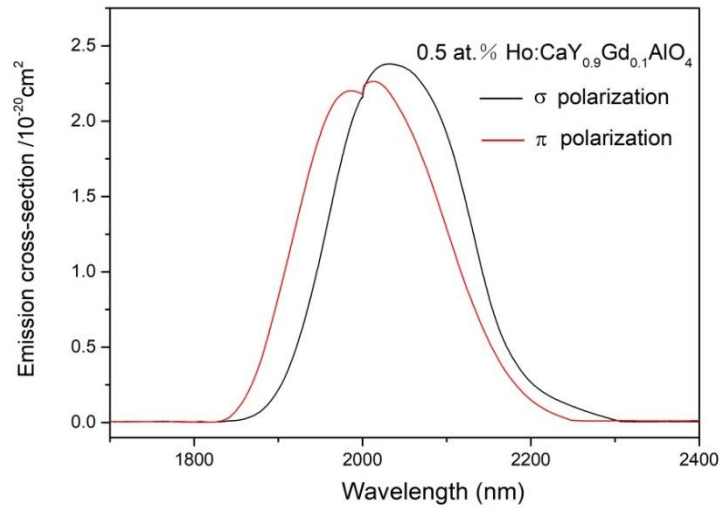


Figure. 3. The emission cross section of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal.

The fluorescence decay curve of ⁵I₇ level at 2050 nm under the excitation of 640 nm is presented in Fig. 4. The fitted curves were obtained by using single exponential function, the lifetime of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal was calculated to be 6.60 ms, which is lower than the calculated result 13.76 ms. According to the measured fluorescence lifetime and calculated lifetime, the quantum efficiency (η) can be calculated by the equation: $\eta = \tau_m / \tau_{rad}$. The ⁵I₇ fluorescence quantum efficiency of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal was obtained to be 48.0%.

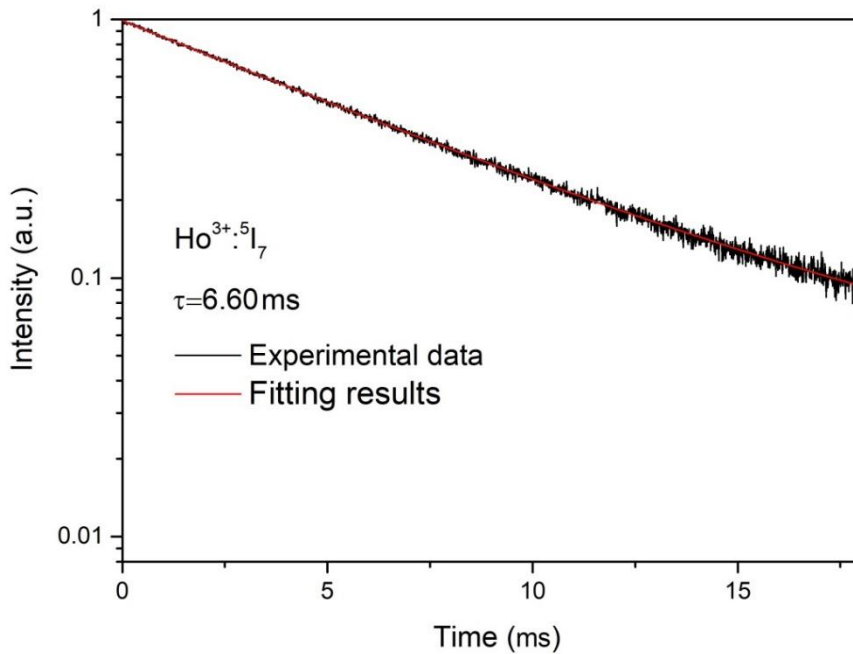


Figure. 4. The fluorescence decay curves of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal.

4. Laser operation

Figure 5 shows a schematic diagram of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal laser pumped by laser

diode (30 W at 1908 nm, core diameter 400 μm , NA=0.22). The pump beam was collimated and focused by a pair of lenses with focal length of 30 mm and 25 mm, respectively. The laser cavity consisted of a plane-plane configuration with the output coupler (OC) with a transmission of 5%, 10%, 20%. The Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystals were a-cut with the dimensions of 4 × 4 × 20 mm³, polished and uncoated for laser experiments. The laser samples were wrapped with indium foil and mounted in a water-cooled copper holder for maintaining at 15°C.

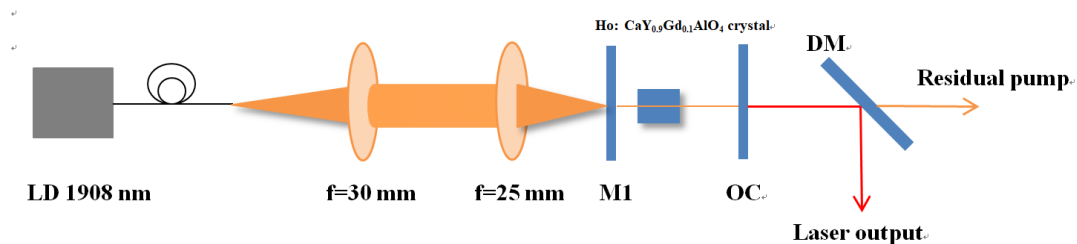


Figure 5. Schematic of LD pumped Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal laser.

Fig. 6 shows results of the CW output power as a function of the pump power. Under the pump power of 27.73 W, the maximum output power of 0.53 W, 0.51 W and 0.18 W were obtained by the output couplers with transmissions of 5%, 10%, and 20%. The corresponding optical efficiency was 3.3%, 3.7%, and 2.5%, respectively. The highest power that we obtained is 0.53 W with the wavelength laser centered at 2088 nm corresponding to the OC with a transmission of 5%, the laser wavelength is at 2080 nm with the OC=10% and at 2083 nm with OC=20%, respectively, as shown in Fig. 7. The slope efficiency of Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal yielded in this work is lower than that of Ho:CaYAlO₄ [12]. By mean of the optimization of crystal quality and the cavity design, much higher average power would be expected. **It is important to mention that the laser operation is strongly connected to the active dopant Ho concentration. The Ho-Ho up conversion phenomenon can be affected by the pumping power and the sample length [32], therefore it is important to grow additional crystal using various Ho dopant concentration and different rod length should be tested.**

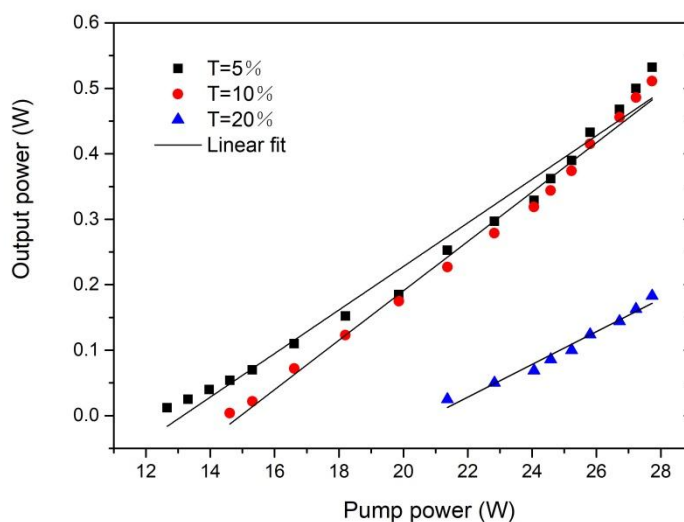


Figure 6. Output power versus pump power with different common OCs.

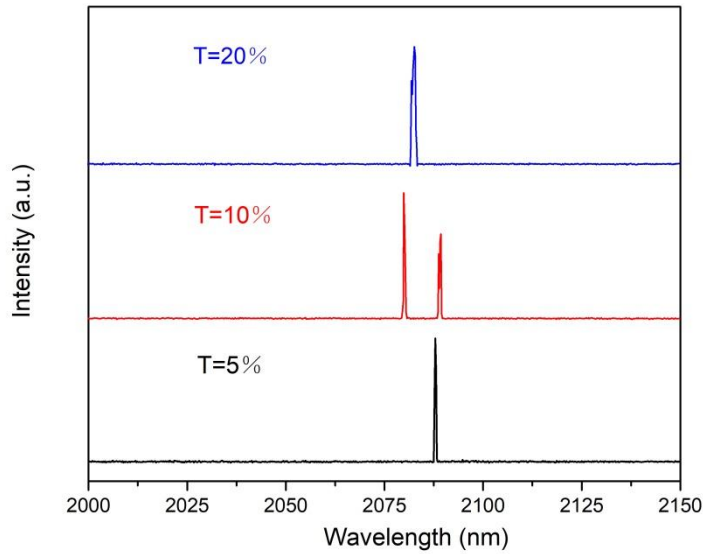


Figure 7. Lasing spectrum of the Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal.

5. Conclusion

In summary, Ho³⁺-doped CaY_{0.9}Gd_{0.1}AlO₄ crystal has been successfully grown by the Czochralski method. The polarized absorption spectra, Judd-Ofelt parameters, polarized emission spectra, fluorescence lifetime were studied. The absorption cross-section of peak at 1922 nm of σ - and 1952 nm of π - polarizations was calculated to be $0.80 \times 10^{-20} \text{ cm}^2$ and $0.75 \times 10^{-20} \text{ cm}^2$. The Judd-Ofelt intensity parameters were calculated to be $3.24 \times 10^{-20} \text{ cm}^2$, $4.03 \times 10^{-20} \text{ cm}^2$, $1.45 \times 10^{-20} \text{ cm}^2$, respectively. The peak emission cross-section of the $^5I_7 \rightarrow ^5I_8$ transition at 2013 nm and 2032 nm are $6.64 \times 10^{-20} \text{ cm}^2$ and $1.90 \times 10^{-20} \text{ cm}^2$ for π - and σ -polarizations by Fuchtbauer-Ladenburg equation, respectively. The fluorescent lifetime at 2050 nm were measured to be 6.60 ms and the 5I_7 fluorescence quantum efficiency was obtained to be 48.0%. The continuous-wave laser operation was demonstrated in the 0.5 at.% Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal pumped by laser diode at 1908 nm. The maximum output power of 0.53 W was obtained, corresponding to the slope efficiency of 3.3%. The results show that Ho:CaY_{0.9}Gd_{0.1}AlO₄ crystal owes excellent spectroscopic properties and is potential for generation of ultrashort pulse around 2 μm wavelength.

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