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Spectroscopic characterization of Yb:CaYAlO₄ shaped crystal fibers

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Abstract: Yb:CaYAlO₄ (Yb:CALYO) shaped crystal fibers with different Yb³⁺ doping concentration were successfully grown by the micro-pulling-down (μ -PD) method. Polarized absorption spectra, emission spectra, as well as the lifetime measurements were performed. The effect of the Yb³⁺ concentration on the structure, absorption, emission and lifetime was systematically studied. The X-ray diffraction (XRD) results show that Yb:CALYO crystal fibers are cubic crystal system, similar with the bulk crystals. The strongest absorption peaks of Yb:CALYO crystal fibers are located at 977 nm for both polarization. Under 905 nm excitation, the strongest emission bands of Yb:CALYO crystal fibers are located at around 980 nm, corresponding to the transition of $^2F_{5/2} \rightarrow ^2F_{7/2}$. The fluorescence lifetime of $^2F_{5/2}$ energy level of Yb:CALYO crystal fibers with concentration of 0.5 at.%, 1 at.%, 2 at.% and 5 at.% was calculated to be 435 μ s, 484 μ s, 514 μ s and 453 μ s, respectively. The experimental results show that Yb:CALYO crystal fiber is a potential laser medium for ultrashort laser operation.

Keywords: Yb:CALYO; μ -PD method; Ultrafast laser; Crystal fiber

1. Introduction

High power femtosecond laser around 1 μm is one of the most active research frontiers in the field of laser science and technology, and has various applications in ultra-fine processing, high-precision ranging, imaging, ultra-fast dynamics, laser fusion and biomedicine [1]. Compared with the Nd^{3+} doped laser gain medium, ytterbium ion (Yb^{3+}) has weak excitation state absorption and relatively long fluorescence lifetime, which is particularly well suited for diode pumping [5]. In addition, the large emission bandwidth is favorable for the generation of ultrashort pulsed laser and various of Yb^{3+} doped host materials have been investigated, including Yb:KYW [6], Yb:YCOB [7], Yb:YAG [8], Yb:Y₂O₃ [9], etc.

Yb:CALYO crystal has attract much attention due to its high thermal conductivity (6.6 W/mK) and negative thermo-optic coefficient. The CALYO crystal has low-symmetry distortions in the local symmetry of the activator center, the corresponding large inhomogeneous broadband spectra is very conducive to the generation of ultrashort pulse laser [11]. In 2011, Tan reported the first femtosecond Yb:CALYO oscillator, which produced 156 fs of laser pulse with an average output power of 740 mW [13]. In 2014, Sévillano reported a Kerr-lens mode-locked Yb:CaGdAlO₄ laser with a pulse width of 32 fs [14]. In 2016, Yu realized a fiber laser pumped Kerr-lens mode-locked Yb:CALYO laser, and obtained a laser with an output power of 250 mW and a pulse duration of 57 fs [15]. In 2018, Tian reported that Kerr-lens mode-locked Yb:CALYO laser directly generated stable 68 fs pulse laser with average power of 1.5 W [16]. In 2021, Ma published an article demonstrating that Kerr-lens mode-locked Yb:CALYO laser generated pulses with less than 5 optical periods, and the resulting pulse duration was as short as 17 fs, corresponding to about 4.68 optical periods [17]. This is also the shortest pulse directly generated by the mode-locked rare earth doped solid state oscillator.

Single crystal fiber is a new type of gain medium between traditional laser bulk crystal and glass fiber. It has the advantages of high aspect ratio, large specific surface area, good heat dissipation, and low nonlinear gain coefficient. The μ -PD method is one of the common method for short growth cycle and low cost of single crystal fiber growth [10], and the diameter of single crystal fiber can reach 300 μm . Yb:CALYO crystal with dimension of $\Phi 2 \times 65 \text{ mm}^3$ was grown by the μ -PD method, and the research mainly focused on the scintillation performance [18].

In this paper, we have successfully grown Yb:CALYO shaped crystal fibers with different

Yb³⁺ doping concentration by the μ -PD method. The spectral properties including polarized absorption spectra, polarized emission spectra and decay curves were measured at room temperature.

2. Experimental

2.1 Crystal growth

Yb:CALYO single crystal fibers were grown by the μ -PD method [19]. The initial raw materials were CALYO crackles grown by the Czochralski method and Yb₂O₃ powder with 5N purity. The dopant concentration of Yb³⁺ ions was 0.5 at. %, 1 at. %, 2 at. % and 5 at.%. The growth rate was 0.3 mm/min with the <100> oriented CALYO crystal as seed under the high purity flowing nitrogen atmosphere. Figure 1 shows a series of Yb:CALYO shaped crystal fibers grown under stable conditions, with length of about 14-16 cm and cross section of 1*1 mm². The crystal fibers are colorless, transparent, crack-free and of good optical quality.

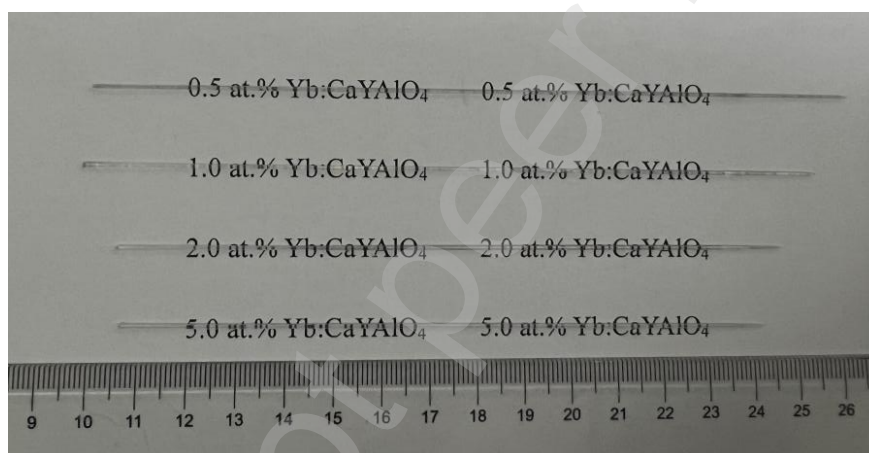


Fig. 1. The photograph of Yb:CALYO shaped crystal fibers.

A small part of the as-grown Yb:CALYO crystal fibers was taken as the samples and ground into powders. The powders were tested by XRD method using Cu-K α radiation (Bruker D2, Germany) at a scan width of 0.01 $^\circ$ within $2\theta = 5^\circ$ -90 $^\circ$, and the setting voltage and current were 30 kV and 10 mA, respectively. The samples for spectral measurements were cut from the as-grown crystal fibers and two surfaces perpendicular to the <100>-growth axis were polished. The polarized absorption spectra were measured with the UH4150 ultraviolet visible near-infrared spectrophotometer produced by Hitachi, Japan, and the measurement range is 850-1100 nm. The polarized fluorescence spectra and fluorescence decay curves were obtained by the FLS1000 fluorescence spectrometer (Edinburgh, UK), under the excitation of 905 nm light source. All the experimental tests were conducted at room temperature.

3. Results and discussion

3.1 Structure

The room temperature diffraction patterns of Yb:CALYO crystal fibers are shown in Fig.2. Compared with the standard diffraction pattern of CALYO crystal, it can be seen that the diffraction angle and relative intensity in the experimental data are basically consistent with the diffraction data of PDF#81-0742 card in the JCPDS diffraction database. The impurity peak appearing at 29.2° was caused by the substitution of Y³⁺ at a high concentration of Yb³⁺ doping. The identification results show that Yb:CALYO crystal fibers also belong to tetragonal system, and the space group is I4/mmm. The lattice parameters of Yb:CALYO crystal fibers was calculated using Jade software and the lattice constants of 0.5 at.% and 5 at.% Yb:CALYO were calculated to be a=0.362 nm, c=1.160 nm, V=0.152 nm³ and a=0.363 nm, c=1.187 nm, V=0.156 nm³, respectively.

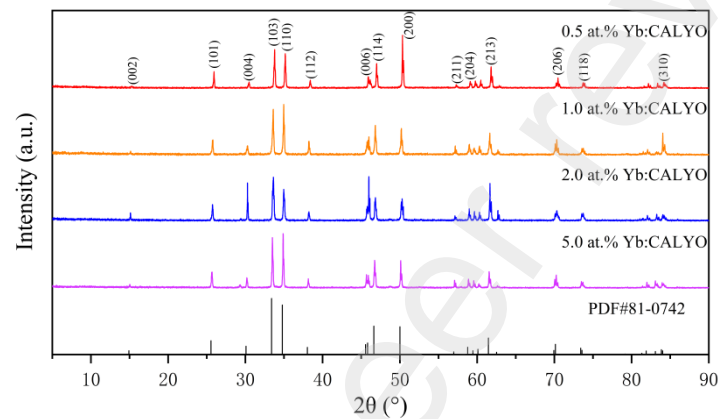


Fig. 2. XRD patterns of Yb:CALYO crystal fiber with a standard pattern of CALYO.

3.2 Optical absorption spectra

Fig. 3 demonstrates the polarized absorption spectra of Yb:CALYO crystal fibers with different dopant concentrations in the wavelength range of 850-1100 nm at room temperature. The absorption bands corresponding to the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb³⁺ ions are around 977 nm for both polarizations, which match well with the emission wavelength of InGaAs laser diodes. Due to the anisotropy of the crystal, the absorption spectra have strong polarization, and the absorption coefficient of the π polarization is generally larger than that of the σ polarization. With increasing Yb³⁺ doping concentration from 0.5 at.% to 5 at.%, the peak absorption coefficient at 977 nm for σ polarization increases from 0.53 cm⁻¹ to 6.72 cm⁻¹, however, peak absorption coefficient for π polarization increases from 2.95 cm⁻¹ to 12.24 cm⁻¹. For 5 at.% Yb:CALYO crystal fiber, the full width at half-maximum (FWHM) of absorption band for σ polarization was 14.8 nm, which is higher than that of 10.0 nm for π polarization, which is smaller than those of 5 at.% Yb:CALYO crystal (15 nm and 11 nm for σ and π polarization, respectively [20]). For the laser diode pumped solid state laser, the emission wavelength of the laser diode will move with the temperature fluctuation, the large absorption bandwidth means that the stable output of the laser can be achieved without complex temperature control system. Due to the strong absorption and wide bandwidth of Yb:CALYO single crystal fibers at around 977 nm, it is beneficial to increase the diode pumping efficiency.

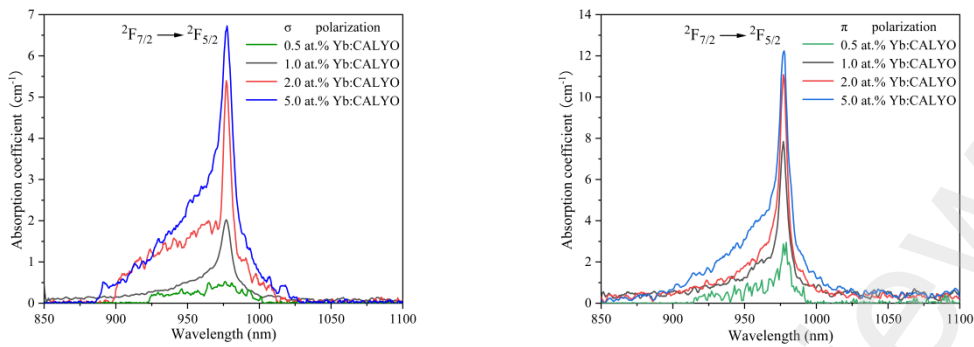


Fig. 3. The polarized absorption spectra of Yb:CALYO crystal fibers.

3.3 Emission spectra

The polarized fluorescence spectra of Yb:CALYO crystal fibers in the range of 925-1150 nm under excitation at 905 nm are indicated in Fig. 4, corresponding to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions. The emission spectra show unresolved zero-line peaks at around 980 nm and broad lines up to 1050 nm, which is due to the rich multisite structure of Yb:CALYO crystal [20]. As the doping concentration increases from 0.5 at.% to 5 at.%, the position of the emission peak shifts from 979 nm to 983 nm for both polarization. As reabsorption phenomenon is a major process in Yb^{3+} -doped laser materials, the wavelength at around 980 nm is not suitable for practical laser output. The FWHMs of emission bands for both polarization increases with the increasing Yb^{3+} doping concentration. For 0.5 at.% Yb:CALYO crystal fiber, the FWHM of the emission band at 979 nm for σ polarization and 983 nm for π polarization is about 15.4 nm and 14.3 nm, respectively. For 5 at.% Yb:CALYO crystal fiber, the FWHM was calculated to be 80.9 nm for σ polarization and 68.9 nm for π polarization, respectively. The considerably large FWHM of 80.9 nm and smooth emission lines indicate that Yb:CALYO crystal fiber is suitable for tunable and ultrashort laser operation.

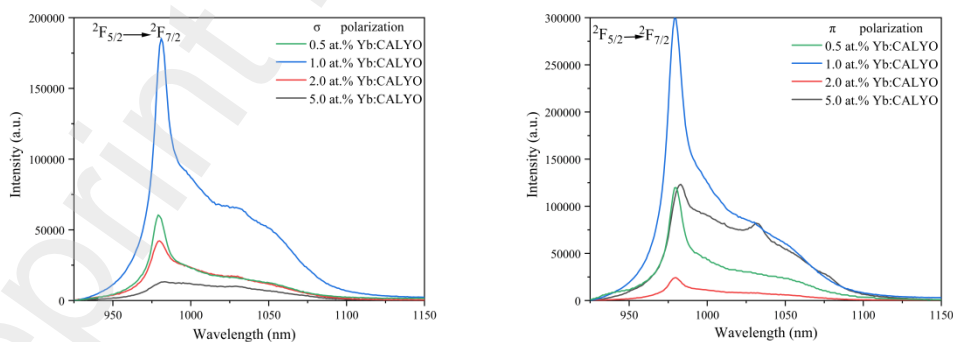


Fig. 4. The polarized fluorescence spectra of Yb:CALYO crystal fibers.

3.4 Fluorescence lifetime

The fluorescence decay curves of the ${}^2F_{5/2}$ level excited by 905 nm at room temperature was presented in Fig. 5. All measured decay curves exhibit a single exponential decaying behavior. The fluorescence lifetime was calculated to be 435 μs , 484 μs , 514 μs and 453 μs for doping concentration of 0.5 at.%, 1.0 at.%, 2.0 at.% and 5.0 at.%, respectively. The value is smaller than that of Yb:YAG (950 μs [21]), Yb:CNGG (791 μs [22]), Yb:KY(WO₄) (600 μs [23]), but slightly larger than that of Yb:CaGdAlO₄ (420 μs [24]) and bulk crystal Yb:CaYAlO₄ (426 μs [11]). The fluorescence lifetime increased with the doping concentration from 0.5 at.% to 2 at.%. Furthermore, increasing the doping concentration decreased the fluorescence lifetime, because of the concentration quenching effect [25]. All results show that Yb:CAYLO crystal fiber may be a promising laser gain medium around 1 μm .

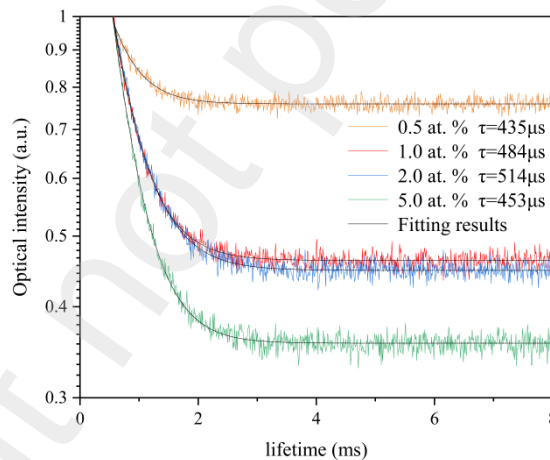


Fig. 5. The fluorescence decay curve of Yb:CALYO single crystal fibers.

4. Conclusion

Yb:CALYO shaped crystal fibers have been successfully grown using the μ -PD method. The XRD results show that Yb:CALYO crystal fibers are cubic crystal system, and the space group is I4/mmm. The broad absorption bands corresponding to the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition enable the crystal fiber to absorb the incident light from InGaAs laser diodes. Under 905 nm excitation, the strongest emission bands of Yb:CALYO crystal fibers are located at 980 nm. For 5 at.% Yb:CALYO crystal fiber, the FWHM was calculated to be 80.9 nm for σ polarization and 68.9 nm for π polarization, respectively. The fluorescence lifetime of 0.5

at.%, 1.0 at.%, 2.0 at.% and 5.0 at.% Yb:CALYO crystal fibers was fitted to be 435 μ s, 484 μ s, 514 μ s and 453 μ s, respectively. All the results show the Yb:CALYO single crystal fiber is potential to achieve ultrashort laser operation.

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