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Growth, structure and spectroscopic properties of Er,Pr:YAP laser crystal

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ABSTRACT

Er^{3+} and Pr^{3+} co-doped YAP laser crystal with high optical quality was grown successfully by the Czochralski method for the first time. By contrast, an Er^{3+} single doped YAP laser crystal was also grown. The cell parameters of the two crystals were obtained by the X-ray Rietveld refinement method. The X-ray rocking curves indicate that the as-grown crystals possess excellent crystalline quality. The absorption spectra show that the crystals are suitable to be pumped by 972 nm LD. The NIR and MIR emission spectra, the up–conversion spectra and the fluorescence decay curves were also measured to investigate the influence of Pr^{3+} ions on the spectroscopic properties. The results indicate the Pr^{3+} ions acting as the deactivator can decrease efficiently the lifetime of the lower laser level $^4I_{13/2}$ of the Er^{3+} ions from 10.72 to 0.489 ms, which would be beneficial to decrease the laser threshold and increase the laser conversion efficiency.

1. Introduction

In recent years, an increasing interest has been aroused on the 2.7–3 μm mid-infrared (MIR) laser crystals, which due to the 2.7–3 μm waveband belongs to the strong water absorption, thus can be widely applied in the medical field, such as ophthalmology, dentistry and laser cosmetic surgery [1–3]. In addition, the 2.7–3 μm laser can be directly used in the field of space military and scientific research because only very little water vapor content in space [4]. Besides, the 2.7–3 μm lasers also have important application in laser remote sensing and LIDAR field [5]. Furthermore, the 2.7–3 μm laser waveband is also an ideal pumping source for the optical parametric oscillator (OPO) or optical parametric generation (OPG) to realize 3–19 μm infrared lasers output, which have significant applications in the fields of atmospheric detection, poisonous gas detection, and optoelectronic countermeasures et al. [3,6,7]. At present, the 2.7–3 μm lasers have been realized on some laser crystals doped with Er^{3+} or Ho^{3+} as the activator ions.

The Er^{3+} serves as an active ion emitting 2.7–3 μm by $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition, but the transition is restricted by the self-terminating effect caused by the lifetime of the upper laser level is much shorter than that of the lower level. This self-terminating “bottleneck” effect can be conquered by means of increasing the doped concentration of Er^{3+} (> 30 at%) or co-doping the deactivation ions [8–12].

$YAlO_3$(YAP) is an attractive candidate as a laser host due to its several excellent characteristics, such as excellent thermal and mechanical properties, natural birefringence [13] and structural anisotropy. The large mechanical strength, high moss hardness (~8.5) and thermal conductivity (~11 W/m/K) make the crystal can operate at high power and high repetition rate. The effects of thermal birefringence can be reduced to negligible levels along the orientation which doesn't coincide with the optic axis of the YAP crystal due to the natural birefringence is much larger than the thermal birefringence [13]. The YAP belongs to a malformed perovskite-like structure and possesses Pbnm space group with orthorhombic symmetry [14], which leads to some unique advantages as a laser host material. For example, the output lasers are linearly polarized lasers, and the quantum yield and branching ratio of the 3 μm emission in Er:YAP is higher than those of Er:YAG crystal [15]. The ions radius of Er^{3+} (0.088 nm) and Y^{3+} (0.090 nm) are almost same, resulting in the effective segregation coefficient of Er^{3+} in the YAP is close to 1. Therefore, the heavily Er doped (10, 20 and 50 at.%) YAP crystals with relatively uniform concentration distribution can be grown easily [16]. Besides, the YAP crystal has the characteristics of high gain along the b-axis, which is suitable for the application of CW laser [14]. However, the YAP crystal tends to crack easily owing to the thermal anisotropy in different crystalline directions. Therefore, the necking down and slow cooling technologies should be adopted to obtain cracking-free YAP crystals in the crystal growth process.

As early as 1987, Stalder et al. have researched the spectroscopy, polarization properties and the laser transitions of the Er:YAP crystal at

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2.7–3 μm medium infrared waveband. They proved the crystal has abundant laser line and they asserted it is possible to excite six more laser lines by using an intracavity polarizer and selectively absorbing filters [17–19]. Moreover, Zeng et al. studied experimentally the time characteristic of the vibration, and the pulsed laser performances of a-axis YAP crystal doped with10 at.% and 20 at.% Er^{3+} ions, and obtained 240 mJ output energy at 2.7 μm with a threshold energy of about 10 J [20]. In recent years, Gu et al. reported the growth and spectroscopic characterization of Yb,Er,Eu:YAP crystal, in which the Yb^{3+} and Eu^{3+} ions act as sensitizer and deactivator for Er^{3+} ions, respectively, resulting in the widening of the absorption band at 978 nm and decreasing of the lifetime ratio between the lower laser level ($^4I_{13/2}$) and upper laser level ($^4I_{11/2}$) [21].

In this paper, the Er:YAP and Er,Pr:YAP crystals with high optical quality were grown by Czochralski method. The Pr^{3+} was chosen as deactivation ions to inhibit the competitive fluorescence and adjust the lifetimes by depleting the population of the $^4I_{13/2}$ energy level. The crystal structure and spectroscopy properties are compared and discussed in detail.

2. Experimental details

2.1. Crystal growth

The Er:YAP and Er,Pr:YAP crystals were grown along the crystalline b-axis using Cz method from a congruent melt with a medium frequency induction heating system. The doping concentrations of the Er^{3+} and Pr^{3+} ions in the initial raw materials are 10 at% and 0.2 at%, respectively. The starting raw materials were Er_2O_3 (5 N), Pr_6O_{11} (5 N), Y_2O_3 (5 N), and Al_2O_3 (5 N) oxide powders, which were weighed accurately according to the molecular formula $Er_{0.1}Y_{0.9}AlO_3$ and $Er_{0.1}Pr_{0.002}Y_{0.898}AlO_3$. The powders were well mixed and pressed into tablets. The crystal growth was carried out in a JGD-60 furnace (CETC26^{th,} China) with an automatic diameter control (ADC) growth system operated at a rotation speed of 7 rpm and a pulling rate of 1 mm/h. An iridium crucible with dimensions of Φ 60 mm × 48 mm was used in high purity argon atmosphere to prevent oxidization. High optical quality Er:YAP and Er,Pr:YAP crystals with a dimension of Φ29 mm × 70 mm were obtained, as shown in Fig. 1. The crystals were annealed in the flow H_2 atmosphere at 1250 °C for 24 h.

2.2. Characterizations

The Er:YAP and Er,Pr:YAP crystal samples with the thickness of 2.5 mm were cut perpendicularly to the growth orientation ⟨010⟩ and optically polished on both faces for the characterization measurements. The crystal structure was determined by XRD using a Philips X'pert PRO X-ray diffractometer equipped with Cu Kα radiation. The diffraction data were recorded at a scan step of 0.0167° in the 2θ range of 10–90°. A high resolution X'pert Pro MPD diffractometer equipped with a Hybrid $K\alpha_1$ monochromator was used to collect the X-ray rocking curve (XRC).

The absorption spectra were measured in a wavelength range of 0.32–3 μm by a spectrophotometer (PE lambda 950). An Edinburgh fluorescence spectrometer (FLSP 920) with an exciting source of 973 nm LD was used to record the fluorescence spectrum from 2.6 to 2.9 μm and the up-conversion luminescence spectra from 0.5 to 0.7 μm. The fluorescence decay curves were recorded by the Edinburgh fluorescence spectrometer (FLSP 920) with the excitation source of Opolette (OPO) 355 I lasers. All measurements were carried out at room temperature.

3. Result and discussion

3.1. X-ray powder diffraction and rietveld refinement

The XRD patterns of the Er:YAP and Er,Pr:YAP crystals and the standard pattern of the YAP phase (ICSD#99419) are shown in Fig. 2. The diffraction peaks are sharp in the measured 2θ range. Compared with the standard pattern of the YAP phase (ICSD #99419), all the diffraction peaks of the Er:YAP and Er,Pr:YAP crystals are consistent with those of the YAP crystal, and only the peak positions have slight difference owing to the doped ions. Hence, the doped ions do not change the perovskite-like structure of the pure YAP crystal and the as-grown crystal still belong to the space group of Pbnm. Strong diffraction peaks are observed and indexed as the (002), (111), (112), (202), (220), (131) and (312) crystallographic planes, corresponding to the 2θ diffraction angles at 23.95°, 26.86°, 34.25°, 42.63°, 49.02°,56.09°and 61.78°, respectively.

Using the structural parameters of ICSD #99419 as the initial values, the structures of the Er:YAP and Er,Pr:YAP crystals are refined with the XRD data by the general structure analysis software (GSAS) package and the results are shown in Fig. 3, Tables 1 and 2. The lattice parameters of the Er:YAP and Er,Pr:YAP crystals are fitted to be: a_1 = 5.180 Å, b_1 = 5.331 Å, c_1 = 7.372 Å and a_2 = 5.181 Å, b_2 = 5.332 Å, c_2 = 7.374 Å, respectively. Compared with the cell parameters: a = 5.180 Å, b = 5.330 Å, c = 7.371 Å of ICSD #99419, the parameters become slight larger after the Er^{3+} and Pr^{3+} ions are

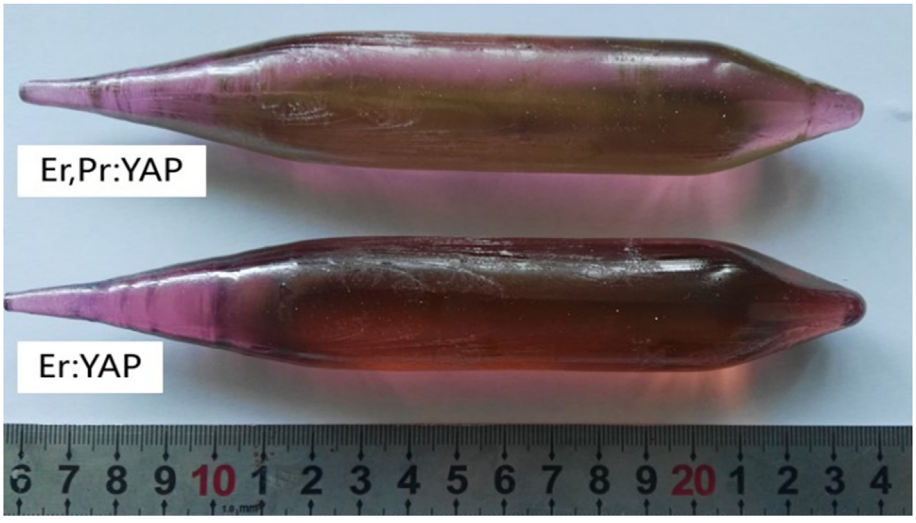

Fig. 1. Photograph of as-grown Er:YAP and Er,Pr:YAP laser crystals.