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

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\begin{abstract}
Er\textsuperscript{3+} and Pr\textsuperscript{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\textsuperscript{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\textsuperscript{3+} ions on the spectroscopic properties. The results indicate the Pr\textsuperscript{3+} ions acting as the deactivator can decrease efficiently the lifetime of the lower laser level \( ^{4}I_{11/2} \) of the Er\textsuperscript{3+} ions from 10.72 to 0.489 ms, which would be beneficial to decrease the laser threshold and increase the laser conversion efficiency.
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1. Introduction

In recent years, an increasing interest has been aroused on the 2.7–3\( \mu \)m mid-infrared (MIR) laser crystals, which due to the 2.7–3\( \mu \)m 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\( \mu \)m 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\( \mu \)m lasers also have important application in laser remote sensing and LIDAR field [5]. Furthermore, the 2.7–3\( \mu \)m laser waveband is also an ideal pumping source for the optical parametric oscillator (OPO) or optical parametric generation (OPG) to realize 3–19\( \mu \)m 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\( \mu \)m lasers have been realized on some laser crystals doped with Er\textsuperscript{3+} or Ho\textsuperscript{3+} as the activator ions.

The Er\textsuperscript{3+} serves as an active ion emitting 2.7–3\( \mu \)m by \( ^{4}I_{11/2} \rightarrow ^{4}I_{13/2} \) transition, but the transition is restricted by the self-terminating effect caused by the lifetime of the upper laser level which 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\textsuperscript{3+} (> 30 at%) or co-doping the deactivation ions [8–12].

Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}(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\( \mu \)m emission in Er:YAP is higher than those of Er:YAG crystal [15]. The ions radius of Er\textsuperscript{3+} (0.088 nm) and Y\textsuperscript{3+} (0.090 nm) are almost same, resulting in the effective segregation coefficient of Er\textsuperscript{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...
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 with 10 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 ($4_{13/2}$) and upper laser level ($4_{11/2}$) [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 $4_{13/2}$ 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 starting raw materials were Er$_2$O$_3$ (5 N), Pr$_6$O$_{11}$ (5 N), Y$_2$O$_3$ (5 N), and Al$_2$O$_3$ (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 (CETC26th, 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 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 Φ 29 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 Xpert 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 Xpert Pro MPD diffractometer equipped with a Hybrid Kα 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 spectometer (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), (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 constants: $a = 5.180$ 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.](image-url)
doped into the YAP crystal and occupy the sites of the Y\(^{3+}\) ions. The larger lattice cell mainly results from the ions radius of the Pr\(^{3+}\) (0.101 nm) is larger than that of the Y\(^{3+}\) (0.090 nm).

### 3.2. X-ray rocking curves

The XRCs of the (010) crystallographic faces of the Er:YAP and Er,Pr:YAP crystals are shown in Fig. 4. The diffraction peaks of these two crystals show symmetrical shape and the full width at half maximum (FWHM) are 0.046° and 0.063°, respectively, which indicate that the two crystals possess good crystalline quality.

### 3.3. Absorption and fluorescence spectra

Figure 5 exhibits the absorption spectra of the Er:YAP and Er,Pr:YAP crystals in the wavelength range of 0.32–3 \(\mu\)m. The absorption peaks of these two crystals are similar to each other, and a wide-band absorption
Fig. 4. XRCs of the Er:YAP and Er,Pr:YAP crystals on the (010) crystallographic face.

Fig. 5. Absorption spectra of the Er:YAP and Er,Pr:YAP crystals. Inset: enlarged curves in the range of 0.95–1.01 μm.

Fig. 6. NIR emission spectra of the Er:YAP and Er,Pr:YAP crystals excited by 973 nm LD.

Fig. 7. MIR emission spectra of the Er:YAP and Er,Pr:YAP crystals excited by 973 nm LD.
characteristic is observed in a wavelength range of 0.95–1.01 μm, which corresponds to the transition of Er3+ ions from the ground state 4I15/2 to the excited state 4I11/2. The FWHM of the 972 nm absorption band for the Er:YAP and Er,Pr:YAP crystals are approximately 35 and 36 nm, and the absorption coefficients are 3.57 and 3.31 cm⁻¹, respectively, which match well with the emission wavelength of the commercially available high power InGaAs LDs. The result indicates that the Er:YAP and Er,Pr:YAP crystals are suitable and desirable for efficient pumping by high-power 970 nm LDs.

The near-infrared (NIR, 1.0–1.7 μm) and mid-infrared (MIR, 2.6–2.9 μm) emission spectra of the Er:YAP and Er,Pr:YAP crystals excited by 973 nm LD are exhibited in Fig. 6 and Fig. 7, respectively. From Fig. 6, we can note that the intensity of NIR emission is significantly quenched after doping the Pr3+ ions, especially in the range of 1.4–1.7 μm. In Fig. 7, a few fluorescence peaks are located in wavelength range of 2.6–2.9 μm, resulting from the stark sub-level transitions from 3H5/2 to 3F4/2 of Er3+ ions. Two relatively strong fluorescence peaks are centered at 2.71 and 2.729 μm, which indicate that the 2.7 μm laser output may be realized on the two crystals.

### 3.4. Energy transfer processes

In order to understand the differences of emission spectra caused by introducing Pr3+, the energy transfer diagram of Er3+ and Pr3+ is presented in Fig. 8. AT denotes the pumping absorption transition, pumped by commercial 973 nm LD, ET1 and ET2 denote energy transfer from 4I11/2 → 3G4 and 4I13/2 → 3F4. ESA1 and ESA2 represent the excited state absorption process from 4I11/2 → 4F7/2 and 4I13/2 → 4F9/2, respectively. The self-terminating “bottleneck” effect of Er3+ can be conquered by means of increasing the doped concentration of Er 3+ (> 30 at%) by inducing up-conversion (UC1) (4I13/2 → 4I15/2) + (4I13/2 → 4I9/2 → 4I11/2) and cross-relaxation (CR) (4S3/2 → H11/2 → 4I15/2) + (4I15/2 → 4I13/2) + (4I15/2 → 4I9/2 → 4I11/2) processes [8,9]. Both processes in favor of population inversion: they produce an even population of the initial (4I11/2) and final (4I13/2) energy levels as a same level. The up-conversion (UC2) (4I11/2 → 4I15/2) + (4I11/2 → 4F7/2 → 4S3/2), followed by the multiphoton transitions to 4S3/2, deactivates the initial laser level, but its negative effect is attenuated by a cross-relaxation mechanism involving 4S3/2 [12].

Another method is co-doping the deactivation ions [9–11], which is adopted to inhibit the competitive fluorescence, at the same time adjust the lifetimes by depleting the population of the 4I13/2 energy level. Experiment finds that the Pr3+ is a suitable ion because its energy level 3F4 is adjacent to level 4I13/2 of Er3+. Wang et al. reported that the efficiencies of energy transfer (ET1 and ET2) were determined as 64.2% and 96.5% in 10 at% Er and 0.17 at% Pr:GGG crystal [11]; and it were 56.7% and 84.6% in the 20 at% Er and 0.3 at% Pr:GYSGG crystal. The near-infrared (NIR, 1.0–1.7 μm) and mid-infrared (MIR, 2.6–2.9 μm) emission spectra of the Er:YAP and Er,Pr:YAP crystals excited by 973 nm LD are exhibited in Fig. 6 and Fig. 7, respectively. From Fig. 6, we can note that the intensity of NIR emission is significantly quenched after doping the Pr3+ ions, especially in the range of 1.4–1.7 μm. In Fig. 7, a few fluorescence peaks are located in wavelength range of 2.6–2.9 μm, resulting from the stark sub-level transitions from 3H5/2 to 3F4/2 of Er3+ ions. Two relatively strong fluorescence peaks are centered at 2.71 and 2.729 μm, which indicate that the 2.7 μm laser output may be realized on the two crystals.

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researched by Chen et al. [9]; Ma et al. researched the influence of the concentration of deactivating ion Pr$^{3+}$ and optimized it in the Er:Pr:CaF$_2$ crystal, they found that the laser performance of the crystal was great improved after lightly doped Pr$^{3+}$, and the efficiencies of energy transfer (ET$_1$ and ET$_2$) were 64.2% and 96.5% in the 3 at% Er and 0.1 at% Pr:CaF$_2$ crystal [10].

3.5. Up-conversion luminescence spectra

The up-conversion luminescence spectra of the Er:YAP and Er,Pr:YAP crystals in a wavelength range of 0.5–0.75 μm excited with 973 nm LD are exhibited in Fig. 9. Two strong up-conversion luminescence bands correspond to $^2H_{11/2}+^4S_{3/2} \rightarrow ^4I_{15/2}$ (green luminescence) and $^4F_{9/2} \rightarrow ^4I_{13/2}$ (red luminescence) transitions of Er$^{3+}$ ions, respectively. In the Er:YAP crystal, the red luminescence is stronger than green luminescence because the excited state absorption process from Er$^{3+}$:$^4I_{13/2}$ (ESA$_2$) is much stronger than the energy transfer conversion process from Er$^{3+}$:$^4I_{11/2}$ (UC$_2$). After co-doping of Pr$^{3+}$, both UC$_2$ and ESA$_2$ processes are weakened especially the latter one, thus the intensity of the green and red emission is weakened, which is in accordance with the results of NIR emission spectra.

3.6. Fluorescence lifetimes

The fluorescence decay curves of the Er:YAP and Er,Pr:YAP crystals excited by OPO pulse lasers are shown in Fig. 10, which exhibit a single exponential decay behavior. The lifetimes of the upper laser level $^4I_{11/2}$ and the lower laser level $^4I_{13/2}$ of the Er,Pr:YAP crystal are fitted to be 0.422 and 0.489 ms, which is much smaller than the lifetimes of laser level of the Er:YAP crystal that are fitted to be 0.895 and 10.72 ms. The results indicate that the Pr$^{3+}$ ions can decrease simultaneously the upper and lower level lifetimes of the ions for the Er,Pr:YAP crystal, which is attributed to the energy transfer processes $^4I_{11/2}$ (Er$^{3+}$) $\rightarrow ^4G_{4}$ (Pr$^{3+}$) and $^4I_{13/2}$ (Er$^{3+}$) $\rightarrow ^4F_{4}$ (Pr$^{3+}$). Besides, the efficiency of energy transfer from the Er$^{3+}$ to Pr$^{3+}$ ions can be calculated based on the following formula:

$$\eta = 1 - \frac{\tau_1}{\tau_2}$$

where $\tau_1$ is the level lifetime of the Er,Pr:YAP crystal, and $\tau_2$ is the level lifetime of the Er:YAP crystal. According to the formula and the aforementioned lifetime values of Er:YAP and Er,Pr:YAP, the energy transfer efficiencies of Er$\rightarrow$Pr in ET$_1$ and ET$_2$ are 52.8% and 95.4%, respectively. It can be seen that the energy transfer efficiencies of Er$\rightarrow$Pr in ET$_2$ is much larger than ET$_1$, the result is in accordance with the aforementioned experimental result of the emission spectra, and which is beneficial to realize population inversion and improve laser efficiency.

4. Conclusions

High optical quality Er:YAP and Er,Pr:YAP crystals were grown successfully by the Cz method. Absorption spectra show that the two crystals are suitable to be pumped by high-power 970 nm InGaAs LD. The MIR emission spectra exhibit two strong peaks at 2.71 and 2.729 μm, which indicate that the two crystals can realize 2.7 μm laser output. The results of the NIR emission spectra, the up-conversion fluorescence spectra and the fluorescence decay curves of the Er:YAP and Er,Pr:YAP crystals show that the deactivator ions Pr$^{3+}$ can greatly inhibit the competitive fluorescence and decrease the lifetime of the lower level $^4I_{13/2}$, which is beneficial to decrease the laser threshold and increase the laser conversion efficiency. From the above, the Er,Pr:YAP crystal is a promising laser medium to realize 2.7 μm laser pumped by 970 nm LD with a high laser performance.

Acknowledgments

This work was financially supported by the National Key Research and Development Program of China (Grant Nos. 2016YFB1102301) and the National Natural Science Foundation of China (NSFC) (51272254, 51702322 and 51502292).

References


