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The micro-pulling-down growth of Tm:LuAG and Tm,Pr:LuAG crystals and optical properties

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Abstract:

Tm³⁺ doped and Tm³⁺, Pr³⁺ co-doped Lu₃Al₅O₁₂ (LuAG) single crystals have been successfully grown by the micro-pulling-down (μ -PD) method. The absorption spectra, fluorescence spectra and lifetimes were investigated at room temperature. In the absorption spectra, the transition centered at 782 nm matches well with the GaAlAs LDs laser pumping. The incorporation of Pr³⁺ into Tm³⁺-doped LuAG crystals significantly enhanced the intensity of 1.5 μ m emission and decreased the fluorescence lifetime of the lower energy level for 1.5 μ m emission from 10.427 ms to 2.603 ms. The results indicate that Tm,Pr:LuAG crystal can be promising candidate for near infrared 1.5 μ m laser materials.

Keywords: Tm, Pr: Lu₃Al₅O₁₂; Micro-pulling-down (μ -PD) method; Near-infrared laser

1. Introduction

Laser sources operating at 1.5 μm region have attracted much attention due to the use for remote sensing, biomedical systems, optical subscriber networks, telecommunication industry, and so on [1-3]. Using an AlGaAs diode laser as pump source, trivalent thulium (Tm^{3+}) can provide laser oscillation at this specific wavelength through the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition channel. However, the transition of Tm^{3+} that generates emission around 1.5 μm is considered to be self-terminating, for the lifetime of $^3\text{F}_4$ energy level is much longer than that of $^3\text{H}_4$ energy level [4]. In order to deal with the unfavorable population bottleneck and depopulate the $^3\text{F}_4$ state efficiently, co-doping sensitive ions like Tb^{3+} , Ho^{3+} and Pr^{3+} ions were proposed to quench the terminal $^3\text{F}_4$ level and increase the emission intensity at around 1.5 μm by means of energy transfer [5-9].

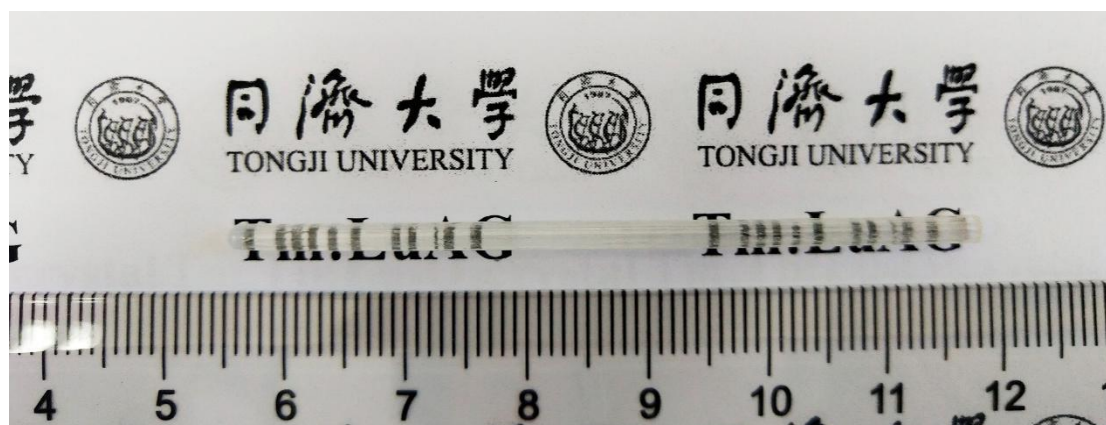
$\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) is a promising laser host material due to its relatively high thermal conductivity, chemical and physical stability [10]. $\text{Tm}:\text{LuAG}$ crystal can be easily grown by the Czochralski method [11] and micro-pulling-down method [12]. In 1995, A diode-pumped $\text{Tm}:\text{LuAG}$ laser was demonstrated with a relatively low optical-to-optical efficiency of 7.3% [13]. For continuous-wave operation, a maximum output power of 4.91 W was reported with a slope efficiency of 25.3 % [14]. To the best of our knowledge, there has no research about the growth and performance of $\text{Tm,Pr}:\text{LuAG}$ crystal.

In this work, $\text{Tm,Pr}:\text{LuAG}$ crystal was grown by the micro-pulling-down method. The spectroscopic properties of $\text{Tm,Pr}:\text{LuAG}$ crystal were reported and Pr^{3+} ion was demonstrated to be an efficient deactivated ion for Tm^{3+} ion by effective energy transfer from $\text{Tm}^{3+} : ^3\text{F}_4$ level to $\text{Pr}^{3+} : ^3\text{F}_2$ level.

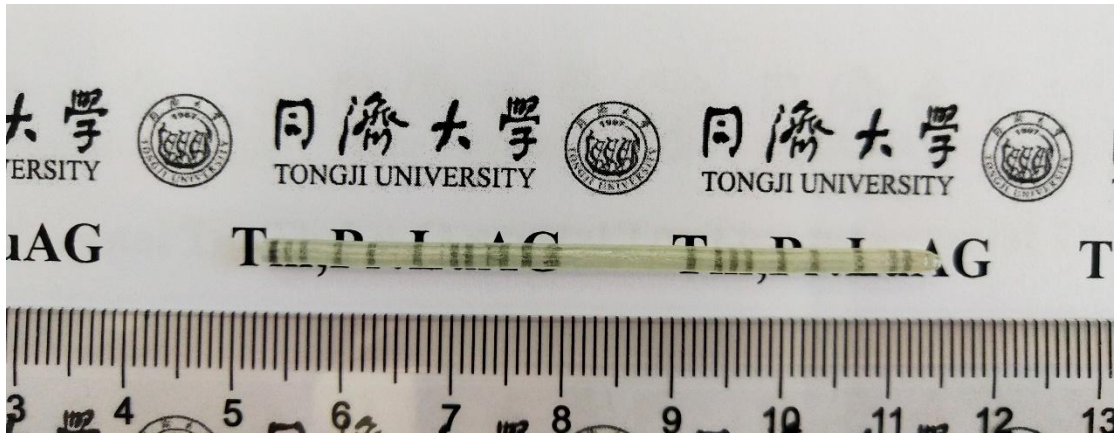
2. Experiments

2.1 Crystal growth

The 2.0 at.% Tm^{3+} , 0.2 at.% Pr^{3+} co-doped LuAG and 2.0 at.% Tm^{3+} single doped LuAG single crystals were grown by the μ -PD method [15, 16]. The Tm_2O_3 , Lu_2O_3 , Al_2O_3 and Pr_6O_{11} powders with purity of 99.999% were prepared as raw materials. After being mixed, the mixtures were shaped into a rod and pressed by cold isostatic, then sintered at 1300 $^\circ\text{C}$ for 12 h in a muffle furnace. A $\langle 111 \rangle$ oriented LuAG crystal was used as seed and the pulling rate was 0.3 mm/min. The growth atmosphere was high-purity flowing argon. Fig.1 shows the obtained $\text{Tm}:\text{LuAG}$ and $\text{Tm,Pr}:\text{LuAG}$ crystals with diameter of about 2 mm. The crystals are transparent and colorless with homogeneous diameter and free of macroscopic defects.



(a)



(b)

Fig. 1. Photographs of the as-grown 2.0 at.% Tm:LuAG (a) and 2.0 at.% Tm, 0.2 at.% Pr:LuAG (b) single crystals.

2.2 Spectral measurements

The Tm:LuAG and Tm,Pr:LuAG crystal samples were cut from the as-grown crystals and two surfaces were polished for measurements. The absorption spectra of the samples were performed by a spectrometer (Lambda 900, Perkin-Elmer UV-VIS-NIR) in the wavelength range of 400-2100 nm. An Edinburgh Instruments FLS 980 spectrophotometer was used to measure the emission spectra and decay curves under the excitation of 790 nm. All the measurements of the samples above were taken at room temperature.

3. Results and discussion

3.1 Absorption spectra

The room temperature absorption spectra of Tm:LuAG and Tm,Pr:LuAG single crystals in the wavelength range of 400-2000 nm are shown in Fig. 2. The five absorption bands of Tm:LuAG crystal centered at 460, 681, 782, 1178 and 1632 nm correspond to the transitions from the ground state 3H_6 to the excited states 1D_2 , 1G_4 , $^3F_{2,3}$, 3H_4 , 3H_5 and 3F_4 , respectively. The absorption band centered at around 1472 nm, corresponding to the $^3H_4 \rightarrow ^3F_4 + ^3F_3$ transition of Pr^{3+} ions, is also clearly in the absorption spectrum of Tm,Pr:LuAG crystal. As is known to all, the transition at 782 nm matches well with AlGaAs LDs pumping sources. The absorption coefficient at 782 nm of Tm:LuAG and Tm,Pr:LuAG was calculated to be 1.23 cm^{-1} and 1.30 cm^{-1} , respectively. Besides, the full width at half maximum (FWHM) of absorption band at 782 nm was 11.4 nm and 15.0 nm, respectively. The FWHM is larger than the value of Tm:LYSO (8nm at 791nm [17]), Tm:YAP (3.9 nm at 777 nm [18]) and Tm:KY₃F₁₀ (3.8nm at 778 nm [19]). The absorption bands of Tm:LuAG and Tm,Pr:LuAG crystals around 782 nm are wide enough to steadily absorb the incident pump power.

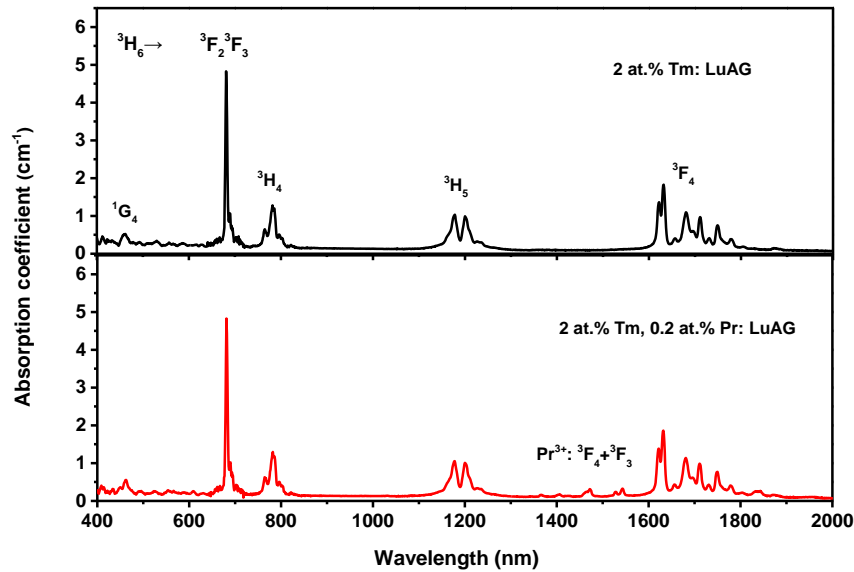


Fig. 2. Room temperature absorption spectra of Tm:LuAG and Tm,Pr:LuAG crystals.

3.2 Fluorescence spectra

Fig. 3 shows the fluorescence spectra of Tm:LuAG and Tm,Pr:LuAG crystals under 790 nm excitation at room temperature. Both samples have similar emission bands around 1431 nm, which correspond to the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition of Tm^{3+} ions. As can be seen from Fig. 3, the intensity of the emission line around 1431 nm increased after the introduction of Pr^{3+} ions. The enhanced fluorescence emission of the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition can justify that the introduction of Pr^{3+} ions can depopulate the $\text{Tm}^{3+} : {}^3\text{F}_4$ level effectively. The results suggest that Tm,Pr:LuAG crystal could be a promising material for 1.5 μm laser generation.

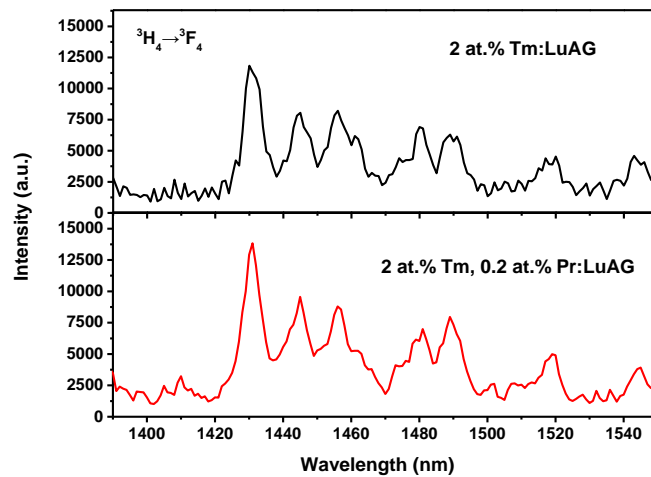


Fig. 3. Room temperature fluorescence spectra of Tm:LuAG and Tm,Pr:LuAG crystals.

3.3 fluorescence lifetime

The room-temperature decay curves of ${}^3\text{H}_4$ and ${}^3\text{F}_4$ levels of Tm:LuAG and Tm, Pr:LuAG crystals excited by 790 nm laser are shown in Fig. 4. For Tm:LuAG crystal, the fluorescence lifetimes of ${}^3\text{H}_4$ and ${}^3\text{F}_4$ level were measured to be 378 μs and 10.427 ms, respectively. It can be easily found that the fluorescence lifetime of the ${}^3\text{F}_4$ terminal level is much longer than that of the ${}^3\text{H}_4$ initial level. Therefore the laser around 1.5 μm is normally self-terminating. In order to depopulate the lower level through the energy transfer process, we introduce Pr^{3+} ions into Tm:LuAG crystal. Fig. 5 shows the energy level scheme of Tm^{3+} and Pr^{3+} ions in LuAG crystal. Under a 790 nm LD excitation, the Tm^{3+} ions are excited from ground state ${}^3\text{H}_6$ to the excited state ${}^3\text{H}_4$. The fluorescence emission at 1.5 μm is due to the $\text{Tm}^{3+}: {}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition. For the 1.8 μm emission, the population of ${}^3\text{F}_4$ level is based on the cross relaxation (CR) $\text{Tm}^{3+}: {}^3\text{H}_4 + {}^3\text{H}_6 \rightarrow {}^3\text{F}_4 + {}^3\text{F}_4$, and the cross relaxation process increased lifetime of ${}^3\text{F}_4$ level [20]. Since the $\text{Pr}^{3+}: {}^3\text{F}_2$ level is adjacent to the $\text{Tm}^{3+}: {}^3\text{F}_4$ level, an effective energy transfer (ET) $\text{Tm}^{3+}: {}^3\text{F}_4 + \text{Pr}^{3+}: {}^3\text{H}_4 \rightarrow \text{Tm}^{3+}: {}^3\text{H}_6 + \text{Pr}^{3+}: {}^3\text{F}_2$ will depopulate the $\text{Tm}^{3+}: {}^3\text{F}_4$ level. To verify the mechanism, the lifetimes of ${}^3\text{H}_4$ and ${}^3\text{F}_4$ levels of Tm,Pr:LuAG crystal are compared with those of Tm:LuAG crystal. By co-doping Pr^{3+} ions into Tm:LuAG crystals, the lifetime of ${}^3\text{F}_4$ level decreased greatly to 2.603 ms, while the lifetime of ${}^3\text{H}_4$ level experienced a slight decrease from 378 μs to 346 μs . The lifetime of ${}^3\text{H}_4$ level of Tm,Pr:LuAG crystal is much higher than the value of 0.5% Tm, 1% Tb:YVO₄ (50 μs [7]), 0.5% Tm:GdScO₃ (265 μs [21]), 1% Tm:KGd(WO₄)₂ (175 μs [22]) and 1.5% Tm:YAG (270 μs [23]). To further investigate the effect of Pr^{3+} ions, the energy transfer efficiency η was calculated according to the following formula:

$$\eta_{ET} = 1 - \tau_{\text{Tm/Pr}} / \tau_{\text{Tm}} \quad (1)$$

where τ_{Tm} and $\tau_{\text{Tm/Pr}}$ are the fluorescence lifetimes of Tm:LuAG and Tm,Pr:LuAG crystals, respectively. The measured fluorescence lifetimes τ and calculated energy transfer efficiency η of Tm:LuAG and Tm,Pr:LuAG crystals are listed in Table 1. The energy transfer efficiency from $\text{Tm}^{3+}: {}^3\text{F}_4$ level to $\text{Pr}^{3+}: {}^3\text{F}_2$ level was calculated to be 75.0%. The results indicate that the co-doping of Pr^{3+} ions can effectively depopulate ${}^3\text{F}_4$ lower level, while has little influence on the ${}^3\text{H}_4$ upper level. Therefore, the co-doping of Pr^{3+} ions into Tm^{3+} doped crystals can be used as an effective way for 1.5 μm laser operation.

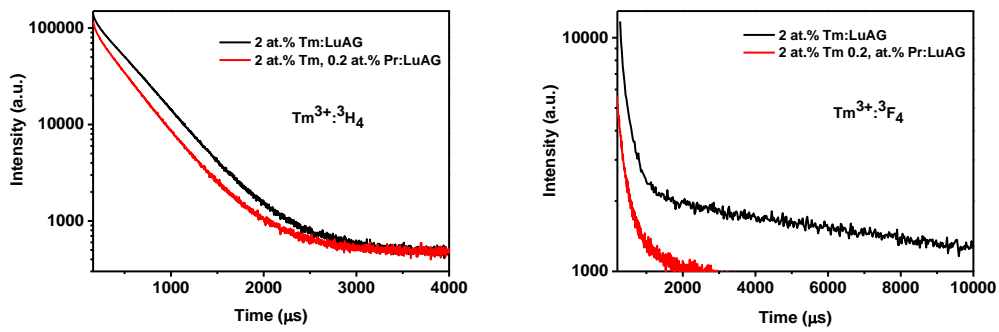


Fig.4. Fluorescence decay curves of the ${}^3\text{H}_4$ and ${}^3\text{F}_4$ manifold of Tm:LuAG and Tm,Pr:LuAG crystals.

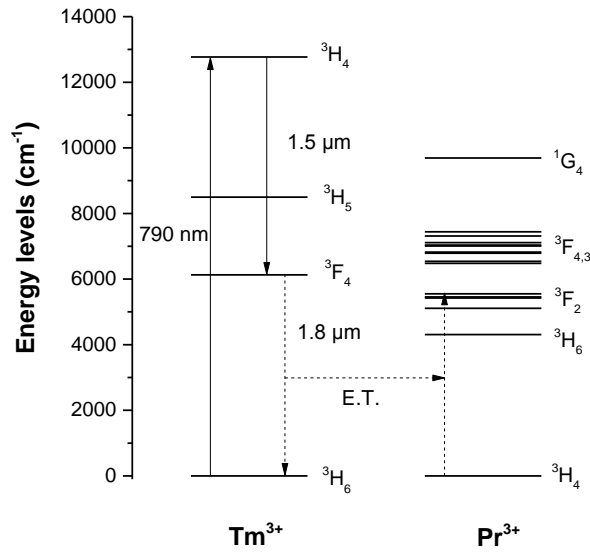


Fig.5. Energy level diagram of $\text{Tm}^{3+}, \text{Pr}^{3+}$ co-doped system.

Table 1 Fluorescence lifetimes τ and fluorescence quantum efficiencies η for the $\text{Tm}:\text{LuAG}$ and $\text{Tm}, \text{Pr}:\text{LuAG}$ crystals.

$\text{Tm}:\text{LuAG}$	$\tau(\mu\text{s})$ ${}^3\text{H}_4$	$\tau(\text{ms})$ ${}^3\text{F}_4$	η ${}^3\text{F}_4$
2%Tm	378	10.427	
2%Tm, 0.2%Pr	346	2.603	75.0%

4. Conclusion

In conclusion, Tm^{3+} and $\text{Tm}^{3+}, \text{Pr}^{3+}$ co-doped LuAG single crystals were successfully grown by the μ -PD method. Compared with $\text{Tm}:\text{LuAG}$ crystal, the absorption coefficient and FWHM at 782 nm of $\text{Tm}^{3+}, \text{Pr}^{3+}$ co-doped LuAG crystal is higher. It was also demonstrated that after the introduction of Pr^{3+} ions, the intensity of 1.5 μm emission increased and the fluorescence lifetime of $\text{Tm}^{3+} : {}^3\text{F}_4$ level decreased greatly from 10.427 ms to 2.603 ms, while the lifetime of $\text{Tm}^{3+} : {}^3\text{H}_4$ level changed little from 378 μs to 346 μs . Pr^{3+} ions can efficiently depopulate the ${}^3\text{F}_4$ lower level, while having little influence on the ${}^3\text{H}_4$ upper level of Tm^{3+} ions. All the results show that $\text{Tm}, \text{Pr}:\text{LuAG}$ crystal could be a potential laser material for eye-safe 1.5 μm laser operation.

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