

Research Article

Optical Spectra Properties and Continuous-Wave Laser Performance of Tm,Y:CaF₂ Single Crystals

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3 at.% Tm, x at.% Y:CaF₂ crystals ($x = 0, 0.5, 1, 2,$ and 3) were grown by the vertical Bridgman method and investigated. Codoping Y³⁺ ions can manipulate the local structure of Tm³⁺ ions in the CaF₂ crystal and then improve the spectroscopic properties. Compared with 3 at.% Tm:CaF₂, 3 at.% Tm, 3 at.% Y:CaF₂ crystal has several advantages. Firstly, the absorption cross section is improved from $0.35 \times 10^{-20} \text{ cm}^{-2}$ to $0.45 \times 10^{-20} \text{ cm}^{-2}$ at 767 nm, and the fluorescence intensity had elevated 3.4 times. Secondly, the linewidth of the fluorescence spectrum and lifetime also increased from 164 nm to 191 nm and from 6.16 ms to 8.15 ms at room temperature, respectively. Furthermore, quantum efficiency improved from 58.2% to 80.3%. The maximum laser output power of 583 mW and slope efficiency of 25.3% were achieved in 3 at.% Tm, 3 at.% Y:CaF₂ crystal under 790 nm diode pumping.

1. Introduction

Calcium fluorides, as laser substrates, possess various advantages of large size, high thermal conductivity, well controlled crystal growth processes, and low nonlinear refractive coefficient. Trivalent rare-earth ions, like Tm, Nd, Pr, doped CaF₂ crystals behave broad, smooth absorption and emission spectra due to heterovalent substitution of Ca²⁺ within the structure without loss of structural integrity [1]. Various RE³⁺ optical centers could be formed in this fluoride by substituting divalent cation ions, and the excessive charge of rare-earth ions is compensated by interstitial fluorine. The Nd³⁺ doped CaF₂ crystal as a laser-pumped-amplifier medium has been abandoned due to a very serious concentration quenching effect which results from the clustering of the neodymium ions and kinds of cross-relaxation type energy transfer processes, which weaken their emission quantum efficiency [2].

However, the [Nd³⁺-Nd³⁺] quenching pairs in clusters can be easily dissociated by codoping buffer ions such as Y³⁺ ions [3–8], La³⁺ ions [9], and Sc³⁺ ions [10]. For example, Nd,Y:CaF₂ crystal, Y³⁺ ions were codoped in Nd:CaF₂ crystal which substitute for Ca²⁺ forming complicated local structure that performs an effect on spectroscopic properties [8].

As the solid-state lasers medium, the doped Tm³⁺ calcium fluoride crystal proves the potential to achieve efficient compact diode-pumped lasers with an oscillation wavelength near 2 μm which could be directly pumped around 790 nm (³H₆ → ³H₄ absorption transition) due to much lower non-radiative losses caused by multiphonon relaxation [11]. Tm ions act both as a sensitizer and activator in a single-doped sample, meaning that a higher concentration is necessary for effective absorption of 800 nm laser excitation. Compared to oxide crystals, pure CaF₂ crystal has a thermal conductivity as high as 10 W/cm·K [12] and low phonon energy

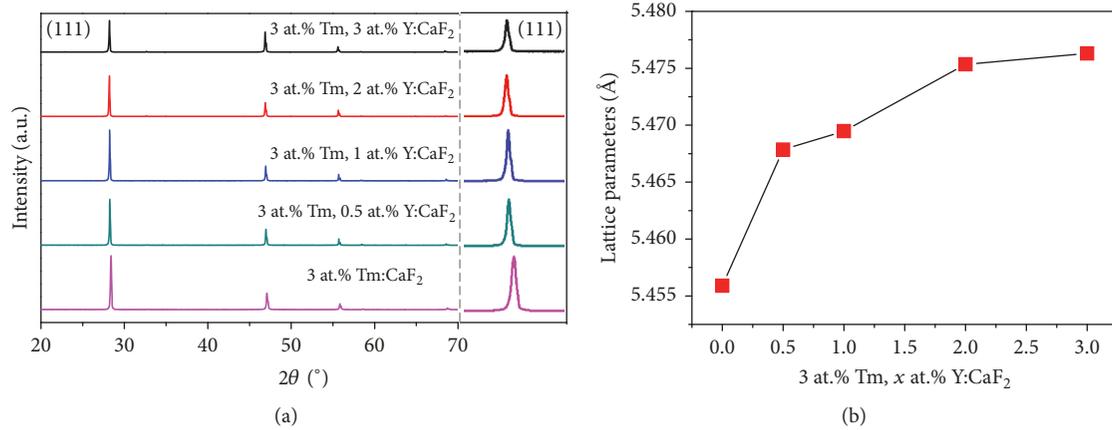


FIGURE 1: The XRD patterns (a) and lattice parameters (b) of 3 at.% Tm, x at.% Y:CaF₂ crystals.

(maximum value of 495 cm⁻¹) [13], making it very suitable for a laser host crystal and becoming one of the first laser hosts in the early 1960 nm. The predecessors have done some researches on Tm³⁺ doped CaF₂ single crystals and found that Tm:CaF₂ crystals possessed broadband absorption and emission properties [11, 14, 15]. The spectroscopic investigation on Tm³⁺ doped crystals indicates that Tm³⁺ ions interactions occur (forming the cross relaxation) at relatively low dopant concentrations (nearly 1%), that is, two excited ions in the ³F₄ upper ground level 7F6 for one absorbed pump photon. The distinction between isolated and clustered ions is observed in the emission spectra due to different doped concentration. Besides, nonradiative processes related to ³H₅-³F₄ induced by [Tm-Tm] clusters in the crystals could result in strong heat generation and distortions reducing quantum efficiency [16]. To achieve higher power laser at 2 μm, one of the efficient ways is to prepare Tm:CaF₂ with higher Tm deponent concentrations avoiding clustering. However, a spectral region around 1.45 μm associated with a ³H₄ → ³F₄ optical transition could be vanished when the Tm³⁺ dopant concentration is beyond 1.34% due to [Tm-Tm] clusters [14], and the energy may be absorbed by the ground stated ³H₆. However, when the concentration of Tm becomes higher, some other possible ways of energy transfer would occur, such as ¹G₄ + ³H₄ → ³F₄ + ¹D₂ [17], ³H₅ → ³H₆ [18], and ³H₅ + photo_{800nm} → ¹G₄. Therefore, we take the advantage of Y³⁺ as buffer ions reported in Nd,Y:CaF₂ [3, 8] crystals to prepare the Tm,Y:CaF₂ crystals to break the [Tm-Tm] clusters and increase the Tm³⁺ emission intensity as well as efficiency in higher concentration, and the laser performance and wide emission spectrum have been expected. Importantly, the incorporation of Y³⁺ ions to the influences of spectroscopic properties in Tm³⁺ doped CaF₂ single crystals had not been investigated systematically.

In this paper, to improve high pump absorption efficiency and high gain per unit length, a series of 3 at.% Tm and x at.% Y:CaF₂ crystals have been grown by the vertical Bridgman method, and spectroscopic properties were studied systematically. We have carried out laser experiments and obtained continuous-wave laser output.

2. Experimental

The single crystal samples, namely, 3 at.% Tm, x at.% Y:CaF₂ (x = 0, 0.5, 1, 2, 3) crystals (at.%, atom percent), were grown by the traditional vertical Bridgman method. High purity fluorides crystalline powders (4N), CaF₂, TmF₃, YF₃, were used as starting materials, and 1 wt% PbF₂ was selected as an oxygen scavenger avoiding oxidation and volatilization additionally. These materials were completely mixed by molar ratios and filled into an assembled platinum crucible. The growth parameters are as follows: the temperature of the melt around 130°C, the pulling rate 0.8 mm/h, the cooling rate 20°C/h. The samples (the same thickness of about 2 mm) were handled with cutting and double-face optically polishing for spectral measurement.

By recording absorption and emission spectra, we investigated the spectroscopic properties of the crystals. The absorption spectra were measured by using a Jasco V-570 UV/VIS/NIR spectrophotometer. The fluorescence spectra and lifetime were obtained with a FLS980 time-resolved fluorimeter with grating blazed at 1820 nm and detected using a Hamamatsu InSb. Measuring of fluorescence spectra was performed under pumping at 808 nm with a CW laser operation. All the measurements were conducted at room temperature.

3. Results and Discussion

3.1. Phase Identification and Crystal Structure. 3 at.% Tm, x at.% Y:CaF₂ crystals (x = 0, 0.5, 1, 2, 3) have been analyzed by powder XRD and behave the purity phase CaF₂ without any impure peaks as shown in Figure 1(a). The XRD patterns of the crystals have matched well with the JCPDS standard card of CaF₂ ICSD 00-075-0363 indicating that the fluorite cubic structure (Fm-3 m) has not been changed by the increasing concentration of yttrium. Tm³⁺ and Y³⁺ ions substitute for Ca²⁺ ions in the CaF₂ lattice, and smaller F⁻ ions have taken placed in the interstitial positions of the empty cubes to compensate the charge and maintain electrical neutrality leading to the smaller Bragg's angles and larger lattice parameters

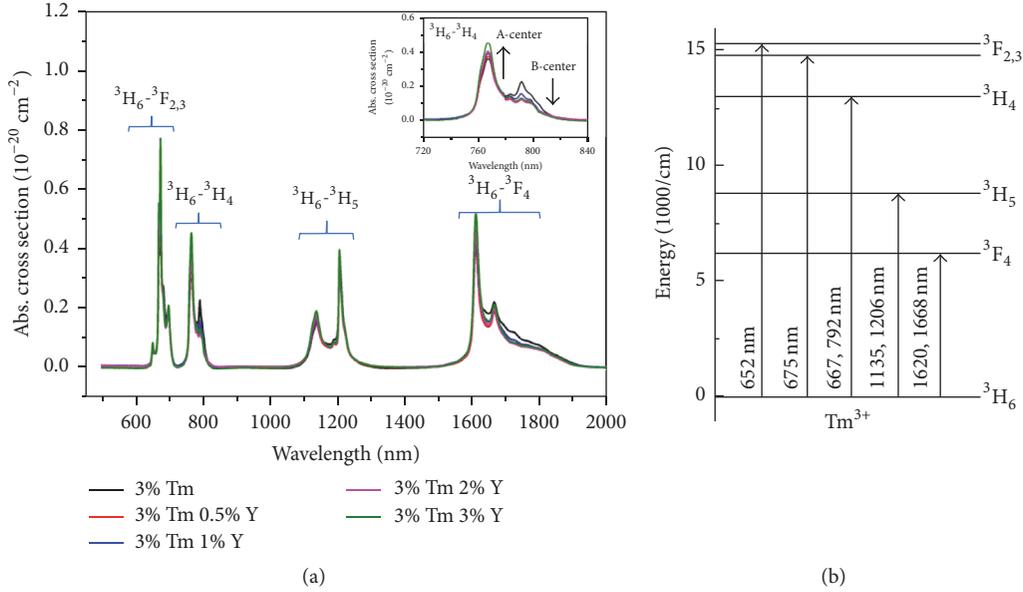


FIGURE 2: Absorption spectra (a) and energy level diagrams (b) of 3 at.% Tm, x at.% Y:CaF₂ crystals at 300 K.

which could be distinguished clearly on the enlarged view of (111) in Figure 1(a). The lattice parameters of series of 3 at.% Tm, x at.% Y:CaF₂ ($x = 0.5, 1, 2, 3$) single crystals are 5.46785 Å, 5.46947 Å, 5.47535 Å, 5.4763 Å, respectively, much larger than 5.4559 Å of Tm:CaF₂, and increase with the rising codoping Y³⁺ ion concentration as shown in Figure 1(b). These observations confirm that Tm³⁺ and Y³⁺ ions had been effectively doped into the host lattice of CaF₂.

3.2. Absorption and Emission Properties. The absorption spectra from 500 nm to 2000 nm at room temperature of 3 at.% Tm, x at.% Y are shown in Figure 2(a). Due to various splitting energy levels of ³H₆ and ³F₄, the absorption bands have been divided into several peaks. Several main absorption bands, ³H₆-³F₂ (652 nm), ³H₆-³F₃ (675 nm), ³H₆-³H₄ (667 nm, 792 nm), ³H₆-³H₅ (1135 nm, 1206 nm), ³H₆-³F₄ (1620 nm, 1668 nm), have been marked in the spectra. Clearly, all the absorption cross sections are increased with the Y ions. Additionally, the absorption ³H₆-³H₄, which is usually used for diode pumping, inset in the picture has been analyzed in detail at 767 nm and 792 nm in the same bands caused by different emission centers, defined as A-center and B-center.

The largest absorption cross section at 767 nm of 3 at.% Tm, 3 at.% Y:CaF₂ improves to $0.45 \times 10^{-20} \text{ cm}^{-2}$, much larger than that reported in [14]. On the other side, the absorption cross section at 792 nm decreases gradually from $0.22 \times 10^{-20} \text{ cm}^{-2}$ to $0.12 \times 10^{-20} \text{ cm}^{-2}$ with the increasing Y ions. Y ions play an important role in modulating spectral performance. The absorption spectra of Tm³⁺ ions can be significantly altered by codoping with Y³⁺ ions. The changeable absorption cross sections indicate that the local structure and symmetry of the calcium fluoride crystal have been modified by changing the amount of deponent codoping Y³⁺ ions. The

increasing phenomenon could be attributed to the stronger crystal field caused by interstitial F⁻ ions in the lattice induced by the codoped Y³⁺ separating the [Tm-Tm] clusters, caused by a considerable high doping concentration 3 at.% much larger than 1.34% [11, 19], to an appropriate distance and forming A-centers instead of B-centers. By doping Y³⁺ ions, B-center has been broken, forming more A-centers as a result. Anyway, it is clear that codoping Tm:CaF₂ with Y³⁺ ions slightly broadens the absorption bands ³H₆-³H₄, which should be profitable for LD pumping. The broad wavelength tunability indicated an efficient ground-state stark splitting with the introduction of Y³⁺ ions in the as-grown Tm,Y:CaF₂ crystal.

The fluorescence spectra of 3 at.% Tm, x at.% Y:CaF₂ crystals, corresponding to ³F₄-³H₆ emission transition of Tm³⁺ around 1.8 μm, excited by 767 nm are reported in Figure 3. The emission spectra of the five crystals consist of four bands, peaking at 1611 nm (6207 cm^{-1}), 1666 nm (6002 cm^{-1}), 1820 nm (5494 cm^{-1}), 1856 nm (5387 cm^{-1}), respectively. The curves of Tm,Y:CaF₂ demonstrate several intense separate local maxima compared to the one of the Tm:CaF₂, indicating that the Y³⁺ ions codoping modulate the emission spectral structure of Tm³⁺ ions in CaF₂ hosts. The emission intensity of 2873 a.u. at 1820 nm of the 3 at.% Tm, 3 at.% Y:CaF₂ crystals is 3.4 times higher than that of the 3 at.% Tm:CaF₂ crystal (842 a.u.), whose value is the largest above all the samples. As has been discussed in the absorption cross sections, Y³⁺ codoping breaks the Tm³⁺ ion clusters and increases the fluorescence quantum efficiency which could also be proved in Table 1. Additionally, the luminescence intensity of the 1.8 μm band is improved by doping Y³⁺.

Figure 4 shows the logarithm of the emission intensity at 1820 nm of Tm³⁺ as a function of the decay time in 3

TABLE 1: The detailed values of σ_{abs} , σ_{em} , τ_{rad} , τ_{em} , η of 3 at.% Tm, x at.% Y:CaF₂ at 1820 nm.

Crystals	$\sigma_{\text{abs}}/\text{cm}^2$	$\sigma_{\text{em}}/\text{cm}^2$	$\tau_{\text{rad}}/\text{ms}$	$\tau_{\text{em}}/\text{ms}$	$\eta/\%$
3 at.% Tm:CaF ₂	0.063	1.206×10^{-20}	10.58	6.16	58.2
3 at.% Tm, 0.5 at.% Y:CaF ₂	0.054	1.026×10^{-20}	11.43	7.25	63.4
3 at.% Tm, 1 at.% Y:CaF ₂	0.057	1.090×10^{-20}	10.24	6.53	63.7
3 at.% Tm, 2 at.% Y:CaF ₂	0.054	1.026×10^{-20}	10.82	7.55	69.8
3 at.% Tm, 3 at.% Y:CaF ₂	0.056	1.088×10^{-20}	10.14	8.15	80.3

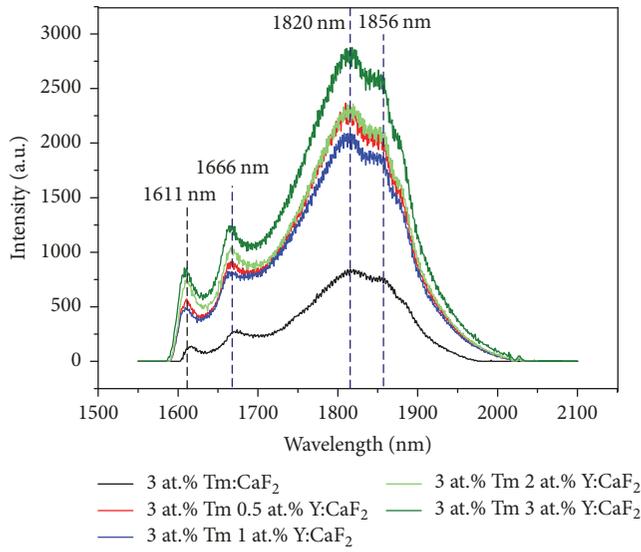


FIGURE 3: Fluorescence spectra for 3F_4 - 3H_6 transition of 3 at.% Tm, x at.% Y CaF₂ crystals at 300 K.

at.% Tm, x at.% Y:CaF₂ crystals excited by 767 nm at room temperature. The straight lines indicated that the decay was consistent with a first-order exponential and the emission lifetimes were labelled as arrows. The emission lifetimes were fitted to be 6.16 ms, 7.25 ms, 6.53 ms, 7.55 ms, 8.15 ms for 3 at.% Tm, x at.% Y:CaF₂ ($x = 0, 0.5, 1, 2, 3$), respectively, which is in the order of 5 ms [11] much shorter than the longer lifetime 15 ms [20]. Due to the higher concentration of Tm³⁺, the emission lifetimes caused by the fluorescence of clustered thulium centers and the tetragonal optical centers are responsible for the longer lifetime 15 ms [11, 20]. It also could be discussed that the emission centers with higher symmetry could extend the emission lifetime of the energy level 3F_4 which could benefit the pump efficiency. The shorter emission lifetime means that in the 3 at.% Tm, x at.% Y:CaF₂ crystals, [Tm-Tm] clusters take a dominant station affecting the lifetime of 3F_4 compared to these tetragonal optical centers. The emission lifetimes of Tm,Y:CaF₂ crystals were longer than that of the Tm:CaF₂ crystal, indicating clearly that

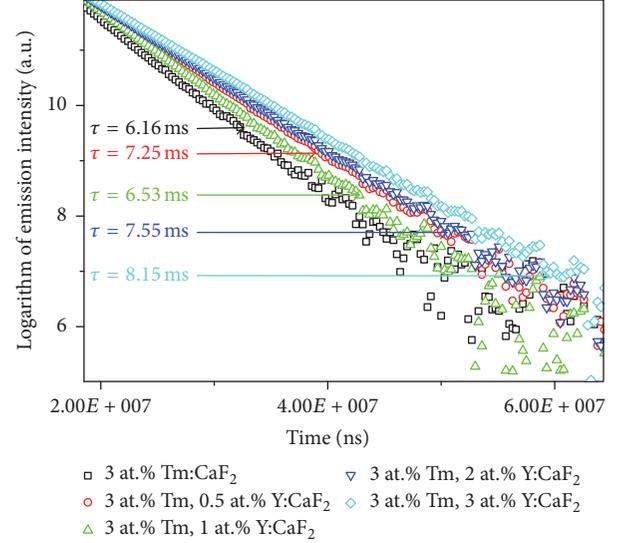


FIGURE 4: Fluorescence lifetimes of energy level 3F_4 of 3 at.% Tm, x at.% Y:CaF₂ crystals.

codoping Y³⁺ ions as buffer ions increase the fluorescence lifetime of Tm ions.

3.3. *Calculations for Spectral Parameters.* In this session, some spectral parameters including the emission cross section σ_{em} , the radiation lifetimes τ_{rad} , the quantum efficiency η , the quality factor $\sigma_{\text{em}} \cdot \tau_{\text{em}}$, the effective linewidth $\Delta\lambda$ have been calculated to measure the quality of these crystals. The emission cross section σ_{em} and the radiation lifetimes τ_{rad} have been calculated by the reciprocity method and the Fuchtbauer-Ladenburg (FL) equation, respectively, and the absorption cross sections σ_{abs} could be obtained from the absorption spectra in Figure 2(a).

$$\sigma_{\text{em}}(\lambda) = \sigma_{\text{abs}}(\lambda) \frac{Z_l}{Z_u} \exp\left[\frac{hc}{k_B T} \left(\frac{1}{\lambda_{\text{ZL}}} - \frac{1}{\lambda}\right)\right], \quad (1)$$

where λ_{ZL} will be referred to as the “zero line” wavelength ($\lambda_{\text{ZL}} = 1666$ nm wavelength associated with the transition between the lowest stark components of each multiplet 3H_6 and 3F_4) and Z_l/Z_u represents the ratio of the partition functions of the lower and upper states and the value is 1.512 [14].

$$\sigma_{\text{em}} = \frac{\lambda_{\text{peak}}^4}{8\pi n^2 \Delta\lambda \cdot \tau_{\text{rad}}}, \quad (2)$$

where λ_{peak} is the wavelength of the maximum emission intensity (here is 1820 nm) and n stands for the refractive index (the refractive index of calcium fluoride is 1.442 at 1820 nm). We can take advantage of (2) for the value of τ_{rad} . In theory, the product of σ_{em} and τ_{rad} is inversely proportional to $\Delta\lambda$. It indicates that the result of the experiment is nearly

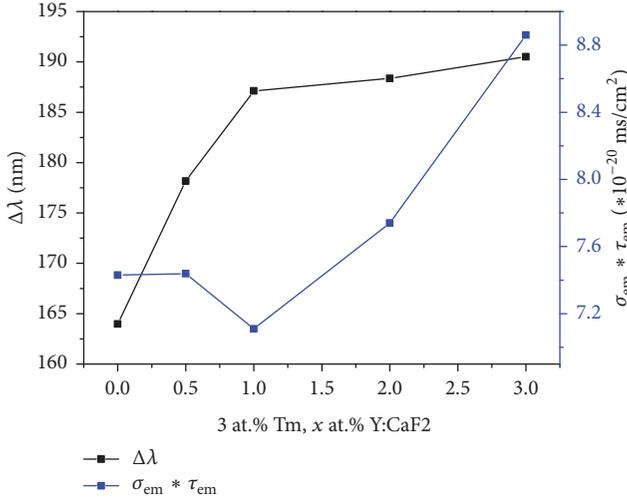


FIGURE 5: $\tau_{\text{rad}} \cdot \sigma_{\text{em}}$ and $\Delta\lambda$ obtained from 3 at.% Tm, x at.% Y:CaF₂ crystals.

in agreement with that of the theory. Equation (2) can also be expressed as

$$\sigma_{\text{em}} \cdot \tau_{\text{em}} = \frac{\lambda_{\text{peak}}^4}{8\pi c n^2} \cdot \frac{1}{\Delta\lambda} \cdot \frac{\tau_{\text{em}}}{\tau_{\text{rad}}} = \frac{\lambda_{\text{peak}}^4}{8\pi c n^2} \cdot \frac{1}{\Delta\lambda} \cdot \eta, \quad (3)$$

where $\lambda_{\text{peak}}^4/8\pi c n^2$ can be regarded as a constant and η is the quantum efficiency. The calculated results have been shown in Table 1 and Figure 5.

The emission cross section σ_{em} varies from $1.026 \times 10^{-20}/\text{cm}^2$ to $1.088 \times 10^{-20}/\text{cm}^2$. The quantum efficiency of emission at 1820 nm is 58.2%, 63.4%, 63.7%, 69.8%, 80.3% for 3 at.% Tm, x at.% Y ($x = 0, 0.5, 1, 2, 3$), respectively. As discussed above, cooping Y ions as buffer ions actually benefit the quantum efficiency increasing the quantum efficiency effectively, indicating that the efficiency of the fluoresce is very sensitive to the cationic coordination [21], and the highest quantum efficiency has been increased to 80.3%.

We can see the difference of $\Delta\lambda$ (where $\Delta\lambda$ is the effective linewidth which can be obtained by measurement) from Figure 4. The change trend of the effective linewidth at 1820 nm is depicted in Figure 5, which is almost increasing with codoping Y³⁺ ion concentration. $\Delta\lambda$ at 1820 nm is 163.97 nm, 178.16 nm, 187.12 nm, 188.37 nm, 190.52 nm for 3 at.% Tm, x at.% Y:CaF₂ ($x = 0, 0.5, 1, 2, 3$), respectively, behaving the superiority for LD pumping. Compared with single-doped one, the effective linewidth of the codoping crystals increased rapidly, and the trend turns out to be saturated when the concentration of Y³⁺ grows higher. It indicates that the effect of Y³⁺ concentration on the effective linewidth causes saturation which is in favor of femtosecond laser output.

3.4. Laser Performance. Taking both emission intensity and lifetime into consideration, two samples, 3 at.% Tm:CaF₂ and 3 at.% Tm, 3 at.% Y:CaF₂, were applied in laser experiments as laser-pumped-amplifier mediums. The size of the crystal is

4 mm × 4 mm × 6 mm and the end faces were optically polished flat and parallel without being coated. The continuous-wave (CW) experiment with a fiber-coupled AlGaAs diode laser as the pump source emitting at 790 nm was carried out at room temperature, and the setup for testing was shown in Figure 6.

In this experiment, the output mirror transmission is 2%, and the folded cavity consisted of three mirrors: M1, M2, and M3, having the same radius of curvature of 10 cm. The pump light was focused into the crystal through a 1:1 optical imaging module. The pump source was provided by a laser diode around 790 nm. The laser output powers of two samples were depicted in Figure 7, we obtained two different laser curves. To the sample, 3 at.% Tm, 3 at.% Y:CaF₂ crystal, its laser slope efficiency and maximum output power of the crystal are 25.3% and 583 mW with the 2% transmission output coupler, while a lower slope efficiency of 15.9% and maximum output power 159 mW were obtained with 3 at.% Tm:CaF₂ crystal. The maximum pump power was limited by the absorption capacity of the 3 at.% Tm:CaF₂ crystal. We found its excited state absorption tended to be saturated when the absorbed pump power was over 1.6 W. To avoid damage, the absorbed pump power of 3 at.% Tm:CaF₂ was set below 1.6 W corresponding to the incident pump power of 3 W, and the absorbed pump power of 3 at.% Tm, 3 at.% Y:CaF₂ crystal was set below 2.5 W corresponding to the incident pump power of 4.5 W.

4. Conclusions

The codoping Y³⁺ ions Tm:CaF₂ crystals were successfully grown by vertical Bridgman method, and the properties of the series crystals were analyzed systematically. Absorption of ³H₆-³H₄ is caused by A-center at 767 nm and B-center at 792 nm, and the absorption cross section of A-center is increased while the absorption cross section of B-center is decrease by codoping Y³⁺. Emission intensity and effective linewidth of emission at 1820 nm are greatly improved when the concentration increased to 3 at.%. The quantum efficiency is enhanced to 80.3% by codoping Y³⁺ ions compared to the undoped crystals. It demonstrates codoping Y³⁺ ions have a positive effect on spectroscopic properties. In laser experiment, we finally obtained a maximum laser output power of 583 mW and slope efficiency of 25.3% in codoped sample.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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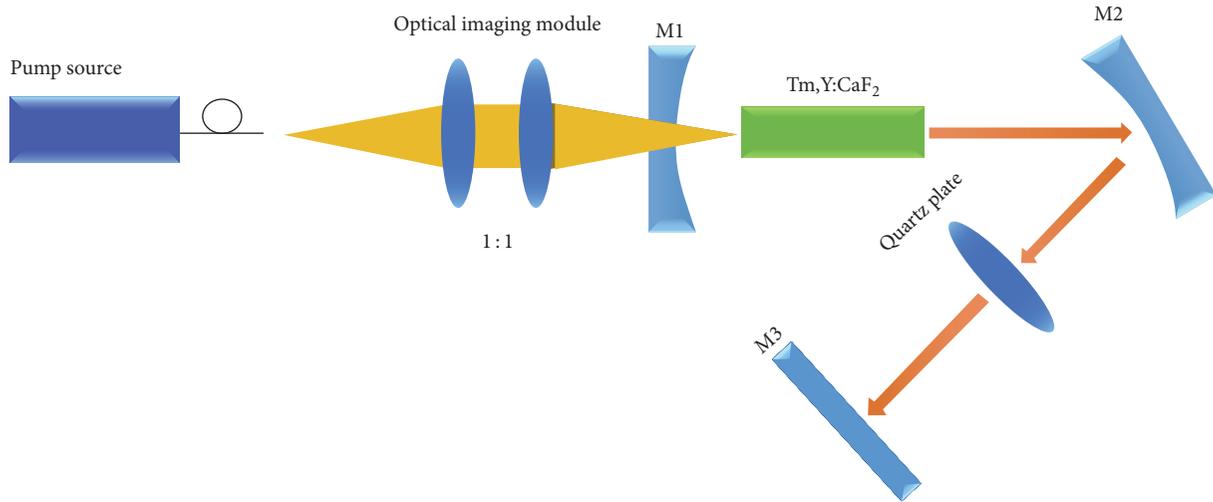


FIGURE 6: Schematic of the experimental setup for 1.8 μm laser operation.

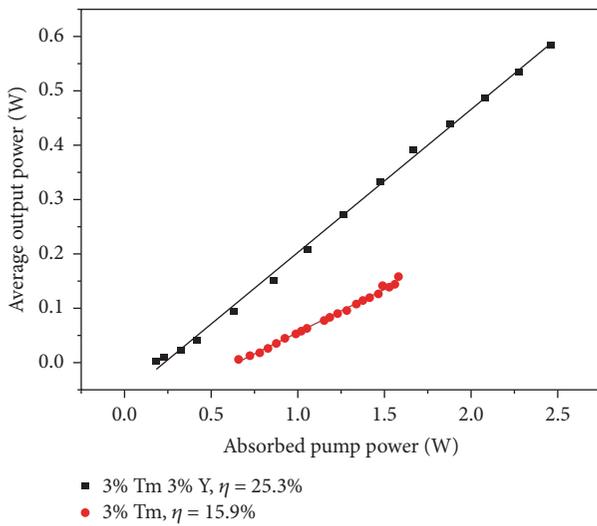


FIGURE 7: Laser output power versus absorbed pump power curve for 3 at.% Tm:CaF₂ and 3 at.% Tm, 3 at.% Y:CaF₂ crystals.

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