Research Article

Optical Spectra Properties and Continuous-Wave Laser Performance of Tm,Y:CaF$_2$ Single Crystals

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3 at.% Tm, x at.% Y:CaF$_2$ crystals ($x = 0, 0.5, 1, 2, \text{ and } 3$) were grown by the vertical Bridgman method and investigated. Codoping Y$^{3+}$ ions can manipulate the local structure of Tm$^{3+}$ ions in the CaF$_2$ crystal and then improve the spectroscopic properties. Compared with 3 at.% Tm:CaF$_2$, 3 at.% Tm, 3 at.% Y:CaF$_2$ crystal has several advantages. Firstly, the absorption cross section is improved from $0.35 \times 10^{-20}$ cm$^2$ to $0.45 \times 10^{-20}$ 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:CaF$_2$ 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 CaF$_2$ crystals behave broad, smooth absorption and emission spectra due to heterovalent substitution of Ca$^{2+}$ within the structure without loss of structural integrity [1]. Various Re$^{3+}$ 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 Nd$^{3+}$ doped CaF$_2$ 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 [Nd$^{3+}$-Nd$^{3+}$] quenching pairs in clusters can be easily dissociated by codoping buffer ions such as Y$^{3+}$ ions [3–8], La$^{3+}$ ions [9], and Sc$^{3+}$ ions [10]. For example, Nd$_2$:Y:CaF$_2$ crystal, Y$^{3+}$ ions were codoped in Nd:CaF$_2$ crystal which substitute for Ca$^{2+}$ forming complicated local structure that performs an effect on spectroscopic properties [8].

As the solid-state lasers medium, the doped Tm$^{3+}$ 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 ($^3$H$_6$→$^3$H$_4$ 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 CaF$_2$ crystal has a thermal conductivity as high as 10 W/cm·K [12] and low phonon energy...
that Tm:CaF incorporation of Y emission spectrum have been expected. Importantly, the in higher concentration, and the laser performance and wide researches on Tm host crystals and becoming one of the first laser host single crystals had not been grown by the traditional vertical Bridgman method. High purity fluorides crystalline powders (4 N), 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 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 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.

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 fluorate cubic structure (Fm-3m) has not been changed by the increasing concentration of yttrium. Tm³⁺ and Y⁺ ions substitute for Ca⁺ 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 angels and larger lattice parameters.
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 $^{3}H_{4}$ and $^{3}F_{4}$, the absorption bands have been divided into several peaks. Several main absorption bands, $^{3}H_{6} - ^{3}F_{4}$ (652 nm), $^{3}H_{4} - ^{3}F_{4}$ (675 nm), $^{3}H_{5} - ^{3}H_{4}$ (667 nm, 792 nm), $^{3}H_{6} - ^{3}H_{5}$ (1135 nm, 1206 nm), $^{2}H_{6} - ^{2}F_{4}$ (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 $^{3}H_{6} - ^{3}H_{4}$, 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:CaF$_{2}$ improves to 0.45 $\times$ 10$^{-20}$ 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$^{-20}$ cm$^2$ to 0.12 $\times$ 10$^{-20}$ cm$^2$ with the increasing Y ions. Y ions play an important role in modulating spectral performance. The absorption spectra of Tm$^{3+}$ ions can be significantly altered by codoping with Y$^{3+}$ 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 Y$^{3+}$ ions. The increasing phenomenon could be attributed to the stronger crystal field caused by interstitial F$^{-}$ ions in the lattice induced by the codoped Y$^{3+}$ 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 Y$^{3+}$ ions, B-center has been broken, forming more A-centers as a result. Anyway, it is clear that codoping Tm:CaF$_{2}$ with Y$^{3+}$ ions slightly broadens the absorption bands $^{3}H_{6} - ^{3}H_{4}$, which should be profitable for LD pumping. The broad wavelength tunability indicated an efficient ground-state stark splitting with the introduction of Y$^{3+}$ ions in the as-grown Tm,Y:CaF$_{2}$ crystal.

The fluorescence spectra of 3 at.% Tm, x at.% Y:CaF$_{2}$ crystals, corresponding to $^{3}F_{4} - ^{3}H_{6}$ emission transition of Tm$^{3+}$ around 1.8 $\mu$m, excited by 767 nm are reported in Figure 2. 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:CaF$_{2}$ demonstrate several intense separate local maxima compared to the one of the Tm:CaF$_{2}$, indicating that the Y$^{3+}$ ions codoping modulate the emission spectral structure of Tm$^{3+}$ ions in CaF$_{2}$ hosts. The emission intensity of 2873 a.u. at 1820 nm of the 3 at.% Tm, 3 at.% Y:CaF$_{2}$ crystals is 3.4 times higher than that of the 3 at.% Tm:CaF$_{2}$ crystal (842 a.u.), whose value is the largest above all the samples. As has been discussed in the absorption cross sections, Y$^{3+}$ codoping breaks the Tm$^{3+}$ ion clusters and increases the fluorescence quantum efficiency which could also be proved in Table 1. Additionally, the luminescence intensity of the 1.8 $\mu$m band is improved by doping Y$^{3+}$.

Figure 4 shows the logarithm of the emission intensity at 1820 nm of Tm$^{3+}$ as a function of the decay time in 3
Table 1: The detailed values of $\sigma_{\text{abs}}$, $\sigma_{\text{em}}$, $\tau_{\text{rad}}$, $\tau_{\text{em}}$, $\eta$ of 3 at.\% Tm, x at.\% Y:CaF$_2$ at 1820 nm.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>$\sigma_{\text{abs}}$/cm$^2$</th>
<th>$\sigma_{\text{em}}$/cm$^2$</th>
<th>$\tau_{\text{rad}}$/ms</th>
<th>$\tau_{\text{em}}$/ms</th>
<th>$\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 at.% Tm:CaF$_2$</td>
<td>0.063</td>
<td>1.206 * 10$^{-20}$</td>
<td>10.58</td>
<td>6.16</td>
<td>58.2</td>
</tr>
<tr>
<td>3 at.% Tm, 0.5 at.% Y:CaF$_2$</td>
<td>0.054</td>
<td>1.026 * 10$^{-20}$</td>
<td>11.43</td>
<td>7.25</td>
<td>63.4</td>
</tr>
<tr>
<td>3 at.% Tm, 1 at.% Y:CaF$_2$</td>
<td>0.057</td>
<td>1.090 * 10$^{-20}$</td>
<td>10.24</td>
<td>6.53</td>
<td>63.7</td>
</tr>
<tr>
<td>3 at.% Tm, 2 at.% Y:CaF$_2$</td>
<td>0.054</td>
<td>1.026 * 10$^{-20}$</td>
<td>10.82</td>
<td>7.55</td>
<td>69.8</td>
</tr>
<tr>
<td>3 at.% Tm, 3 at.% Y:CaF$_2$</td>
<td>0.056</td>
<td>1.088 * 10$^{-20}$</td>
<td>10.14</td>
<td>8.15</td>
<td>80.3</td>
</tr>
</tbody>
</table>

Figure 3: Fluorescence spectra for $^3F_4$-$^3H_6$ transition of 3 at.\% Tm, x at.\% Y CaF$_2$ crystals at 300 K.

Figure 4: Fluorescence lifetimes of energy level $^3F_4$ of 3 at.\% Tm, x at.\% Y:CaF$_2$ crystals.

3.3. Calculations for Spectral Parameters. In this session, some spectral parameters including the emission cross section $\sigma_{\text{em}}$, the radiation lifetimes $\tau_{\text{rad}}$, the quantum efficiency $\eta$, 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 $\sigma_{\text{em}}$ and the radiation lifetimes $\tau_{\text{rad}}$ have been calculated by the reciprocity method and the Fuchtbauer-Ladenburg (FL) equation, respectively, and the absorption cross sections $\sigma_{\text{abs}}$ could be obtained from the absorption spectra in Figure 2(a).

$$\sigma_{\text{em}} (\lambda) = \sigma_{\text{abs}} (\lambda) \frac{Z_1}{Z_n} \exp \left[ \frac{hc}{k_B T} \left( \frac{1}{\lambda_{\text{ZL}}} - \frac{1}{\lambda} \right) \right],$$

where $\lambda_{\text{ZL}}$ 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 $Z_1/Z_n$ represents the ratio of the partition functions of the lower and upper states and the value is 1.512 [14].

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

where $\lambda_{\text{peak}}$ 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 $\tau_{\text{rad}}$. In theory, the product of $\sigma_{\text{em}}$ and $\tau_{\text{rad}}$ is inversely proportional to $\Delta \lambda$. It indicates that the result of the experiment is nearly...
3.4. Laser Performance. Taking both emission intensity and lifetime into consideration, two samples, 3 at.% Tm:CaF$_2$ and 3 at.% Tm, 3 at.% Y:CaF$_2$, 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:CaF$_2$ 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:CaF$_2$ crystal. The maximum pump power was limited by the absorption capacity of the 3 at.% Tm:CaF$_2$ 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:CaF$_2$ 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:CaF$_2$ crystal was set below 2.5 W corresponding to the incident pump power of 4.5 W.

4. Conclusions

The codoping Y$^{3+}$ ions Tm:CaF$_2$ crystals were successfully grown by vertical Bridgman method, and the properties of the series crystals were analyzed systematically. Absorption of $^2$H$_4$-H$_4$ 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 Y$^{3+}$. Emission intensity and effective linewidth of emission at 1820 nm are greatly improved when the concentration increased to 3 at.%. The quantum efficiency has been enhanced 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 Y$^{3+}$ 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:CaF$_2$(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 Y$^{3+}$ grows higher. It indicates that the effect of Y$^{3+}$ concentration on the effective linewidth causes saturation which is in favor of femtosecond laser output.

Conlicts 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.

References


