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Highly efficient CW laser operation in 4 at. % Tm$^{3+}$ and 4 at. % Y$^{3+}$ codoped CaF$_2$ crystals

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Tm:CaF$_2$ and Tm,Y:CaF$_2$ single crystals were prepared by the temperature gradient technique. The spectral properties of Tm,Y:CaF$_2$ single crystals were investigated and compared with those of Tm:CaF$_2$. It was demonstrated that codoping with Y$^{3+}$ ions could efficiently improve the spectroscopic properties. Tm,Y:CaF$_2$ crystals have larger absorption cross-sections at the pumping wavelength, larger mid-infrared stimulated emission cross-sections, and much longer fluorescence lifetimes of the upper laser level (Tm$^{3+}$:3H$_4$ level) than Tm:CaF$_2$ crystals. Continuous-wave (CW) lasers around 1.97 $\mu$m were demonstrated in 4.0 at. % Tm,4.0 at. % Y:CaF$_2$ single crystals under 792 nm laser diode (LD) pumping. The best laser performance has been demonstrated with a low threshold of 0.368 W, a high slope efficiency of 54.8%, and a maximum output power of 1.013 W.

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As we know, the quenching effect will occur due to defects and impurities introduced by increasing concentration of rare-earth ions. We found that codoping of Y^{3+} ions in Tm:CaF\textsubscript{2} can alleviate the cluster quenching effect and improve the spectral performance. 4 at. % Tm, 4 at. % Y:CaF\textsubscript{2} demonstrated the laser performance with a high slope efficiency of 54.8% and a maximum output power of 1.013 W. To the best of our knowledge, this is the highest slope efficiency and largest power reported in Tm\textsuperscript{3+}-doped CaF\textsubscript{2} crystals.

Tm:CaF\textsubscript{2} and Tm\textsubscript{3+}, Y:CaF\textsubscript{2} crystals were grown by the temperature gradient technique (TGT). The raw materials of grown crystals are CaF\textsubscript{2}, TmF\textsubscript{3}, and YF\textsubscript{3}. To prevent oxidation in the growing process, 1 wt. % PbF\textsubscript{2} was added to the starting materials. All of the raw materials used for our experiment were of 99.99% purity. The weighed chemical powders were mixed thoroughly and then sealed in the graphite crucibles during the process of growth. The crystal samples were cut and then polished into a size of 10 mm × 10 mm × 2 mm for spectral measurements.

The room temperature absorption spectra were measured using a Jasco V-570 UV/visible (VIS)/near-IR (NIR) spectrophotometer. Fluorescence spectra were obtained using an FLS 980 time-resolved fluorimeter with grating blazed at 1820 nm and detected using a Hamamatsu InSb. Fluorescence decay curves measured at 1820 nm were obtained with FLS 980 spectrophotometers under an 808 nm pulse laser excitation with the frequency of 9 Hz and duration of 10 μs. All of the measurements were carried out at room temperature.

Figure 1 shows the X-ray diffraction (XRD) patterns of 4% Tm:CaF\textsubscript{2} and 4% Tm\textsubscript{3+}, 4% Y:CaF\textsubscript{2} crystals compared with the standard pattern of the pure CaF\textsubscript{2} phase. No impurity peaks are found, and all of the diffraction peaks of the Tm:CaF\textsubscript{2} and Tm\textsubscript{3+}, Y:CaF\textsubscript{2} crystals are in good agreement with those of the pure CaF\textsubscript{2} phase. These suggested that Tm\textsuperscript{3+} and Y\textsuperscript{3+} ions have substitutionally entered the Ca\textsuperscript{2+} sites and the doping ions do not change the perovskite-like structure of the pure CaF\textsubscript{2} crystal. The structural parameters of these crystals were obtained by fitting the XRD data using the software JADE 6.0. The lattice parameters of 4% Tm, 4% Y:CaF\textsubscript{2} crystal is a bit larger than those of 4% Tm:CaF\textsubscript{2} crystal. It is well in agreement with the fact that the radius of Y\textsuperscript{3+} is greater than that of Tm\textsuperscript{3+}.

Figure 2 shows the room temperature absorption spectra of 4% Tm:CaF\textsubscript{2} and 4% Tm\textsuperscript{3+}, 4% Y:CaF\textsubscript{2} crystals in the wavelength range of 720–880 nm. There are three strong absorption peaks centered at 767, 784, and 792 nm, corresponding to the transitions from the ground state to the higher levels of Tm\textsuperscript{3+}.

The absorption coefficient and absorption cross-section at the strongest absorption peak of 767 nm in 4% Tm\textsubscript{3+}, 4% Y:CaF\textsubscript{2} crystal are enhanced from 2.85 cm\textsuperscript{-1} and 0.34 × 10\textsuperscript{-21} cm\textsuperscript{2} to 4.54 cm\textsuperscript{-1} and 4.7 × 10\textsuperscript{-21} cm\textsuperscript{2}, respectively, compared with 4% Tm:CaF\textsubscript{2} crystal. The larger absorption cross-section means a higher pump absorbing efficiency. The increasing of the absorption cross-section benefits from the stronger crystal field induced by codoping of Y\textsuperscript{3+} ions. While the crystallographic Ca\textsuperscript{2+} sites were occupied by the Y\textsuperscript{3+} ions, the compensation ions F\textsuperscript{−} were introduced to fill the vacancies of cubic lattices. This leads to distorted crystallographic sites and a stronger crystal field around Tm\textsuperscript{3+}.

According to the known absorption cross-section based on the reciprocity method, the emission cross-sections were calculated and shown in Fig. 3:

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Fig. 1. XRD patterns of the Tm:CaF\textsubscript{2} and Tm\textsubscript{3+}, Y:CaF\textsubscript{2} crystals.

Fig. 2. Absorption spectra of Tm:CaF\textsubscript{2} and Tm\textsubscript{3+}, Y:CaF\textsubscript{2} crystals.

Fig. 3. Emission spectra of the Tm:CaF\textsubscript{2} and Tm\textsubscript{3+}, Y:CaF\textsubscript{2} crystals.
\[ \sigma_{\text{em}}(\lambda) = \frac{\sigma_{\text{abs}}(\lambda) Z_L}{Z_u} \exp \left( \frac{E_{ZL} - \frac{hc}{\lambda} - kT}{kT} \right). \]  

(1)

where \( Z_u \) and \( Z_L \) are the partition functions of the lower and upper levels, \( E_{ZL} \) is the zero line energy defined as the energy gap between \(^3\)\(\text{H}_6\) and \(^3\)\(\text{F}_4\) manifolds, \( h \) is Planck’s constant, \( k \) is Boltzmann’s constant, and \( T \) is temperature. Here, the zero line is 1666 nm, and \( Z_u/Z_L \) is 1.512\(^{[1]}\). There are three emission peaks located at 1611, 1666, and 1820 nm, respectively. The emission cross-section of 4\% Tm,4\% Y:CaF\(_2\) crystal was calculated to be \( 0.45 \times 10^{-20} \text{ cm}^2 \) at 1820 nm, which is increased by 40.96\% compared with the value of \( 0.32 \times 10^{-20} \text{ cm}^2 \) in 4\% Tm:CaF\(_2\) crystal. The emission cross-section is enhanced by the incorporation of 4\% Y\(^3\)\(\text{+}\) ions. There are two reasons to be concerned for the phenomenon. On the one hand, part of the f-f forbidden transition between \(^3\)\(\text{F}_4\) and \(^3\)\(\text{H}_6\) energy levels of Tm\(^{3+}\) ions was relieved by a stronger crystal field, as discussed above for absorption cross-sections. That is to say, higher absorption intensity results in a stronger emission in Tm:Y:CaF\(_2\) crystal. On the other hand, it was pointed out that the Y\(^{3+}\) ions enter the lattice predominantly in the vicinity of the Tm\(^{3+}\) ions\(^{[2]}\). Thus, coded Y\(^{3+}\) ions may separate the clustered Tm\(^{3+}\) ions in the lattice at an appropriate distance. As a result, the probability of cross-relaxation between Tm\(^{3+}\) ions was increased, and there will be more population inversion on the upper energy level. The emission was improved accordingly. Table 1 shows the comparison of the emission cross-section between our work and the Tm laser in other oxide hosts reported. The value of the Tm:Y:CaF\(_2\) crystal is lower than those of YAG, YAlO\(_3\) (YAP), and C\(_{22}\)H\(_{36}\)NNaO\(_7\)S (SSO) but higher than that of CaYAlO\(_4\). The data indicate that laser energy conversion efficiency of Tm:SSO is lower than those of YAP and CaF\(_2\). In addition, the full widths at half-maximum of the emission peaks at 1820 nm of these samples were similar, which were about 200 nm.

The fluorescence decay curves of these samples excited by 808 nm pulsed lasers show a single exponential decay behavior, which are shown in Fig. 4. By fitting the decay curves, the lifetimes are obtained to be 2.99 and 3.94 ms in 4\% Tm:CaF\(_2\) crystal and 4\% Tm,4\% Y:CaF\(_2\) crystal, respectively. The longer lifetime in Tm:Y:CaF\(_2\) crystal further proved that codoping Y\(^{3+}\) is beneficial to luminescence. Moreover, compared to other oxide-based laser materials, the lifetime of Tm:Y:CaF\(_2\) crystal is relatively long, which is listed in Table 1. Also, longer lifetime also means higher quantum efficiency.

As the absorption and emission cross-section were calculated, the gain cross-section \( \sigma_g \) could be estimated by the following equation:

\[ \sigma_g = P \cdot \sigma_{\text{abs}} - (1 - P) \cdot \sigma_{\text{em}}, \]

(2)

where parameter \( P \) is the relative inverted population of the involved levels. The gain cross-sections of 4\% Tm:CaF\(_2\) and 4\% Tm,4\% Y:CaF\(_2\) crystals with the \( P \) varying from 0 to 0.4 were estimated and illustrated in Fig. 5. Obviously, the gain cross-section becomes positive when the population inversion level reaches 10\%. In particular, the value of Tm:Y:CaF\(_2\) is almost two times higher than that of Tm:CaF\(_2\) crystal when the value of \( P \) is equal to 0.4.

CW laser operations were carried out by inserting an uncoated Tm:Y:CaF\(_2\) sample inside a plane-concave laser resonator with water cooling at 13°C, and the setup was shown in Fig. 6. The pump source was a fiber-coupled 792 nm diode laser, delivering a maximum power of 30 W with a core diameter of 105 \( \mu \text{m} \) and a numerical aperture of 0.22. The pump beam was expanded into the gain medium by a coupling system of 1:2. M1 was a flat mirror (more than 90\% transmission at the pump wavelength and more than 99\% reflectivity at the lasing wavelength); M2 was a concave mirror having a radius of 100 mm with output transmissions of 2\%, 5\%, and 10\% around 2.0 \( \mu \text{m} \),

\[ \begin{array}{|c|c|c|c|c|}
\hline
\text{Hosts} & \text{Emission Cross-section (cm}^{-2}\text{)} & \text{Emission Lifetime (ms)} & \text{P} \text{\(_{\text{out}}\)} (\text{W}) & \eta (\%) \\
\hline
\text{Tm:YAG} & 2.9 \times 10^{-20} & 0.25 & 0.593 & 18.9 \text{[27]} \\
\text{Tm:SSO} & 6 \times 10^{-21} & 1.1 & 0.934 & 25.9 \text{[28,29]} \\
\text{Tm:CaYAlO}_4 & 2.5 \times 10^{-21} & 2.68-2.9 & 0.24 & 28 \text{[30,31]} \\
\text{Tm:YAP} & 2.09 \times 10^{-19} & 48.3 & 10.5 & 46 \text{[32,33]} \\
\text{Tm:CaF}_2 & 3.2 \times 10^{-21} & 2.99 & - & - \\
\text{Tm,Y:CaF}_2 & 4.5 \times 10^{-21} & 3.94 & 1.013 & 54.8 \text{This work} \\
\hline
\end{array} \]

Fig. 4. Fluorescence decay curves at (a) 4\% Tm:CaF\(_2\) and (b) 4\% Tm,4\% Y:CaF\(_2\).

Table 1. Emission Cross-section, Emission Lifetime, and Laser Parameters of Tm-doped Hosts
The experiments were done at output powers of 0.976 and 0.867 W, respectively. In or-
transmissions of 2% and 10%, respectively. The maximum efficiencies are 49.9% and 53.6% by using the OCs with power of 1.013 W, which is remarkable. The laser slope efficiency is lower than those of oxide materials. The laser output was 0.976 W were achieved by using the 5% transmissive output coupler (OC). To the best of our knowledge, this is the highest slope efficiency and largest power reported in Tm:CaF2 crystals. A comparative study for laser properties of Tm:Y:CaF2 with other oxide hosts is shown in Table 1. The value of Tm:Y:CaF2 crystal is 54.8%, which is the highest in these hosts. The data indicate that the laser energy conversion efficiency of Tm:Y:CaF2 is lower than those of oxide materials. The laser output power is 1.013 W, which is remarkable. The laser slope efficiencies are 49.9% and 53.6% by using the OCs with transmissions of 2% and 10%, respectively. The maximum output powers are 0.976 and 0.867 W, respectively. In order to protect the crystal, the experiments were done at low incident pump powers. Therefore, higher output power can be achieved with the increasing pump power.

In summary, CaF2 crystals doped with Tm3+ ions and Y3+ ions are obtained by the TGT. The fluorescence emissions around 1820 nm, corresponding to F4 → H6 transitions of Tm3+, were observed under the excitation of an 808 nm LD. The emission intensity at 1820 nm increased with codoping of Y3+ ions. Under LD pumping, a maximum CW output power of 1.013 W and a slope efficiency of 54.8% were obtained in the 4% Tm:4% Y:CaF2 crystal. Further studies will focus on Y3+ doping concentration in Tm:CaF2 for potential CW lasers.

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