Mid-IR Optical Property of Dy:CaF\textsubscript{2}-SrF\textsubscript{2} Crystal Fabricated by Multicrucible Temperature Gradient Technology

Lihe Zheng \textsuperscript{1}, Jianbin Zhao \textsuperscript{1}, Yangxiao Wang \textsuperscript{2}, Weichao Chen \textsuperscript{3,}*\textsuperscript{,} Fangfang Ruan \textsuperscript{4,}*\textsuperscript{,} Hui Lin \textsuperscript{5}, Yanyan Xue \textsuperscript{6}, Jian Liu \textsuperscript{6}, Yang Liu \textsuperscript{1}, Ruiqin Yang \textsuperscript{1}, Haifeng Lu \textsuperscript{1}, Xiaodong Xu \textsuperscript{7} and Liangbi Su \textsuperscript{2}

1 Key Laboratory of Yunnan Provincial Higher Education Institutions for Optoelectronics Device Engineering, School of Physics and Astronomy, Yunnan University, Kunming 650500, China; zhenglihe@ynu.edu.cn (L.Z.); jianbinzhao@mail.ynu.edu.cn (J.Z.); liuyang1@mail.ynu.edu.cn (Y.L.); yangruiqin@mail.ynu.edu.cn (R.Y.); 294327027@qq.com (H.L.)

2 Key Laboratory of Transparent Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China; wangtim@student.sic.ac.cn (Y.W.); suliangbi@sic.ac.cn (L.S.)

3 School of Technology, Pu’er University, Pu’er 665000, China

4 Department of Medical Imaging, Hangzhou Medical College, Hangzhou 310053, China

5 Engineering Research Center of Optical Instrument and System, Ministry of Education and Shanghai Key Lab of Modern Optical System, University of Shanghai for Science and Technology, Shanghai 200093, China; linh81120163.com

6 School of Physics Science and Engineering, Tongji University, Shanghai 200092, China; xueyanyan@c163.com (Y.X.); 1910102@tongji.edu.cn (J.L.)

7 Jiangsu Key Laboratory of Advanced Laser Materials and Devices, School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, China; xdxu79@jsnu.edu.cn

* Correspondence: weichaochen2010@foxmail.com (W.C.); ruan.f@hmc.edu.cn (F.R.)

Abstract: Dy\textsuperscript{3+}-doped CaF\textsubscript{2}-SrF\textsubscript{2} crystals with various Dy\textsuperscript{3+} dopant concentrations were synthesized by multicrucible temperature gradient technology (MC-TGT). Dy:CaF\textsubscript{2}-SrF\textsubscript{2} crystals were fluoride structured and crystallized in cubic \textit{Fm\textsubscript{3}m} space group, as characterized by X-ray diffraction. The crystallographic site concentration was calculated from the measured density by Archimedes’ hydrostatic weighing principle. The optical transmission reached over 90\% with a sample thickness of 1.0 mm. The Sellmeier dispersion formula was obtained following the measured refractive index in a mid-IR range of 1.7–11 µm. Absorption coefficients of 6.06 cm\textsuperscript{-1} and 12.71 cm\textsuperscript{-1} were obtained at 804 nm and 1094 nm in 15\% Dy:CaF\textsubscript{2}-SrF\textsubscript{2} crystal. The fluorescence spectra of 15 at.% Dy:CaF\textsubscript{2}-SrF\textsubscript{2} showed the strongest wavelength peak at 2919 nm with a full width at half maximum (FWHM) of 267 nm under an excitation wavelength of 808 nm. The fluorescence lifetimes were illustrated for different Dy\textsuperscript{3+} dopant levels of 5\%, 10\% and 15\%. The results indicate that the Dy:CaF\textsubscript{2}-SrF\textsubscript{2} crystal is a promising candidate for compact mid-IR lasers.

Keywords: Dy:CaF\textsubscript{2}-SrF\textsubscript{2}; crystal growth; temperature gradient technology; midinfrared crystal; Sellmeier dispersion formula

1. Introduction

Midinfrared (mid-IR) lasers are considered of great importance due to their wide applications in fundamental and practical fields such as directional infrared countermeasures, atmospheric monitoring, biomedicine, medical laser, optical communication and high-energy physics [1]. Directly pumped mid-IR solid-state lasers have attracted significant attention due to their advantages such as simple system composition, compact size, high efficiency and high output power. Active ions and host materials are both important in obtaining diode laser pumped solid-state lasers.

Rare-earth ions (Tm\textsuperscript{3+}, Er\textsuperscript{3+}, Ho\textsuperscript{3+} and Dy\textsuperscript{3+}) are the preferred active ions for laser emission in the mid-IR spectral range. Tm\textsuperscript{3+}, Er\textsuperscript{3+}, Ho\textsuperscript{3+} ions have been reported with 2–3 µm lasing in crystalline or glass hosts such as Tm:YAG [2], Tm:YLF [3], Tm:ZBLAN [4].
2. Materials and Methods

2.1. Crystal Growth

Dy:CaF$_2$-SrF$_2$ crystal boules, with Dy$^{3+}$ concentrations of 5 at.%, 10 at.% and 15 at.%, were fabricated by multicrucible temperature gradient technology (MC-TGT). TGT is a directional solidification technique adapted for the growth of high-temperature crystals [26]. The traditional TGT method allows for one-crucible crystal growth. To enhance growth efficiency, we developed an MC-TGT that allows obtaining multiple crystal boules in the one-growth process [22]. Six crucibles were fixed in the furnace. Benefiting from the azeotrope properties of CaF$_2$-SrF$_2$, no crystal seed was used. A stable temperature gradient was then built around the crucible to conduct latent heat and to promote crystallization. The starting materials were CaF$_2$, SrF$_2$ and DyF$_3$ powders with purity higher than 99.995%. The raw materials were mixed according to Ca/Sr molar ratio of 1:1 before placing it in a graphite crucible. Then, 1 wt.% PbF$_2$ was added to remove oxygen. The melting points of DyF$_3$, CaF$_2$ and SrF$_2$ are 1360 °C, 1420 °C and 1477 °C, respectively. The furnace was insulated for 3 h at 1530 °C while evacuating to 10$^{-3}$ Pa. The cooling rate for crystal growth was set at 1.5 °C/h. After growth, the crucible was cooled to room temperature.
at a cooling rate of 20 °C/h. The Dy:CaF\textsubscript{2}-SrF\textsubscript{2} crystals were then cut and processed for subsequent tests.

2.2. Characterizations

The segregation coefficient of Dy\textsuperscript{3+} ion in the CaF\textsubscript{2}-SrF\textsubscript{2} host was detected by inductively coupled plasma atomic emission spectrometry (ICP-AES). The sample was cut from the initial part of the crystal and then ground into fine powder in an agate mortar. The solvent was a mixture of phosphoric acid and boric acid. After obtaining the weight percentage of Dy\textsuperscript{3+}, Ca\textsuperscript{2+} and Sr\textsuperscript{2+} in the solvent, the dopant level of Dy\textsuperscript{3+} was calculated. The segregation coefficient could thus be calculated by dividing the measured dopant value of Dy\textsuperscript{3+} by the theoretical value. The segregation coefficient was measured for the sample adjacent to the initial part of the as-grown crystal boule.

The structure of Dy:CaF\textsubscript{2}-SrF\textsubscript{2} crystal was measured by a powder-X-ray diffractometer (P-XRD, RIGAKU TTRIII-18KW, Tokyo, Japan) using a Cu target at room temperature. The scan rate was 3°/min. The raw data from the P-XRD pattern were analyzed to fix the diffraction peak by comparing with the standard Power Diffraction File (PDF) data from Jade software. The diffractograms were gathered by Origin software.

The refractive index in the mid-IR spectral range was characterized using an infrared ellipsometer (J.A. Woollam IR-Vase II, Lincoln, NE, USA). The single crystal along the growth axis was cut with a diameter of 20 mm and a thickness of 1 mm. One surface was polished, while the other surface was kept rough for measurement. The measured data were then analyzed by nonlinear fitting by Origin software to obtain dispersion formula.

The optical quality of as-grown crystal boules was characterized by mid-IR transmission spectra with a sampling step of 2.8 nm (Bruker TENSOR27, Karlsruhe, Germany). Absorption spectra were measured with a UV/vis/NIR spectrophotometer (Varian Cary 5000, Palo Alto, CA, USA) using Xe light as a pump source. Fluorescence spectra were measured with an 808 nm pump source (Edinburg Instruments FLS1000, Livingston, UK) and an InSb detector. As a comparison, a 1320 nm pump source from a pulse generator (Thurlby Thandar Instruments TGP 110, Huntingdon, UK) was used for fluorescence spectra, emitting at 1200–3500 nm, recorded by a digital phosphor oscilloscope with sampling rate of 1.25 GS/s and frequency of 100 MHz (Tektronix TDS 3012C, Beaverton, OR, USA). The fluorescence lifetime measurement was carried out by a computer-controlled transient digitizer decay curve of emission under a pump wavelength of 808 nm. Single crystals with a thickness of 1 mm along the growth axis were polished and then used for the above-mentioned spectroscopic measurements. All measurements were performed at room temperature.

3. Results and Discussion

3.1. Crystal Structure and Optical Quality

The traditional TGT method allows for one-crucible crystal growth. To enhance growth efficiency, we developed an MC-TGT that allows obtaining multiple crystal boules in the one-growth process. Figure 1 shows the obtained Dy:CaF\textsubscript{2}-SrF\textsubscript{2} crystal boules up to 20 mm in diameter and 68 mm in length. The as-grown yellow boules are homogeneous without bubbles. The dopants of Dy\textsuperscript{3+} ions are 5 at.%, 10 at.% and 15 at.%. The segregation coefficient of Dy\textsuperscript{3+} ion in 5 at.% Dy:CaF\textsubscript{2}-SrF\textsubscript{2} and 15 at.% Dy:CaF\textsubscript{2}-SrF\textsubscript{2} is 1.0, while that in 10 at.% Dy:CaF\textsubscript{2}-SrF\textsubscript{2} is 0.96. This indicates the high solubility of Dy\textsuperscript{3+} ion in the CaF\textsubscript{2}-SrF\textsubscript{2} host lattice.

![Figure 1](https://via.placeholder.com/150.png?text=Figure%201%20As-grown%20Dy:CaF\textsubscript{2}-SrF\textsubscript{2}%20crystal%20boules%20using%20MC-TGT.%20(a)%205at.%%20Dy;%20(b)%2010at.%%20Dy;%20(c)%2015at.%%20Dy.)

**Figure 1.** As-grown Dy:CaF\textsubscript{2}-SrF\textsubscript{2} crystal boules using MC-TGT. (a) 5 at.% Dy; (b) 10 at.% Dy; (c) 15 at.% Dy.
The method of Archimedes’ hydrostatic weighing principle aids in the determination of density following Equation (1).

\[ \rho = \frac{m_1 \cdot \rho_1}{m_1 - m_2} \]  

(1)

Here, \( m_1 \) and \( m_2 \) are sample weights measured in air and in water, respectively. \( \rho_1 \) is the density of water marked as 1 g cm\(^{-3} \). \( \rho \) is the sample density in air to be determined. The test results are listed in Table 1.

| Crystals            | \( m_1 \) (g) | \( m_2 \) (g) | \( \rho \) (g/cm\(^3\)) |
|---------------------|---------------|---------------|------------------------|
| 5% Dy:CaF\(_2\)-SrF\(_2\) | 12.24010      | 9.20478       | 4.03256                |
| 10% Dy:CaF\(_2\)-SrF\(_2\) | 14.00670      | 10.69937      | 4.23505                |
| 15% Dy:CaF\(_2\)-SrF\(_2\) | 13.22491      | 10.28247      | 4.49454                |

Figure 2 gives the measured XRD pattern of Dy:CaF\(_2\)-SrF\(_2\) crystal compared with that of pure CaF\(_2\) referring to PDF Number 75-0363 and that of pure SrF\(_2\) referring to PDF Number 06-0262. The main three strongest peaks in CaF\(_2\) are located at 2\( \theta \) of 28.272\(^\circ\) for (111), 47.008\(^\circ\) for (200) and 55.764\(^\circ\) for (311), while those in SrF\(_2\) are located at 2\( \theta \) of 26.57\(^\circ\) for (111), 44.123\(^\circ\) for (200) and 52.273\(^\circ\) for (311). In the case of Dy:CaF\(_2\)-SrF\(_2\) crystal, the three strongest peaks are located at 2\( \theta \) of 27.46\(^\circ\), 45.52\(^\circ\) and 53.96\(^\circ\). The diffraction angles 2\( \theta \) of Dy:CaF\(_2\)-SrF\(_2\) situates in-between those of CaF\(_2\) and SrF\(_2\). This indicates that Dy:CaF\(_2\)-SrF\(_2\) crystal is fluorite structured and crystallizes in the cubic \( Fm\overline{5}m \) space group.

Figure 2. XRD pattern of Dy:CaF\(_2\)-SrF\(_2\) crystal.

The optical quality of polished Dy:CaF\(_2\)-SrF\(_2\) crystals was characterized by transmission spectra. Figure 3 gives the transmission spectra of Dy:CaF\(_2\)-SrF\(_2\) at 2–11 \( \mu \)m. The transmission curves in Figure 3 are based on measured raw data subtracting the background without considering the reflections on both surfaces. It shows that the transmission of all three polished samples is above 90% from 4 to 9 \( \mu \)m. The infrared transmittance cut-off wavelength is around 11 \( \mu \)m. It could be concluded that the crystallinity and optical quality of Dy:CaF\(_2\)-SrF\(_2\) crystal boules are good.

Figure 3. Transmission spectra of Dy:CaF\(_2\)-SrF\(_2\) crystal.
3.2. Refractive Index in the Mid-IR Spectral Range

Figure 4 gives the refractive index of Dy:CaF$_2$-SrF$_2$ in the mid-IR spectral range of 1.7–11 $\mu$m. As seen from Figure 4, the refractive index of Dy:CaF$_2$-SrF$_2$ increases along with a higher dopant level of Dy$^{3+}$. The Sellmeier dispersion formula is used for nonlinear fitting. The dispersion formula for Dy:CaF$_2$-SrF$_2$ with Dy$^{3+}$ dopant levels of 5%, 10% and 15% is thus achieved and described in Equations (2)–(4), respectively. The reduced Chi-square is 2.70 $\times$ 10$^{-5}$. The adjusted $R^2$ is 0.9986.

$$\begin{align*}
n^2 - 1 & = 0.20292 + \frac{0.69272\lambda^2}{\lambda^2 - 0.94855^2} + \frac{0.87102\lambda^2}{\lambda^2 - 60.10^2} + \frac{5.64914\lambda^2}{\lambda^2 - 45.04^2} \quad (2) \\
n^2 - 1 & = 0.21687 + \frac{0.70758\lambda^2}{\lambda^2 - 0.97111^2} + \frac{1.84394\lambda^2}{\lambda^2 - 70.44^2} + \frac{6.11963\lambda^2}{\lambda^2 - 48.55^2} \quad (3) \\
n^2 - 1 & = 0.20292 + \frac{0.73684\lambda^2}{\lambda^2 - 0.97075^2} + \frac{2.30876\lambda^2}{\lambda^2 - 69.93^2} + \frac{6.15892\lambda^2}{\lambda^2 - 50.30^2} \quad (4)
\end{align*}$$

Figure 4. Refractive index of Dy:CaF$_2$-SrF$_2$ in the mid-IR spectral range of 1.7–11 $\mu$m.
3.3. Absorption and Emission Spectra

Figure 5 shows the room-temperature absorption spectra in the spectral range of 650–1900 nm and the assignment of energy level in Dy:CaF\textsubscript{2}–SrF\textsubscript{2} crystals. The assignment of energy level could refer to that in Dy:BaY\textsubscript{2}F\textsubscript{8} [27]. In the mid-IR region, Dy\textsuperscript{3+} ions show broad absorption bands in 5\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2} crystal peaks at 804 nm, 907 nm, 1092 nm, 1276 nm and 1714 nm corresponding to absorption coefficients of 2.12 cm\textsuperscript{-1}, 2.69 cm\textsuperscript{-1}, 4.04 cm\textsuperscript{-1}, 2.54 cm\textsuperscript{-1} and 1.18 cm\textsuperscript{-1}, respectively. In the case of 10\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2} crystal, the absorption coefficients are 3.56 cm\textsuperscript{-1}, 4.46 cm\textsuperscript{-1}, 7.08 cm\textsuperscript{-1}, 4.47 cm\textsuperscript{-1} and 2.02 cm\textsuperscript{-1}, corresponding to absorption band peaks at 804 nm, 908 nm, 1093 nm, 1273 nm and 1716 nm. For 15\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2} crystal, it gives the strongest absorption coefficients of 6.06 cm\textsuperscript{-1}, 7.56 cm\textsuperscript{-1}, 12.71 cm\textsuperscript{-1}, 8.25 cm\textsuperscript{-1} and 3.63 cm\textsuperscript{-1}, corresponding to absorption band peaks at 804 nm, 907 nm, 1094 nm, 1277 nm and 1716 nm. The absorption band peaks at 1308 nm and 1720 nm correspond to energy level transitions of \(6\text{H}_{15/2} \rightarrow 6\text{H}_{9/2}, 6\text{F}_{11/2}\) and \(6\text{H}_{15/2} \rightarrow 6\text{H}_{11/2}\) in Dy\textsuperscript{3+} ion. With the increase in Dy\textsuperscript{3+} ion dopant levels from 5\% to 15\%, the absorption coefficient becomes 2.8–3.3 times stronger. Broad absorption bands are profitable in increasing the diode-pumping efficiency, as laser diodes typically emit in a narrow spectral range and present a thermal shift in the peak wavelength.

![Figure 5](image_url)

Figure 5. Absorption coefficient of Dy:CaF\textsubscript{2}–SrF\textsubscript{2} crystal at 650–1900 nm.

Table 2 gives the calculated absorption cross-section of Dy\textsuperscript{3+} according to the expression \(\sigma_{abs} = \alpha/N\). Here, \(\alpha\) is the absorption coefficient of Dy\textsuperscript{3+}. \(N\) is the concentration of Dy\textsuperscript{3+} ions with \(1.21 \times 10^{21}\) ion\textsuperscript{−3}, \(2.42 \times 10^{21}\) ion\textsuperscript{−3} and \(4.03 \times 10^{21}\) ion\textsuperscript{−3} in 5\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2}, 10\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2} and 15\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2}, respectively.

| Crystal         | \(\sigma_{abs} (\times 10^{-20}\text{ cm}^{2})\) |
|-----------------|---------------------------------------------|
|                 | 804 nm | 907 nm | 1094 nm | 1287 nm |
| 5\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2} | 0.176   | 0.223   | 0.335    | 0.211    |
| 10\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2} | 0.147   | 0.184   | 0.293    | 0.185    |
| 15\% Dy:CaF\textsubscript{2}–SrF\textsubscript{2} | 0.150   | 0.187   | 0.315    | 0.205    |
Figure 6 shows the emission spectra and peak assignment of Dy:CaF$_2$-SrF$_2$ crystal in the mid-IR range under excitation wavelengths of 808 nm and 1320 nm. In the case of using a pump wavelength of 1320 nm, as shown in Figure 6a, the fluorescence band peak at 1970 nm, corresponding to the energy level transition from $^6\text{H}_{9/2}$ to $^6\text{H}_{15/2}$, was detected with an intensity variation in the order of the Dy$^{3+}$ doping concentration. The strongest fluorescence intensity appears in 5% Dy:CaF$_2$-SrF$_2$, while the lowest fluorescence intensity appears in 15% Dy:CaF$_2$-SrF$_2$. It is interesting to note that the intensity of the fluorescence band peak at 2882 nm is not affected by the Dy$^{3+}$ doping concentration.

![Emission spectra](image)

**Figure 6.** Emission spectra of Dy:CaF$_2$-SrF$_2$ crystal under different pump source. (a) 1320 nm pump; (b) 808 nm pump.

Figure 6b shows the emission spectra by using an excitation wavelength of 808 nm. The emission intensity of 10% Dy:CaF$_2$-SrF$_2$ is the lowest, while that of 15% Dy:CaF$_2$-SrF$_2$ is the highest. In order to illustrate the mid-IR fluorescence bands, nonlinear fittings for multiple peaks are used in the form of the Lorentz function. Taking 15% Dy:CaF$_2$-SrF$_2$ for example, the full width at half maximum (FWHM) is 267 nm for the emission band peak at 2919 nm, corresponding to the energy level transition from $^6\text{H}_{13/2}$ to $^6\text{H}_{15/2}$ of Dy$^{3+}$ ion. In the case of Dy:CaF$_2$-SrF$_2$ with Dy$^{3+}$ dopant levels of 10% and 5%, the values of FWHM are both 237 nm. All emission bands peak at 2913 nm.

Figure 7 gives the measured fluorescence lifetime curves for the energy transfer channel $^6\text{H}_{13/2} \rightarrow ^6\text{H}_{15/2}$ of Dy$^{3+}$ ions in Dy:CaF$_2$-SrF$_2$ crystals. The obtained fluorescence lifetime curves are processed with nonlinear fitting according to the second-order exponential formula (ExpDec2), as described in Equation (5).

$$ y = A_0 + A_1 e^{-\frac{t}{t_1}} + A_2 e^{-\frac{t}{t_2}} $$  

(5)

![Fluorescence lifetime curves](image)

**Figure 7.** Measured and nonlinear fitted fluorescence lifetime curves in Dy:CaF$_2$-SrF$_2$. (a) 5% Dy; (b) 10% Dy; (c) 15% Dy.

Here, $A_0$, $A_1$, $A_2$, $t_1$ and $t_2$ are constant values that could be obtained from the fitting results. Accordingly, the second-order exponential formula for Dy:CaF$_2$-SrF$_2$ with various
Dy\(^{3+}\) dopant levels is thus written in Equations (6)–(8). The average fluorescence lifetime could be obtained from Equation (9). The fluorescence lifetimes are calculated as 743.6 µs, 339.2 µs and 194.7 µs for Dy:CaF\(_2\)–SrF\(_2\) with Dy\(^{3+}\) dopant levels of 5%, 10% and 15%, respectively. The reduction of fluorescence lifetime along with a higher Dy\(^{3+}\) concentration could be attributed to the increase in interstitial fluoride ions. The mechanism could be described in the defect reaction equation as shown in Equation (10). It would be interesting to investigate the mechanism of enhancing fluorescence intensity while maintaining lifetime in future work.

\[
y = 1046.495 + 331.646e^{-\frac{\tau}{2343.164}} + 4722.538e^{-\frac{\tau}{4722.538}} + 1046.495 + 331.646e^{-\frac{\tau}{2343.164}} + 4722.538e^{-\frac{\tau}{4722.538}} + 1046.495 + 331.646e^{-\frac{\tau}{2343.164}} + 4722.538e^{-\frac{\tau}{4722.538}} \quad (6)
\]

\[
y = 793.798 + 5605.837e^{-\frac{\tau}{339.964}} + 60.970e^{-\frac{\tau}{104.241}} + 793.798 + 5605.837e^{-\frac{\tau}{339.964}} + 60.970e^{-\frac{\tau}{104.241}} + 793.798 + 5605.837e^{-\frac{\tau}{339.964}} + 60.970e^{-\frac{\tau}{104.241}} \quad (7)
\]

\[
y = 1050.882 + 2892.258e^{-\frac{\tau}{194.744}} + 2892.258e^{-\frac{\tau}{194.744}} + 1050.882 + 2892.258e^{-\frac{\tau}{194.744}} + 2892.258e^{-\frac{\tau}{194.744}} + 1050.882 + 2892.258e^{-\frac{\tau}{194.744}} + 2892.258e^{-\frac{\tau}{194.744}} \quad (8)
\]

\[
\tau = \frac{A_1I_1^2 + A_2I_2^2}{A_1I_1 + A_2I_2} \quad (9)
\]

\[
\text{DyF}_3^{3+} \rightarrow \text{SrF}_2^{2-} \text{Dy}_{\text{Ca/Sr}} + 2F + F' \quad (10)
\]

4. Summary

This paper concerns the important issue of novel emissive materials for laser applications in the significant mid-IR range. Dy\(^{3+}\)-doped CaF\(_2\)–SrF\(_2\) crystals with fluorite structure and cubic \(Fm\overline{3}m\) space group were synthesized by MC-TGT. The crystallographic site concentrations were up to \(4.034 \times 10^{21}\) ions·cm\(^{-3}\) in 15 at.% Dy:CaF\(_2\)–SrF\(_2\). The optical transmission of Dy:CaF\(_2\)–SrF\(_2\) crystal reached over 90% with a sample thickness of 1.0 mm. The Sellmeier dispersion formula for 1.7–11 µm was obtained from the refractive index. The strongest absorption coefficients of 6.06 cm\(^{-1}\), 7.56 cm\(^{-1}\), 12.71 cm\(^{-1}\), 8.25 cm\(^{-1}\) and 3.63 cm\(^{-1}\) were obtained in 15% Dy:CaF\(_2\)–SrF\(_2\) crystal corresponding to absorption band peaks at 804 nm, 907 nm, 1094 nm, 1277 nm and 1716 nm. The value of FWHM was 267 nm for the emission band peak at 2919 nm in 15% Dy:CaF\(_2\)–SrF\(_2\) under an excitation wavelength of 808 nm. The fluorescence lifetime in 5% Dy:CaF\(_2\)–SrF\(_2\) was 3.8 times longer than that in 15% Dy:CaF\(_2\)–SrF\(_2\). Further research work will focus on the enhancement of lifetime while maintaining strong emission in the mid-IR spectral range.

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References
1. Xue, Y.Y.; Xu, X.D.; Su, L.B.; Xu, J. Research Progress of Mid-infrared Laser Crystals. J. Synth. Cryst. 2020, 49, 1347–1360.
2. Cao, D.; Meng, Q.; Du, S.; Xu, J.; Guo, Y.; Yang, J.; Bo, Y.; Zhang, J.; Cui, D.; Xu, Z. A 200 W diode-side-pumped CW 2 µm Tm:YAG laser with water cooling at 8 °C. Appl. Phys. B 2011, 103, 83–88. [CrossRef]
3. Wang, S.Q.; Huang, H.T.; Chen, H.W.; Liu, X.; Liu, S.D.; Xu, J.L.; Shen, D.Y. High efficiency nanosecond passively Q-switched 2.3 μm Tm:YLF laser using a ReSe₂-based saturable output coupler. *OSA Contin.* 2019, 2, 1676–1682. [CrossRef]

4. Lancaster, D.G.; Gross, S.; Ebendorff-Heidepriem, H.; Fuerbach, A.; Withford, M.J.; Monro, T.M. 2.1 μm waveguide laser fabricated by femtosecond laser direct-writing in Ho⁺³⁺:ZBLAN glass. *Opt. Lett.* 2012, 37, 996–998. [CrossRef] [PubMed]

5. Sottile, A.; Damiano, E.; Rabe, M.; Bertram, R.; Klümper, D.; Tonelli, M. Widely tunable, efficient 2 μm laser in monocristalline Tm³⁺:SrF₂. *Opt. Express* 2016, 26, 5368–5380. [CrossRef] [PubMed]

6. Duan, X.M.; Shen, Y.J.; Zhang, Z.; Su, L.B.; Dai, T.Y. A passively Q-switching of diode-pumped 2.08 μm Ho:CaF₂ laser. *Infrared Phys. Technol.* 2019, 103, 103071. [CrossRef]

7. Majewski, M.R.; Jackson, S.D. Highly efficient mid-infrared dysprosium fiber laser. *Opt. Lett.* 2016, 41, 2173–2176. [CrossRef] [PubMed]

8. Woodward, R.I.; Majewski, M.R.; Bhatarhan, G.; Hudson, D.D.; Fuerbach, A.; Jackson, S.D. Watt-level dysprosium fiber laser at 3.15 μm with 73% slope efficiency. *Opt. Lett.* 2018, 43, 1471–1474. [CrossRef] [PubMed]

9. Djeu, N.; Hartwell, V.E.; Kaminskii, A.A.; Butashin, A.V. Room-temperature 3.4-μm Dy:BaYbF₃ laser. Opt. Lett. 1997, 22, 997–999. [CrossRef]

10. Barnes, N.P.; Allen, R.E. Room temperature Dy:YLF laser operation at 4.34 μm. *IEEE J. Quantum Electron.* 1991, 27, 277–282. [CrossRef]

11. Jelinkova, H.; Doroshenko, M.E.; Osiko, V.V.; Jelinková, M.; Šulc, J.; Němec, M.; Vyhídal, D.; Badikov, V.V.; Badikov, D.V. Dysprosium thioalgalase: Source of mid-infrared radiation at 2.4, 4.3, and 5.4 μm. *Appl. Phys. A* 2016, 122, 738. [CrossRef]

12. Jelinkova, H.; Doroshenko, M.E.; Jelinková, M.; Šulc, J.; Osiko, V.V.; Badikov, V.V.; Badikov, D.V. Dysprosium-doped PbGa₂S₄ laser generating at 4.3 μm directly pumped by 1.7 μm laser diode. *Opt. Lett.* 2013, 38, 3040–3043. [CrossRef]

13. Nostrand, M.C.; Page, R.H.; Payne, S.A.; Krupke, W.F.; Schunemann, P.G. Room-temperature laser action at 4.3–4.4 μm in CaGa₂S₄:Dy³⁺. *Opt. Lett.* 1999, 24, 1215–1217. [CrossRef]

14. Zhang, F.; Zhu, H.T.; Liu, J.; He, Y.F.; Jiang, D.P.; Tang, F.; Su, L.B. Tunable Yb:CaF₂-SrF₂ laser and femtosecond mode-locked performance based on semiconductor saturable absorber mirrors. *Opt. Appl.* 2016, 55, 8359–8362. [CrossRef] [PubMed]

15. Jiang, B.B.; Zheng, L.H.; Jiang, D.P.; Yin, H.D.; Zheng, J.G.; Yang, Q.H.; Cheng, G.F.; Su, L.B. Growth and optical properties of ytterbium and rare earth ions codoped CaF₂-SrF₂ eutectic solid-solution (RE = Y³⁺, Gd³⁺, La³⁺). *J. Rare Earths* 2021, 39, 390–397. [CrossRef]

16. Ma, F.; Su, F.; Zhou, R.; Ou, Y.; Xie, L.; Liu, C.; Jiang, D.; Zhang, Z.; Wu, Q.; Su, L.; et al. The defect aggregation of RE³⁺ (RE = Y, La ∼ Lu) in MF₂ (M = Ca, Sr, Ba) fluorites. *Mater. Res. Bull.* 2020, 125, 110788. [CrossRef]

17. Ruan, F.F.; Yang, L.; Hu, G.; Wang, A.M.; Xue, Y.Y.; Yang, L.L.; Wang, Z.X.; Wu, S.H.; He, Z.L. Luminescence Properties of Dy³⁺ Doped Lanthanum Fluoride Crystal by Multi-crucible Temperature Gradient Technology. *Chin. J. Luminesc.* 2021, 42, 158–164. [CrossRef]

18. Renaud, E.; Robelin, C.; Heyrman, M.; Chartrand, P. Thermodynamic evaluation and optimization of the (LiF + NaF + KF + MgF₂ + CaF₂ + SrF₂) system. *J. Chem. Thermodyn.* 2001, 33, 661–669. [CrossRef]

19. Klimm, D.; Rabe, M.; Bertram, R.; Uecker, R.; Pither, L. Phase diagram analysis and crystal growth of solid solutions Ca₁₋ₓSrₓF₂. *J. Cryst. Growth* 2008, 310, 152–155. [CrossRef]

20. Karimov, D.N.; Komar’kova, O.N.; Sorokin, N.I.; Bezhanov, V.A.; Chernov, S.P.; Popov, P.A.; Sobolev, B.P. Growth of congruently melting Caₓ₄₋₅Ca₄₋₅Sr₄F₁₂ crystals and study of their properties. *Crystallogr. Rep.* 2010, 55, 518–524. [CrossRef]

21. Xu, J.W.; Zhou, Y.Z.; Zhou, G.Q.; Xu, K.; Deng, P.Z.; Xu, J. Growth of large-sized sapphire boules by temperature gradient technique (TGT). *J. Cryst. Growth* 1998, 193, 123–126. [CrossRef]

22. Johnson, L.F.; Guggenheim, H.J. Laser emission at 3 μm from Dy³⁺ in Ba₂YF₆. *Appl. Phys. Lett.* 1973, 23, 96–98. [CrossRef]