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Full Length Article Yb³⁺, Er³⁺: CeF₃ crystals: Growth, first-principles simulation, and near-infrared optical properties

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ABSTRACT

 Yb^{3+} , Er^{3+} : CeF₃ crystals were successfully grown via Bridgman-Stockbarger technique, and their structure and physicochemical properties were characterized and analyzed. The results have shown that the maximum phonon vibrational frequency of the crystals is 391 cm⁻¹. Under 980 nm excitation, Yb^{3+} ions doping can effectively improve the luminescence intensity at 1550 nm. The maximum luminescence intensity was achieved at the Yb^{3+} ion concentration of 3 at.%. The energy transfers, concentration quenching mechanisms and the factors affecting the fluorescence decay time were investigated in detail. The band gap structure, density of states and charge distribution of Yb^{3+} , Er^{3+} : CeF₃ crystals were studied in depth by first principles simulation. This work proves that Yb^{3+} , Er^{3+} : CeF₃ crystals have great potential for the near-infrared laser applications.

1. Introduction

Near-infrared emission realized by rare earth doped crystals has been widely used in fiber amplifiers, solid-state lasers, telecommunications, optoelectronics and remote sensing [1-3]. In addition, with the development and deepening of medical technology, the application of near-infrared optical imaging to complete the diagnosis and multi-level scanning of tissues or organs has become the mainstream, which makes this kind of crystals more and more concerned. Er³⁺ ions have a wide near-infrared emission range of 1500-1600 nm, which is applicable in optical communication, eye safety measurement and spectroscopy, and has been mentioned in many related studies on Er^{3+} ion doped crystals. However, single rare earth element doping cannot further improve the luminous intensity, so it is urgent to expand the diversity of rare earth doping and the selectivity of crystal matrices to further improve the luminous performance of crystal [4–7]. Yb³⁺ ions, as a kind of rare earth ions, serve as sensitizers to enhance the luminescent properties of other rare earth ions, besides their near-infrared emission applications at 1030 nm [8]. Especially, Yb^{3+} ions have a simple energy level structure,

which is conducive to reducing the influence of non-radiative relaxation in the process of energy transfer, as well as a huge absorption cross-section at the pump at 980 nm. Therefore, they can partner with Er^{3+} ions as co-doped rare earth ions to improve the luminous intensity and fluorescence lifetime at 1550 nm [9–11].

CeF₃ crystals are commonly used as scintillators and magneto-optical crystal materials [12]. In recent years, they have also been found to be excellent matrix materials of laser crystals. For example, Yang et al. studied the growth and optical properties of Dy³⁺:CeF₃ and Ho³⁺:CeF₃ crystals [13,14]. The advantages of this crystal in the field of yellow light and mid-infrared laser output are demonstrated. However, there are few related studies in the near-infrared field, which cannot explain the application value of CeF₃ crystals in the near-infrared field [15]. In order to further study the optical properties and laser application potential of CeF₃ crystals in the near-infrared field, combined with the high optical output performance of Yb³⁺ and Er³⁺ ions in the near-infrared field, therefore, studying the growth and near-infrared luminescence characteristics of CeF₃ crystals doped with Er³⁺ and Yb³⁺ ions has become an urgent task [16].

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Fig. 1. The photo of the grown crystal.

In this study, Yb³⁺, Er³⁺: CeF₃ crystals were grown via Bridgman-Stockbarger method. The phase structure of the crystals was carefully analyzed via XRD, Raman and density tests. Combined with firstprinciples simulation, the changes of crystal structure before and after doping were explored experimentally, and the effects of rare earth doping on the crystal structure and luminescent properties were discussed as well. The near-infrared spectral parameters of the crystals were measured around 1.5 μ m, and their potential in the laser field was characterized according to absorption cross-section and emission crosssection calculations, which further expanded the application value of the crystal.

2. Crystal growth

The crystals were grown through the Bridgeman-Stockbarger method. First, the raw materials CeF₃, YbF₃ and ErF₃ and oxygen scavenger PbF₂ (2 wt%) were weighed and mixed according to the stoichiometric ratio, and the mixtures were dried and purified by fluorination to reduce the influence of impurities and water of crystallization. Next, the processed raw materials were put into a platinum crucible that was evacuated and welded to seal. Finally, the crucible was put into the descending furnace and the temperature was raised to 1650 °C to start the crystal growth. During the growth process, the descending rate of the crucible was adjusted to 1 mm/h, and the cooling rate was set at 35 °C/h. After the growth was completed, the obtained crystals (see Fig. 1) were taken out from the crucible for further testing.

3. Analysis and discussion

3.1. Crystal structure analysis

Fig. 2 (a) displays the XRD diffraction patterns of CeF₃ crystals with different Yb³⁺ ion doping concentrations. All crystals showed the same diffraction peaks, which corresponded exactly to the CeF₃ crystal standard card (JCPDS No.08-0045). No impurity peaks were observed in the XRD diffractograms, indicating that Yb^{3+} and Er^{3+} ions were successfully intercalated into the CeF₃ lattice. Moreover, the hexagonal phase structure of CeF₃ crystals remained unchanged because the difference between the rare earth ion radii was small; in this respect, the lower doping concentration did not affect the overall shape and structure of the crystal. Fig. 2 (b) depicts a map of the corresponding peak position of the crystal at 28–28.3°. Compared with the standard card, as the doping concentration of Yb³⁺ ions increases, the peak is significantly shifted toward the larger angles, which is mainly due to the fact that $Ce^{3+}(1.143 \text{ Å})$ are replaced by $Er^{3+}(1.004 \text{ Å})$ and $Yb^{3+}(0.985 \text{ Å})$. According to the Bragg formula, the upshift of the diffraction peaks would indicate that the interplanar spacing in the crystal decreases, which also confirms that the Yb³⁺ and Er³⁺ ions are effectively introduced into the lattice. Fig. 3 displays a simulated lattice structure of CeF₃ doped with Yb^{3+} and Er^{3+} ions, which can intuitively explain the whole doping process.

3.2. Raman spectroscopy analysis

The phonon frequency of lattice vibration is an important factor affecting the optical properties of crystal. High phonon frequencies will cause part of the transition energy to be absorbed by phonons, resulting in a decrease in the radiative transition. Therefore, it is necessary to test



Fig. 3. Simulation of a CeF_3 lattice structure doped with Yb^{3+} and Er^{3+} ions.



Fig. 2. The XRD diffraction patterns of Yb^{3+} , Er^{3+} : CeF_3 crystals, (a) XRD patterns at different Yb^{3+} doping concentrations; (b) XRD peak shifts.



Fig. 4. Raman spectra of 3 at. % Yb^{3+} ,1 at. % Er^{3+} : CeF_3 crystal, the vibrational peaks at 238, 321, 391 and 650 cm⁻¹.

Table 1 Density values of crystals with different Yb^{3+} doping concentrations.

doping density	Density(g⋅cm ⁻³)	
1 at. % Yb ³⁺	6.1905	
2 at. % Yb ³⁺	6.2005	
3 at. % Yb ³⁺	6.2215	
4 at. % Yb ³⁺	6.2262	
5 at. % Yb ³⁺	6.2435	



Fig. 5. Crystal density as a function of Yb³⁺ doping concentration.

Raman spectra to characterize the phonon frequency of Yb³⁺, Er³⁺: CeF₃ crystal. Fig. 4 depicts the Raman spectrum of 3 at. % Yb³⁺, 1 at. % Er³⁺: CeF₃ crystal, revealing the vibrational peaks at 238, 321, 391 and 650 cm⁻¹. Typically, the Raman peak with the highest intensity refers to the maximum phonon energy of the material [17]. Therefore, the maximum phonon frequency of Yb³⁺, Er³⁺: CeF₃ crystal is only that at 391 cm⁻¹, which is similar to some other binary fluorides (The maximum phonon frequency of the LaF₃ crystal is 350 cm⁻¹), but much lower than in common oxide crystals or glass materials (above 1000 cm⁻¹) [18,19]. In laser applications, Yb³⁺, Er³⁺: CeF₃ crystal is easier to achieve particle number inversion and improve the overall light output efficiency.



Fig. 6. Absorption spectra of Yb^{3+} , Er^{3+} : CeF_3 crystal in a range of 250–1750 nm at room temperature.



Fig. 7. The differential charge density obtained after simulation optimization and calculation of Yb^{3+} , Er^{3+} : CeF₃ crystal.

3.3. Crystal density analysis

The density test was performed according to the Archimedes drainage method. To reduce the margin of error, each sample was tested more than 3 times, and the corresponding densities are shown in Table 1. The density change is shown in Fig. 5. As the Yb^{3+} doping concentration increases, the density of the crystal also increases. This may be due to the higher atomic masses of the Yb^{3+} and Er^{3+} dopants, when the lattice structure does not change significantly, the overall mass of the crystal increases, which is reflected in the increase in macroscopic density. In addition, there is no proportional change trend between doping concentration and density. This may be due to the difference in the quality of crystal growth, which causes the content of rare earth ions doped into the crystal is not fully follow the set chemical. As a result, there would be differences between the real and theoretical doping amounts.

3.4. Absorption spectroscopy

The UV–Vis absorption absorption spectra of Yb³⁺, Er^{3+} : CeF₃ crystals were recorded in a range of 250–1750 nm at room temperature (the



Fig. 8. (a) Band gap structure of Yb³⁺, Er³⁺: CeF₃ crystal; (b) Band gap value obtained via absorption spectrum calculation.

scanning step was 1 nm). Fig. 6 reveals the absorption bands centered at 1550, 975, 860, 652, 520, 487, 451 and 371 nm, corresponding to the transition of $\rm Er^{3+}$ ions from the ground state ${}^{4}I_{15/2}$ to the excited states ${}^{4}I_{13/2}$, ${}^{4}I_{11/2}$, ${}^{4}I_{9/2}$, ${}^{4}F_{9/2}$, ${}^{4}F_{7/2}$, ${}^{4}F_{5/2}$ and ${}^{4}G_{11/2}$, respectively. With the increase of Yb^{3+} ion doping concentration, the absorption intensity at 980 nm increases obviously. This corresponds to the Yb^{3+} ion transition from ${}^{2}F_{7/2}$ to ${}^{2}F_{5/2}$ (where the absorption bands of Yb^{3+} and Er^{3+} ions overlap).

3.5. First-principles simulation and analysis

In this study, Vasp software was used for structural optimization and simulation. For the matrix atom, the U value of the 4f orbital of Ce was set at 5 eV and the 2p orbital of F was set at 4.5 eV. The Yb³⁺ and Er³⁺ elements were not added with U value. The cut-off energy was set at 500 eV. A PBE + U method was used for calculation.

Fig. 7 depicts the differential charge density obtained after simulation optimization and calculation. It can be observed that, after Yb^{3+} and Er^{3+} doping, the electrons near Ce^{3+} ions in the original matrix are polarized and drawn to Yb^{3+} and Er^{3+} ions, which increases the charge density near the doped ions. Although the overall spatial structure does not change greatly, the deviation of electron density will exert a significant impact on the optical properties of the crystal.

Fig. 8 (a) shows the band structure of Yb^{3+} , Er^{3+} : CeF₃ crystal obtained by simulation. The horizontal coordinate shows a set path of the Brillouin zone $(G \rightarrow X \rightarrow H \rightarrow C \rightarrow H \rightarrow Y \rightarrow G)$, and a zero point corresponds to the Fermi level E_F. The calculated band gap value is about 3.91 eV. Compared with the band gap found from the absorption spectrum in Fig. 8 (b), the difference between them is about 0.2 eV. This may be due to the margin of error during experiments, or the differences between the spatial structures, doping ion concentrations and U values set in the simulation and experiment. Compared with the band structure of pure CeF3 material simulated by Hui Miao et al., it can be found that the doping of rare earth ions Yb^{3+} and Er^{3+} did not change the indirect transition properties of the crystal [20]. In particular, the valence band of CeF₃ is also located below the Fermi level, so the f-f and p-f matrix elements of the imaginary part of the dielectric function caused by the interband transition have large values, so Yb³⁺, Er³⁺: CeF₃ crystal has high photoluminescence activity [21]. In addition, Yb^{3+} ion doping creates multiple new energy levels between 0 and 4 eV, which effectively improves the transition probability of electrons from the valence band to the conduction band, reduces the energy loss, and improves the photon energy absorption efficiency [22]. Moreover, doping makes the conduction band in the range of 6–8 eV more unstable and the coupling degree decreases, which is beneficial to improve the active state of the



Fig. 9. Total state density of Yb^{3+} , Er^{3+} : CeF_3 crystal, the contributions of 4f and 5d electronic states from Yb^{3+} and Er^{3+} and Ce^{3+} ions.

luminescence process and enhance the energy transfer.

In order to further study the contribution of cations in the Yb³⁺, Er³⁺: CeF₃ crystal to the optical properties, the total state density of the crystal was calculated, as shown in Fig. 9. It can be seen that, compared with Yb³⁺ and Er³⁺ ions, the contributions of 4f and 5d electronic states from Ce³⁺ ions are significant, which indicates that the role of Ce³⁺ ions cannot be ignored in the luminescence process.

In order to see the contribution degree and spatial position of each electronic state more directly, the densities of states of different cations were decomposed. As shown in Fig. 10, the 4f and 5d electronic states of Ce^{3+} ions are distributed on both sides of the Fermi level [23]. The 5d and 6s states of Er^{3+} ions and 6s and 5d states of Yb^{3+} ions are more concentrated and coupled, indicating that there are more energy transfer processes between the two ions [24]. Moreover, the electrons from the 4f states of Er^{3+} and Yb^{3+} ions are delocalized and may exist in the higher conduction band [25], having more optical emission wavelengths and thereby offering more options in near-infrared optical applications.

3.6. Near-infrared spectroscopy analysis

Fig. 11 displays the NIR emission spectra of Yb^{3+} , Er^{3+} : CeF₃ crystal at an excitation wavelength of 980 nm. It can be seen that the wide



Fig. 10. Density of states in Yb³⁺, Er³⁺: CeF₃ crystal: two-direction projections of (a)–(b) Ce³⁺; (c)–(d) Er³⁺; (e)–(f) Yb³⁺ ions.



Fig. 11. NIR emission spectra of Yb³⁺, Er³⁺: CeF₃ crystal.

emission band is centered at 1550 nm, resulting from the emission process of the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition in Er^{3+} ions [26,27]. As the Yb³⁺ doping concentration increases, the emission intensity rises, indicating that Yb³⁺ ions can effectively transfer energy to Er^{3+} ions and improve their luminescence intensity. At the Yb³⁺ doping concentration of 3 at. %, the luminescence intensity reaches its maximum and then decreases with a further increase in dopant content, which is due to the so-called concentration quenching.

In order to further explore the luminescence mechanism of Yb³⁺, Er³⁺: CeF₃ crystals, their up-conversion spectra were excited by a 980 nm LD, and the strong green emission and weak red emission responses are given in Fig. 12. The green emission region is mainly formed by the superposition of two main emission bands at 525 and 545 nm, which are derived from the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transitions in Er³⁺ ions [28–30]. The rather weak red emission near 652 nm is due to the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition in the Er³⁺ ion [31–34].

The luminescence mechanism of Yb^{3+} , Er^{3+} : CeF₃ crystal can be well



Fig. 12. Up-conversion luminescence spectra of Yb^{3+} , Er^{3+} : CeF_3 crystal.

analyzed by combining the 980 nm NIR and up-conversion luminescence spectra. Fig. 13 displays a schematic diagram of energy level transitions between Yb³⁺, Er³⁺ and Ce³⁺ ions in the crystal according to the luminescence process. In general, Ce³⁺ ions can inhibit and quench up-conversion luminescence to some extent, leading to the decrease in up-conversion intensity of Yb^{3+} , Er^{3+} or Yb^{3+} , Ho^{3+} co-doped materials, but improve the energy enhancement at the ${}^{4}I_{13/2}$ energy level and the luminescence intensity at 1550 nm [35,36]. For a CeF₃ crystal matrix, the maximum phonon energy (\hbar_{ω}) is about 391 cm⁻¹, and the energy difference between the ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ transition of Er^{3+} ion ($\Delta E_{Er} \approx 3656$ cm⁻¹) and the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition of Ce^{3+} ion ($\Delta E_{Ce} \approx 2170$ cm⁻¹) is $\Delta E \approx 1486 \text{ cm}^{-1}$ [37]. Assume that the phonons involved in the energy transfer have the equal energy. When the number of phonons involved is small, there is an effective cross relaxation between the two energy levels. As a result, the probability of non-radiative ${}^{4}I_{11/2}$ - ${}^{4}I_{13/2}$ transition increases, and the concentration of resident electrons at the ${}^{4}I_{13/2}$ energy level increases significantly [38]. In addition, a large amount of energy absorbed by the Yb^{3+} ions is also transferred to the ${}^{4}I_{11/2}$ energy level of Er^{3+} ions and back to the ${}^{4}\mathrm{I}_{13/2}$ energy level through a non-radiative



Fig. 13. Energy level transitions and energy transfer between Yb^{3+} , Er^{3+} and Ce^{3+} ions in Yb^{3+} , Er^{3+} : CeF_3 crystal.



Fig. 14. Near-infrared luminescence decay curve of $\rm CeF_3$ crystal co-doped with $\rm Yb^{3+}$ and $\rm Er^{3+}$ ions.

relaxation process. Besides, the energy of 980 nm excitation light absorbed by the Yb³⁺ ion is much higher than the energy consumed to increase the electron population at the ${}^{4}I_{13/2}$ level of the Ce³⁺ ion [39]. Therefore, when Yb³⁺ and Er³⁺ ions are both embedded in the CeF₃ crystal, the energy transfer process will be mainly from Yb³⁺ to Er³⁺ ions, being much efficient than that between Er³⁺-Ce³⁺ and Er³⁺-Er³⁺. As a result, the emission intensity at 1550 nm will be further increased [40].

3.7. Luminescence decay curve analysis

Fig. 14 depicts the experimental attenuation curve associated with a near-infrared luminescence process of the Yb³⁺ and Er³⁺ co-doped CeF₃ crystal. The excitation wavelength is 980 nm (⁴I_{13/2} energy level) and the emission wavelength is 1550 nm (⁴I_{15/2} energy level). A three-index exponential function is used for fitting this curve:

$$y = A_1 \times exp\left(\frac{-x}{t_1}\right) + A_2 \times exp\left(\frac{-x}{t_2}\right) + A_3 \times exp\left(\frac{-x}{t_3}\right) + y_0$$
(2)

This allows one to achieve the highest data fitting degree (99.998%). Then, the fitting parameters $A_{1,2,3}$ and $t_{1,2,3}$ are substituted into the formula for calculating the luminescence decay curve as follows:

Table 2

1

Luminescence decay curve of CeF_3 crystals doped with Yb^{3+} and Er^{3+} ions.

Yb ³⁺ doping concentration (at.%)	Luminescence decay curve(ms)	Corresponding energy level
1 2 3 4 5	0.1034 0.1186 0.1146 0.1332 0.1396	${}^4\!I_{13/2} \to {}^4\!I_{15/2}$

$$r = \frac{A_1 t_1^2 + A_2 t_2^2 + A_3 t_3^2}{A_1 t_1 + A_2 t_2 + A_3 t_3}$$
(3)

The luminescence decay parameters of Yb^{3+} , Er^{3+} : CeF_3 crystals are shown in Table 2.

According to the luminescence decay curve, with the increase of Yb³⁺ ion doping concentration, the fluorescence lifetime in the range of 980–1550 nm gradually increases, which is attributed to the larger absorption cross-section of Yb³⁺ ions at 980 nm, as compared to that of Er^{3+} ions. Therefore, when excited at 980 nm, Yb³⁺ ions absorb more photon energy at 980 nm, resulting in the higher energy distribution at the ⁴I_{13/2} energy level of Er^{3+} ions. Therefore, in the process of radiation relaxation, it shows a longer decay time, and this trend of increasing fluorescence life is beneficial to the application in lasers and other related fields. It is also noteworthy that Er^{3+} ions have a certain self-absorption effect, which affects the near-infrared emission at 1550 nm [7,8,13]. Thus, the experimentally measured lifetime of Er^{3+} -doped crystals may differ from the calculated one due to the error caused by self-absorption.

3.8. Energy transfer and quenching mechanism

Generally, it is believed that the non-radiative relaxation process between energy levels is mainly caused by one of three effects: exchange interaction, radiation reabsorption, and multi-level interaction. These are mainly related to the critical distance between ions, which will lead to different interaction mechanisms. Therefore, the critical distance between Yb³⁺ and Er³⁺ ions in the crystal can be calculated according to the formula below:

$$R_c \approx 2 \left[\frac{3V}{4\pi X_c Z} \right]^{\frac{1}{3}} \tag{4}$$

where v is the unit cell volume of CeF₃ crystal and X_c is the sum of the concentrations of Yb³⁺ and Er³⁺ ions (the critical concentration), respectively. Z is the number of cations in the lattice center. Given the standard card of CeF₃ crystal (JCPDS 08–0045), the V, X_c and Z parameters of CeF₃ are 318.9, 0.06 and 6, respectively. Thus, the critical distance R_c is about 11.9176.

When the critical distance between ions exceeds 5, there is no forbidden band transition mechanism between them. It is generally believed that the concentration quenching in this case comes from the electric interaction mechanism in the multi-level interaction. The electrical interaction between ions can be further refined into three kinds of interactions, namely dipole-dipole interaction, dipole-quadrupole interaction and quadrupole-quadrupole interaction [5]. These specific interactions can be calculated and distinguished as follows:

$$\frac{I}{X} = Kx \left(x \right) \left(x \right) \left(x \right)^{\frac{d}{2}} \right]^{-1}$$
(5)

formula (5) can be further simplified as follows:

$$\log\left(\frac{I}{x}\right) = A - \frac{\theta}{3}\log x \tag{6}$$

where I is the emission intensity, X represents the doping concentration



Fig. 15. Logarithmic ratio and fitting curve of emission intensity and concentration of CeF_3 crystal doped with Yb^{3+} and Er^{3+} ions.



Fig. 16. Schematic diagram of concentration quenching of ${\rm CeF_3}$ crystal doped with ${\rm Yb^{3+}}$ and ${\rm Er^{3+}}$ ions.

of sensitizer Yb³⁺, and K and β are the constant parameters under the same excitation conditions. When the calculated θ values are close to 6, 8 and 10, the corresponding interaction types are dipole-dipole interaction, dipole-quadrupole interaction and quadrupole-quadrupole interaction [30].

Fig. 15 depicts the logarithmic ratio of a crystal emission intensity to the doping concentration in the case of the near-infrared emission at 1550 nm under 980 nm excitation. The slope, namely $-\theta/3$ value, can be obtained by linear fitting, which is -0.91755, Therefore, the θ value is hence about -2.7527, the θ value is close to 6. So it can be considered that the electric interaction between Er^{3+} ions in the CeF₃ crystal matrix is dipole-dipole interaction. Fig. 16 displays a schematic diagram of concentration quenching of Yb³⁺, Er³⁺ ion-doped CeF₃ crystal, which can clearly show the influence of concentration quenching on the ions in the crystal lattice.

3.9. J-O parameter calculation

The J-O theory provides a standard research method for the optical transition properties of trivalent rare earth ion-doped luminescent materials [41]. By using the J-O intensity parameter Ω_t (t = 2, 4, and 6), some important dynamic parameters such as radiative transition rate, optical alkalinity, or degree of structural symmetry can be obtained. First, the experimental and theoretical spectral line intensities of the ground state (LJ) level to transition (L'J') of the 4fⁿ electronic

Table 3 Ω_t (t = 2, 4 and 6) values of Yb³⁺, Er³⁺: CeF₃ crystals.

Doping concentration	Ω_2	Ω_4	Ω_6	Error δ ($ imes$ 10 ⁻⁶)
1 at. %Yb ³⁺	0.08	0.51	0.73	0.67
2 at. %Yb ³⁺	0.06	0.42	0.31	0.41
3 at. %Yb ³⁺	0.18	0.13	0.27	0.2
4 at. %Yb ³⁺	0.01	0.23	0.25	0.3
5 at. %Yb ³⁺	0.05	0.13	0.25	0.2



Fig. 17. Absorption cross-section of Yb^{3+} , Er^{3+} : CeF₃ crystal.

configuration in rare earth ions are defined as:

$$S_{exp}(J \to J') = \frac{3hc(2J+1)}{8\pi^3 e^2} \frac{9n}{(n^2+2)^2 \lambda} \frac{1}{0.43N_0 l} \int OD(\lambda) d\lambda$$
(7)

$$f_{cal} = f_{ed} + f_{md} = \frac{8\pi^2 mcv}{3he^2(2J+1)} \left(\frac{\left(n^2 + 2\right)^2}{9n} S_{ed} + nS_{md} \right)$$
(8)

where h is Planck's constant, J is the total angular momentum of the ground state, e is the electron charge, m is the electron mass, c is the speed of light, and n is the refractive index of the crystal. The transition process is usually the electric dipole transition, where the magnetic dipole transition is several orders of magnitude less than that of the electric dipole and can therefore be neglected. The required J-O parameters can be calculated according to the following formula:

$$f_{ed}(J \to J') = \sum_{t=2,4,6} \Omega_t \left| 4f^n[S, L] J U^{(t)} 4f^n[S', L'] J' \right|^2 \tag{9}$$

A system of linear equations should be then solved to obtain the value of Ω_t (t = 2, 4, 6), and the error between the experimental and theoretical values must be determined to ensure the accuracy of the calculation. The calculation results are shown in Table 3.

The intensity parameter can be used as a reference to characterize structural properties [42], where Ω_2 is usually related to the coordination symmetry and covalency of the lattice field in the crystal. In general, crystals with larger Ω_2 indicate greater covalency. For the Yb³⁺, Er³⁺: CeF₃ crystal, it is clear from the calculations that it is a typical ionic crystal with extremely weak covalency. In addition to Ω_2 , Ω_4 and Ω_6 also showed an overall decreasing trend with the increase of doping concentration. This indicates that the higher the doping concentration, the lower the anionic stability and the higher the active state.



Fig. 18. Emission cross-section of Yb^{3+} , Er^{3+} doped CeF_3 crystal.

3.10. Absorption cross-section, emission cross-section, and gain coefficient

The absorption cross-section (σ_{abs}) can be calculated using the Beer-Lambert formula as follows:

$$\sigma_{abs} = \frac{2.303 \lg(I_0/I)}{NI}$$
(10)

where $lg(I_0/I)$ represents the absorption intensity, N is the concentration of doped rare earth ions, and I is the thickness of the crystal. Fig. 17 shows the calculated absorption cross-section of the Yb³⁺, Er³⁺: CeF₃ crystal.

The Füchtbauer-Ladenburg (FL) formula is usually used to calculate the emission cross-section of crystalline materials as follows:

$$\sigma_{emi} = \frac{\lambda^4 A_{rad}}{8cn^2} \times \frac{\lambda I(\lambda)}{\int \lambda I(\lambda) d\lambda}$$
(11)

where λ represents the wavelength, n is the refractive index, c is the speed of light, $I(\lambda)$ is the spectral intensity of luminescence at a wavelength λ , and Arad is the spontaneous emission transition probability. Fig. 18 depicts the calculated emission cross-section of Yb^{3+}, Er^{3+}: CeF_3 crystal.

According to the absorption cross-section and emission cross-section, the gain cross-section and gain coefficient of the crystal can be further calculated. Both are used to characterize the threshold condition for realizing the population inversion between energy levels in the crystal material. formula (12)and (13) as follows:

$$P = \frac{N_{ex}}{N} \tag{12}$$

$$\sigma_{\mathcal{G}(\lambda)} = N[P\sigma_{emi}(\lambda) - (1 - P)\sigma_{emi}(\lambda)]$$
(13)

P is the inversion ratio of the excited state particles, N is the concentration of ions, N_{ex} is the volumetric density of excited ions. formula (13) is equivalent to the net gain value between the emission cross-section and the absorption cross-section, where N is the concentration of doping ions. In order to better analyze and characterize the gain of near-infrared 1550 nm emission of crystals doped with different Yb³⁺ ion concentrations, the corresponding gain cross-sections, calculated for the samples(different P values (0, 0.2, 0.4, 0.6, 0.8, 1)) under consideration, are given in Fig. 19(a)–(e).

On this basis, the corresponding point at 1550 nm is linearly fitted. Fig. 20 displays the fitting values of gain coefficients for different doping concentrations. It can be seen that as the doping concentration increases, the P value corresponding to the 0 point tends to decrease, from 80.80% to 69.11%, which also shows that the increase of doping ions increases the probability of population inversion and reduces the threshold condition. Therefore, increasing the doping concentration of the crystal is beneficial to obtain laser output under low power conditions.



Fig. 19. Gain cross-sections of crystals with different doping concentrations.



Fig. 20. Gain coefficients at 1550 nm at different doping concentrations.

4. Conclusions

The Yb³⁺, Er^{3+} : CeF₃ crystals were successfully grown by a crucible descending method. The lattice structure, phonon vibrational energy and density of the grown crystals were studied via X-ray diffraction, Raman spectroscopy and density measurement. The physical and chemical parameters of crystals were characterized and analyzed as well. The results showed that co-doping with Yb^{3+} and Er^{3+} ions did not significantly alter the crystal structure. Raman spectroscopy revealed that the crystals had a maximum leptonic vibrational frequency of about 391 cm⁻¹, being only a half that of the oxide crystal, which contributed to the radiative transition probability. Under 980 nm excitation, the Yb^{3+} ions effectively enhanced the luminescence intensity at 1.55 μ m. The highest luminescence intensity was achieved at the Yb³⁺ ion concentration of 3 at. The energy transfer process and concentration quenching mechanism between the $^2F_{7/2} \rightarrow {}^{\bar{2}}F_{5/2}$ transition in Yb^{3+} ions and the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition in Er³⁺ ions were investigated in detail by combining the up-conversion spectra, the absorption spectra, the fluorescence decay curves, and the factors affecting the fluorescence decay time. Besides, the structural parameters, absorption crosssections, emission cross-sections, gain cross-sections and gain coefficients of the crystals were calculated and analyzed. The band gap structure, density of states and charge distribution were also obtained via first-principles simulation to explore the effect of electronic structure on the luminescent properties of Yb^{3+} , Er^{3+} : CeF_3 crystals. The findings of this study reveal that Yb³⁺, Er³⁺: CeF₃ crystals have great potential in the near-infrared fields of application such as laser and near-infrared systems.

Author contribution

Weiling Yang: Conceptualization, Data curation, Formal analysis, Writing – original draft, Later revision, English translation, theoretical calculation. Crystal growth experiment. Zhuang Leng: Investigation, Supplementary experimental data, data test. Crystal growth experiment. Xiliang Jiang: Supplementary experimental data, data test. Literature search, data collection. Crystal growth experiment. Ce Li: Investigation, Methodology. Literature search, data collection. Huisheng Liu: Supplementary experimental data, data test. Zhiming Shi: Structural model optimization, first-principles simulation, Data processing, Theoretical analysis. Keke Huang: Project funding, theoretical guidance. Fanming Zeng: Conceptualization, Supervision, Funding acquisition, Resources, Supervision, Manuscript revision, theoretical guidance. Chun Li: Conceptualization, Supervision, Funding acquisition, Resources, Supervision, test guide. Hai Lin: Investigation, Methodology. Zhongming Su: Conceptualization, Supervision, Funding acquisition, Resources, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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