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Evaluation of spectroscopic properties of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal for use in mid-infrared lasers

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Houping Xia^{1,2}, Jianghe Feng³, Yan Wang¹, Jianfu Li¹, Zhitai Jia⁴ & Chaoyang Tu¹

$\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal was firstly grown by Czochralski method. Detailed spectroscopic analyses of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ were carried out. Besides better absorption characteristic, the spectra of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ show weaker up-conversion and near-infrared emissions as well as superior mid-infrared emission in comparison to Er^{3+} : $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals. Furthermore, the self-termination effect for Er^{3+} 2.7 μm laser is suppressed successfully because the fluorescence lifetime of the $^4\text{I}_{13/2}$ lower level of Er^{3+} decreases markedly while that of the upper $^4\text{I}_{11/2}$ level changes slightly in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal. The sensitization effect of Yb^{3+} and deactivation effect of Pr^{3+} ions as well as the energy transfer mechanism in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal were also studied in this work. The introduction of Yb^{3+} and Pr^{3+} is favorable for achieving an enhanced 2.7 μm emission in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal which can act as a promising candidate for mid-infrared lasers.

In recent years, novel mid-infrared lasers with outputs in the range of 2.7–3 μm have received extensive attention owing to enormous potential applications in medicine, sensing, light detection, *etc.*^{1–3} Er^{3+} can act as active ions achieving 2.7–3 μm lasers through its $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ transition, which has been extensively investigated. However, a detrimental self-termination bottleneck effect is possible for this transition, because of the shorter lifetime of upper laser level ($^4\text{I}_{11/2}$) than that of the lower one ($^4\text{I}_{13/2}$). Previous researches have shown that increasing Er^{3+} concentration or co-doping with proper sensitive ions (such as Pr^{3+} , Ho^{3+} , Tm^{3+} , *etc.*) can inhibit the self-termination bottleneck^{4–10}. However, high doping concentration of Er^{3+} may lead to poor quality of crystal. So co-doping with proper sensitive ions is a better choice. Additionally, Yb^{3+} can also be introduced into Er^{3+} -doped materials to improve absorption properties because of effective energy transfer between Yb^{3+} and Er^{3+} ^{11–14}. Predictably, Er^{3+} , Re^{3+} ($\text{Re}^{3+} = \text{Pr}^{3+}$, Ho^{3+} , Tm^{3+} , *etc.*) and Yb^{3+} triply doped crystals without heavily doping of Er^{3+} might demonstrate excellent mid-infrared lasers performance. For example, Chen *et al.* developed a novel mid-infrared crystal $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Ho}^{3+}$: GYSGG¹⁵ in which Yb^{3+} can broaden the absorption band as well as shift the pumping peak to the optimum position, meanwhile, Ho^{3+} ions can nearly retain the lifetime of $^4\text{I}_{11/2}$ level and decrease that of $^4\text{I}_{13/2}$ level intensely. Therefore, Er^{3+} , Yb^{3+} and Re^{3+} ($\text{Re}^{3+} = \text{Pr}^{3+}$, Ho^{3+} , Tm^{3+} , *etc.*) triply doped crystals are worth studying as mid-infrared lasers candidates.

Among the various matrix materials of mid-infrared solid-state lasers, fluoride, aluminate and gallate crystals are excellent for their low phonon energy, high thermal stability, stable chemical durability and

¹Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 350002, PR China. ²University of Chinese Academy of Sciences, Beijing 100039, PR China. ³State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China. ⁴State Key Laboratory of Crystal Materials, Shandong University, Ji'nan 250100, PR China. Correspondence and requests for materials should be addressed to C.T. (email: tcy@fjirm.ac.cn) or Z.J. (email: jiazhitm@icm.sdu.edu.cn)

Figure 1. The view of anionic layer Ga₂O (a), 3D network (b) and the Raman spectrum of SrGdGa₃O₇ (c).

so on^{4,5,16,17}. The spectroscopic properties and laser operations of Er³⁺ doped CaF₂, LiYF₄, Y₃Al₅O₁₂, CaYAlO₄, CaGdAlO₄, YSGG, GSGG and GGG crystals have been reported^{4,5,17–21}. In this work, SrGdGa₃O₇ single crystal was chosen as the host matrix because it has lower melting point (about 1600 °C)²² as compared with the above aluminate and gallate crystals, and, large-sized crystals with high optical quality can be obtained more easily by using Czochralski technique.

SrGdGa₃O₇ single crystal belongs to the large family ABGa₃O₇ (A = Ca, Sr, Ba; B = Gd, La)²². It crystallizes in $P\bar{4}2_1m$ space group and features a layered structure (Fig. 1(a,b)). The Ga³⁺ ions exhibit two kinds of slight distorted tetrahedral environments hereafter referred to as Ga₁ and Ga₂. Ga₁O₄ and Ga₂O₄ tetrahedra are alternately interconnected via corner-sharing to form anionic layer of [Ga₃O₇]^{5−} in *ab*-plane. Between the layers, the Sr²⁺ and Gd³⁺ cations are distributed randomly in the ratio of 1:1, which results in certain structural disorder. Therefore, the absorption and emission lines of Er³⁺ ions would be inhomogeneously broadened in Er³⁺ ions doped SrGdGa₃O₇ crystal. The broadening of absorption band is favorable for diode pumping and the broadening of emission band is very beneficial for tunable or ultra fast laser output. In addition, the Raman spectrum in Fig. 1(c) shows that SrGdGa₃O₇ single crystal has relative low phonon energy (~680 nm^{−1}), which is similar to its isostructural SrLaGa₃O₇ crystal²³. The low phonon energy conduces to the decrease of the multiphonon relaxation rate for Er³⁺: ⁴I_{11/2} → ⁴I_{13/2} transition, and therefore decreasing the populations on ⁴I_{13/2} state^{12,24,25}.

This work aims to study the spectroscopic performance with focus on 2.7 μm emissions and the roles of Yb³⁺ and Pr³⁺ in Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystal. To the best of our knowledge, Yb³⁺, Er³⁺ and Pr³⁺ triply doped single crystal was firstly investigated.

Materials and Methods

Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ single crystal was successfully grown by Czochralski method. The initial concentrations of Er³⁺, Yb³⁺ and Pr³⁺ were 15 at.%, 5 at.% and 0.15 at.%, respectively. 15 at.% Er³⁺/5 at.% Yb³⁺: SrGdGa₃O₇, 15 at.% Er³⁺: SrGdGa₃O₇ and 5 at.% Yb³⁺: SrGdGa₃O₇ single crystals were also grown for comparison. The used chemicals were SrCO₃ (A.R. grade) and Gd₂O₃, Er₂O₃, Yb₂O₃, Pr₂O₃, Ga₂O₃ (4N purity). In order to compensate the evaporation losses of Ga₂O₃ in the growing process, excess 1.0 wt.% Ga₂O₃ was added to the starting materials. The crystal growth was carried out in a DJL-400 furnace with N₂ atmosphere protection, and an Ir crucible with the diameter of 50 mm and the height of 30 mm was used. A <001> orientated SrGdGa₃O₇ seed crystal was used. The pulling rate varied from 1 to 1.5 mm/h and the crystal rotation speed was kept at 8–15 r/m. Finally, the crystal was cooled to room temperature at a rate of 10–25 K/h.

The concentrations of Er³⁺, Yb³⁺ or Pr³⁺ ions in every crystal were measured by using an inductively coupled plasma atomic emission spectrometry (ICP-AES, Ultima2, Jobin-Yvon). The absorption spectra were measured using a Perkin-Elmer UV-VIS-NIR Spectrometer (Lambda-900). The emission spectra and fluorescence lifetime were measured using an Edinburgh Instruments Fluorescence Spectrometer. Samples with dimensions of 10.0 × 10.0 × 0.9 mm³ were optically polished for spectral measurement. The experimental conditions were maintained exactly same for measurement of each group of spectra in order to get the comparable results.

Results and Discussion

Ions concentrations. The concentrations of Er³⁺, Yb³⁺ and Pr³⁺ ions in Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystal are measured to be 5.06×10^{20} ions·cm^{−3}, 1.08×10^{20} ions·cm^{−3} and 0.36×10^{20} ions·cm^{−3}, respectively. The concentrations of Er³⁺ and Yb³⁺ ions in Er³⁺/Yb³⁺: SrGdGa₃O₇ crystal are 4.83×10^{20} ions·cm^{−3} and 1.04×10^{20} ions·cm^{−3}, respectively. While the Er³⁺ concentration in Er³⁺: SrGdGa₃O₇ crystal is 4.86×10^{20} ions·cm^{−3} and Yb³⁺ concentration in Yb³⁺: SrGdGa₃O₇ crystal is 1.12×10^{20} ions·cm^{−3}.

Figure 2. Absorption spectra of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals at room temperature.

Figure 3. Up-conversion emission spectra of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals under excitation of 980 nm.

Absorption spectra. Room temperature absorption spectra of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals are shown in Fig. 2. For Er^{3+} : $\text{SrGdGa}_3\text{O}_7$ crystal, the absorption spectrum consists of six main absorption bands centered at 487, 522, 651, 802, 980 and 1536 nm, which correspond to the transitions from $^4I_{15/2}$ to $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$, respectively. Among them the wide absorption band centered at 980 nm with a full width at half maximum (FWHM) of 31 nm matches the commercial 980 nm InGaAs laser diodes (980 nm LDs) very well. The absorption cross-section at 980 nm is calculated to be $2.1 \times 10^{-21} \text{ cm}^2$. As compared with the absorption spectrum of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$ crystal, there is almost no change in the intensity and location of the characteristic absorption bands of Er^{3+} ions in $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal. But, there is a much stronger absorption band in the range of 936 to 1015 nm with a FWHM of 40 nm, which is involved both the contributions from Yb^{3+} and Er^{3+} ions, owing to the transition from $^2F_{7/2}$ to $^2F_{5/2}$ of Yb^{3+} ions and the transition from $^4I_{15/2}$ to $^4I_{11/2}$ of Er^{3+} ions (Inset of Fig. 2). Its absorption peak is also located at 980 nm and the absorption cross-section is calculated to be $3.6 \times 10^{-21} \text{ cm}^2$. Thus, the introduction of Yb^{3+} ions not only enhanced absorption intensity but also widened the absorption band, which makes $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal more suitable for 980 nm LDs pumping. Furthermore, as seen in the absorption spectrum of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal in the inset of Fig. 2, the absorption band centered at 980 nm is very similar to that in $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal owing to the existence of Yb^{3+} ions in both crystals. For Pr^{3+} ions, a weak characteristic absorption band corresponding to the transition from 3H_4 to 3F_2 of Pr^{3+} ions is observed.

Emission spectra. The up-conversion emission spectra within 500–725 nm of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals are measured under excitation of 980 nm, as shown in Fig. 3. In the spectra of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$ crystal, the observable green and red up-conversion emission bands which centered at 550 and 677 nm are assigned to Er^{3+} : ($^2H_{11/2}$, $^4S_{3/2}$) $\rightarrow$ $^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions, respectively. Compared with Er^{3+} : $\text{SrGdGa}_3\text{O}_7$ crystal, the up-conversion

Figure 4. Near-infrared emission spectra of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals.

Figure 5. Mid-infrared emission spectra of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals.

emission spectrum of $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal shows tiny changes in intensity while that of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal exhibits much weaker intensity.

The near-infrared emission spectra of three crystals within the range of 1425–1650 nm excited by 980 nm are shown in Fig. 4. For $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal, the intensity of the 1553 nm emission corresponding to Er^{3+} : $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ is stronger than that of Er^{3+} single-doped $\text{SrGdGa}_3\text{O}_7$. Generally, the strong near-infrared emission is a hindering factor for 2.7 μm laser output, thus the sole introduction of Yb^{3+} into Er^{3+} : $\text{SrGdGa}_3\text{O}_7$ crystal is not beneficial to the realization of 2.7 μm lasers. However, the addition of Pr^{3+} can significantly inhibit the harmful near-infrared emission as shown in the spectra of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal.

Figure 5 displays the mid-infrared emission spectra in the range of 2500–3100 nm excited by an optical parametric oscillator (OPO) laser at 980 nm. The broad mid-infrared emission band centered at 2718 nm can be assigned to the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ transition of Er^{3+} . There is almost no difference in the emission spectrum shape and peak position of the three crystals. However, it is obvious that the strongest 2.7 μm emission existed in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal. The intensity is about 5 times of that in Er^{3+} : $\text{SrGdGa}_3\text{O}_7$ crystal. The enhanced mid-infrared emission is also obtained in $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal. As an important parameter affecting the potential 2.7 μm laser performance, the stimulated emission cross-section, can be calculated by the following equation^{5,26}:

$$\sigma_e(\lambda) = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{\text{eff}} \tau_m} \quad (1)$$

where λ_p is the emission peak wavelength, c is the velocity of light, n is the refractive index which can be obtained in²⁷, λ_{eff} is the effective line width of the emission band^{11,26} and τ_m is the measured lifetime. The obtained emission cross-sections of Er^{3+} : $\text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystals are all listed in Table 1.

Crystals	σ_a at 980nm (10^{-21} cm ²)	$^4I_{11/2}$, σ_e (10^{-19} cm ²)	Er ³⁺ : $^4I_{13/2}$		Er ³⁺ : $^4I_{11/2}$		Yb ³⁺ : $^2F_{5/2}$
			τ_f (ms)	η_t (ET ₃)	τ_f (ms)	η_t (ET ₂)	
Er ³⁺ : SrGdGa ₃ O ₇	2.1	1.64	10.81		0.62		
Er ³⁺ /Yb ³⁺ : SrGdGa ₃ O ₇	3.5	1.75	10.58		0.63		0.47
Er ³⁺ /Yb ³⁺ /Pr ³⁺ : SrGdGa ₃ O ₇	3.6	2.57	1.02	90.6%	0.44	29.0%	0.38

Table 1. Spectroscopic data for Er³⁺: SrGdGa₃O₇, Er³⁺/Yb³⁺: SrGdGa₃O₇ and Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ laser crystals.

Figure 6. Decay curves of Er³⁺: $^4I_{11/2}$ level in Er³⁺: SrGdGa₃O₇, Er³⁺/Yb³⁺: SrGdGa₃O₇ and Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystals.

Figure 7. Decay curves of Er³⁺: $^4I_{13/2}$ level in Er³⁺: SrGdGa₃O₇, Er³⁺/Yb³⁺: SrGdGa₃O₇ and Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystals.

Fluorescence lifetimes. The decay curves of Er³⁺: $^4I_{11/2}$ and $^4I_{13/2}$ levels in Er³⁺: SrGdGa₃O₇, Er³⁺/Yb³⁺: SrGdGa₃O₇ and Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystals are shown in Fig. 6 and 7, respectively. For Er³⁺: SrGdGa₃O₇ crystal, the decay curves both show single exponential decaying behavior and the fluorescence lifetimes can be fitted with

$$I(t) = A + B \exp(t/\tau). \quad (2)$$

However, the decay curves of $^4I_{11/2}$ and $^4I_{13/2}$ levels of Er³⁺ in Er³⁺/Yb³⁺: SrGdGa₃O₇ and Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystals show multi-exponential behavior, which can be obtained by fitting with

$$I(t) = A + B_1 \exp(t/\tau_1) + B_2 \exp(t/\tau_2) + \dots + B_n \exp(t/\tau_n). \quad (3)$$

Then, the fluorescence lifetimes are calculated by

Figure 8. Decay curves of $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ level in $\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystals.

$$\tau = \frac{B_1\tau_1^2 + B_2\tau_2^2 + \dots + B_n\tau_n^2}{B_1\tau_1 + B_2\tau_2 + \dots + B_n\tau_n} \quad (4)$$

The fluorescence lifetimes are listed in Table 1, too. When compared with $\text{Er}^{3+}: \text{SrGdGa}_3\text{O}_7$, the fluorescence lifetimes of ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$ levels of Er^{3+} only change slightly in $\text{Er}^{3+}/\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal. However, the fluorescence lifetimes of ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$ levels of Er^{3+} both decrease in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal, which is mainly due to energy transfer via $\text{Er}^{3+}: {}^4\text{I}_{11/2} \rightarrow \text{Pr}^{3+}: {}^1\text{G}_4$ and $\text{Er}^{3+}: {}^4\text{I}_{13/2} \rightarrow \text{Pr}^{3+}: {}^3\text{F}_4$. The declining degree of the lifetime of ${}^4\text{I}_{13/2}$ level is much larger than that of ${}^4\text{I}_{11/2}$ level. To be more specific, the lifetime of ${}^4\text{I}_{11/2}$ level is reduced to 1/1.4 while the lifetime of ${}^4\text{I}_{13/2}$ level is reduced to 1/10.6 as compared with that in $\text{Er}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal. Based on the fluorescence lifetimes, the energy transfer efficiency from Er^{3+} to Pr^{3+} in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal can be obtained from the following equation^{4,5,8}:

$$\eta_t = 1 - \tau_{\text{DA}}/\tau_{\text{A}} \quad (5)$$

where τ_{DA} is the lifetime of Er^{3+} in the existence of Pr^{3+} , and τ_{A} is the lifetime of Er^{3+} in the absence of Pr^{3+} . The calculated energy transfer efficiencies of $\text{Er}^{3+}: {}^4\text{I}_{11/2} \rightarrow \text{Pr}^{3+}: {}^1\text{G}_4$ and $\text{Er}^{3+}: {}^4\text{I}_{13/2} \rightarrow \text{Pr}^{3+}: {}^3\text{F}_4$ are about 29.0% and 90.6%, respectively. That means the lifetime of the $\text{Er}^{3+}: {}^4\text{I}_{13/2}$ level decreases much quicker than that of $\text{Er}^{3+}: {}^4\text{I}_{11/2}$ level in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal. Consequently, co-doping Pr^{3+} can significantly decrease the lifetime of the lower level ($\text{Er}^{3+}: {}^4\text{I}_{13/2}$) and almost has no effect on that of the upper level ($\text{Er}^{3+}: {}^4\text{I}_{11/2}$), which indicates the self-termination problem in the crystal can be greatly inhibited.

To explore the sensitization effect of Yb^{3+} in $\text{SrGdGa}_3\text{O}_7$ crystals, the decay curves of $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ energy levels in $\text{Er}^{3+}/\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$, $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ and $\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystals are measured and shown in Fig. 8. For $\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal, the decay curve is single exponential, while the decay curve of $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ in $\text{Er}^{3+}/\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal shows multi-exponential behavior. The fitted fluorescence lifetimes are also listed in Table 1. The energy transfer efficiency from Yb^{3+} ions to Er^{3+} ions can also be obtained from $\eta_t = 1 - \tau_{\text{DA}}/\tau_{\text{D}}$, where τ_{DA} is the lifetime of Yb^{3+} ions in $\text{Er}^{3+}/\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal, τ_{D} is the lifetime of Yb^{3+} ions in $\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal. The energy transfer efficiency is calculated to be 44.7%. For $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal, the decay curve of $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ also shows multi-exponential behavior and the fitted fluorescence lifetime is shorter than that in $\text{Er}^{3+}/\text{Yb}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal. The corresponding energy transfer efficiency is calculated to be 55.3%. This suggests that the energy transfer between Yb^{3+} and Pr^{3+} exists in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal. Nevertheless, this small proportion of energy shows no obvious negative effect on the $2.7 \mu\text{m}$ emission in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal, which is shown in above experimental results. In conclusion, Yb^{3+} is a practicable sensitizer to enhance the $2.7 \mu\text{m}$ emission in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal, that is, Yb^{3+} ions can effectively transfer pumping energy to Er^{3+} ions and thus enhance the absorption efficiency of Er^{3+} ions obviously. Furthermore, higher Yb^{3+} concentrations may result in an increase in energy transfer efficiency between Yb^{3+} and Er^{3+} because the efficiency of energy transfer between Yb^{3+} and other ions partly depends on Yb^{3+} ions' density¹¹.

Energy transfer diagram. Based on the analyses of measurements above, the possible energy transfer processes in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal can be interpreted by the energy transfer diagram in Fig. 9. When $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}: \text{SrGdGa}_3\text{O}_7$ crystal is pumped, populations on $\text{Yb}^{3+}: {}^2\text{F}_{7/2}$ level and populations on $\text{Er}^{3+}: {}^4\text{I}_{15/2}$ level are excited to $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ and $\text{Er}^{3+}: {}^4\text{I}_{11/2}$ levels by ground state absorption. Then

Figure 9. The energy transfer diagram among Yb^{3+} , Er^{3+} and Pr^{3+} ions in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Pr}^{3+}$: $\text{SrGdGa}_3\text{O}_7$ crystal.

an anticipated energy transfer progress $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow \text{Er}^{3+}: {}^4\text{I}_{11/2}$ (ET_1) takes place and increases the populations on $\text{Er}^{3+}: {}^4\text{I}_{11/2}$ level, which leads to an enhanced $2.7\text{ }\mu\text{m}$ emission. Although the enhanced $2.7\text{ }\mu\text{m}$ emission can increase the populations on $\text{Er}^{3+}: {}^4\text{I}_{13/2}$ level subsequently, the competitive near-infrared emission is still weakened because of the effective energy transfer $\text{Er}^{3+}: {}^4\text{I}_{13/2} \rightarrow \text{Pr}^{3+}: {}^3\text{F}_4$ (ET_3) which deactivates the population on the $\text{Er}^{3+}: {}^4\text{I}_{13/2}$ state effectively. Furthermore, with the decrease of populations on the $\text{Er}^{3+}: {}^4\text{I}_{11/2}$ state as a result of the enhanced $2.7\text{ }\mu\text{m}$ emission and the energy transfer progress $\text{Er}^{3+}: {}^4\text{I}_{11/2} \rightarrow \text{Pr}^{3+}: {}^1\text{G}_4$ (ET_2), the cross-relaxation ${}^4\text{I}_{11/2} + {}^4\text{I}_{11/2} \rightarrow {}^4\text{F}_{7/2} + {}^4\text{I}_{15/2}$ (CR) from the $\text{Er}^{3+}: {}^4\text{I}_{11/2}$ state decreases. Consequently, the red and green up-conversion emissions are decreased significantly. Further, the decrease of near-infrared and up-conversion emission is beneficial to the $2.7\text{ }\mu\text{m}$ emission conversely. So the enhanced $2.7\text{ }\mu\text{m}$ emission is a result of comprehensive effect of above progresses.

Conclusion

Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystal was grown successfully by Czochralski method, Er³⁺/Yb³⁺: SrGdGa₃O₇ and Er³⁺ and Yb³⁺ singly doped SrGdGa₃O₇ crystals were also grown for spectral comparison. The crystals were evaluated by absorption, up-conversion emission, near-infrared and mid-infrared emissions, and luminescence decay measurements. The relevant absorption and emission cross-sections as well as fluorescence lifetimes were calculated and compared. Studies showed that Yb³⁺ ions acted as a sensitizer for Er³⁺ due to the energy transfer via Yb³⁺: ²F_{5/2} → Er³⁺: ⁴I_{11/2} in Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystal, which increased the absorption cross-section with peak at 980 nm. At the same time, due to the existence of Pr³⁺, two energy transfer routes Er³⁺: ⁴I_{11/2} → Pr³⁺: ¹G₄ and Er³⁺: ⁴I_{13/2} → Pr³⁺: ³F₄ occurred and the corresponding energy transfer efficiencies were determined to be 29.0% and 90.6%, respectively. As a result, strongest mid-infrared emissions as well as weakest up-conversion and near-infrared emissions were shown in Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ as compared with Er³⁺: SrGdGa₃O₇ and Er³⁺/Yb³⁺: SrGdGa₃O₇ crystals. Furthermore, the fluorescence lifetimes of Er³⁺: ⁴I_{11/2} and ⁴I_{13/2} levels both decreased in Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystal. But the decrease extent of the lifetime of lower level ⁴I_{13/2} is much larger than that of upper level ⁴I_{11/2}. The lifetime of the ⁴I_{13/2} state decreases from 10.81 ms in Er³⁺: SrGdGa₃O₇ crystal to 1.02 ms in Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystal by 10 times. Obviously, the self-saturation for the Er³⁺ 2.7 μm laser is inhibited to a great degree. These results indicate that the doping of Yb³⁺ and Pr³⁺ is helpful to achieve an enhanced 2.7 μm emission and Er³⁺/Yb³⁺/Pr³⁺: SrGdGa₃O₇ crystal could be considered as an excellent candidate for mid-infrared lasers.

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Author Contributions

H.X., J.F. and J.L. contributed to the growth of crystals. Y.W. and Z.J. contributed to the data analysis and scientific discussion. H.X. conceived the experiments and wrote the manuscript. C.T. supervised the project and reviewed the manuscript. All authors assisted in manuscript preparation.

Additional Information

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