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Energy Transfer and Cross-Relaxation Induced Efficient 2.78 µm Emission in Er$^{3+}$/Tm$^{3+}$: PbF$_2$ mid-Infrared Laser Crystal

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Abstract: An efficient enhancement of 2.78 µm emission from the transition of Er$^{3+}$: $^4_{11/2} \rightarrow ^4_{13/2}$ by Tm$^{3+}$ introduction in the Er/Tm: PbF$_2$ crystal was grown by the Bridgman technique for the first time. The spectroscopic properties, energy transfer mechanism, and first-principles calculations of as-grown crystals were investigated in detail. The co-doped Tm$^{3+}$ ion can offer an appropriate sensitization and deactivation effect for Er$^{3+}$ ion at the same time in PbF$_2$ crystal under the pump of conventional 800 nm laser diodes (LDs). With the introduction of Tm$^{3+}$ ion into the Er$^{3+}$: PbF$_2$ crystal, the Er/Tm: PbF$_2$ crystal exhibited an enhancing 2.78 µm mid-infrared (MIR) emission. Furthermore, the cyclic energy transfer mechanism that contains several energy transfer processes and cross-relaxation processes was proposed, which would well achieve the population inversion between the Er$^{3+}$: $^4_{11/2}$ and Er$^{3+}$: $^4_{13/2}$ levels. First-principles calculations were performed to find that good performance originates from the uniform distribution of Er$^{3+}$ and Tm$^{3+}$ ions in PbF$_2$ crystal. This work will provide an avenue to design MIR laser materials with good performance.

Keywords: 2.78 µm mid-infrared emission; Er/Tm; PbF$_2$ laser crystal; energy transfer mechanism; first-principles calculation

1. Introduction

Over the past several decades, mid-infrared (MIR) solid-state lasers operating around 2.7–3 µm have received extensive attention for numerous applications in medicine surgery, communications, remote sensing, pollution monitoring, and military countermeasures, etc. [1–5]. Additionally, 2.7–3 µm lasers are suitable pump sources for longer wavelength mid-infrared or long-infrared (8–12 µm) laser applications utilizing the optical parametric oscillators [6,7].

Up to now, many kinds of rare-earth ions in favorable ~3 µm MIR emissions have been analyzed, such as erbium ion (Er$^{3+}$): $^4_{11/2} \rightarrow ^4_{13/2}$ [8], holmium ion (Ho$^{3+}$): $^5_{I_6} \rightarrow ^5_{I_7}$ [9], and dysprosium ion (Dy$^{3+}$): $^6_{H_{15/2}} \rightarrow ^6_{H_{13/2}}$ [10]. Among them, the Er$^{3+}$ ion-doped single crystal has been deemed as the effective source for ~3 µm laser operation, benefiting from its abundant energy levels, such as GSGG [11], YSGG [12], YAP [13], Lu$_2$O$_3$ [14], GdScO$_3$ [15], SrF$_2$ crystals [16], NdVO$_4$ [17], InVO$_4$ crystals [18], etc. As investigated, the Er$^{3+}$ ion can be directly pumped utilizing 808 or 980 nm commercial laser diodes (LDs).
corresponding to Er$^{3+}$ ion absorption transitions from ground state $^4I_{15/2}$ to $^4I_{9/2}$, $^4I_{11/2}$ levels, respectively. To take further advantage of this, a co-doping suitable sensitization ion having strong absorption around 980 nm or 800 nm would improve the absorption efficiency, such as Yb$^{3+}$, Nd$^{3+}$, or Tm$^{3+}$ ions [19–21]. However, the fluorescence lifetime of the $^4I_{11/2}$ level (the upper) is fairly shorter than that of the $^4I_{13/2}$ level (the lower) of Er$^{3+}$ ion, causing the possible termination of 2.7 µm mid-infrared emissions [22]. Therefore, the shortcoming of the intrinsic self-terminating “bottleneck” effect of Er$^{3+}$ ion is important to consider. On one hand, the self-terminating “bottleneck” effect can be restrained by the energy transfer up-conversion (UC) process: $^2I_{13/2} \rightarrow ^4I_{15/2} + ^4I_{9/2}$, which needs heavy doping of Er$^{3+}$ ion (>30 at.%). The UC process can simultaneously depopulate the $^4I_{13/2}$ level and populate the $^4I_{11/2}$ level via non-radiative transition from $^4I_{9/2}$ to $^4I_{11/2}$ levels. However, excessive Er$^{3+}$ doping concentrations will generate the inclusion defects in as-grown crystal and degenerate the crystal quality and thermal performance, which is not conducive to laser output efficiency [23,24]. On the other hand, we can focus attention on co-doping a suitable deactivation ion for Er$^{3+}$ ion to suppress the self-terminating effect, such as Pr$^{3+}$, Ho$^{3+}$, Dy$^{3+}$, or Tm$^{3+}$ ions [25–28]. These deactivation ions can dramatically reduce the population of lower Er$^{3+}$ $^4I_{11/2}$ levels, thereby achieving efficient 2.7 µm mid-infrared emission. Based on the above investigation, it is noteworthy that Tm$^{3+}$ ion can simultaneously serve as sensitization and deactivation effects for Er$^{3+}$ ion [29,30].

In recent years, fluoride crystals have attracted numerous attention in the field of mid-infrared lasers, such as the β-PbF$_2$ crystal [31]. The PbF$_2$ crystal exhibits its intrinsic advantages. The PbF$_2$ crystal has lower phonon energy (257 cm$^{-1}$), compared with GdLiF$_4$ (432 cm$^{-1}$), LiYF$_4$ (442 cm$^{-1}$), LuLiF$_4$ (400 cm$^{-1}$) and BaY$_2$F$_8$ (415 cm$^{-1}$) crystals [32–34]. Such low phonon energy is conducive to reducing the non-radiative transition probability and enhancing the spontaneous radiation transition probability between $^4I_{11/2}$ and $^4I_{13/2}$ levels of Er$^{3+}$ ion [35]. Moreover, the PbF$_2$ crystal is optically transparent in the region of 0.25–15 µm, which is broader than other fluoride crystals, such as LiYF$_4$ (0.12–8.0 µm), BaY$_2$F$_8$ (0.2–9.5 µm), and KYF$_4$ (0.15–9.0 µm). Additionally, another issue to consider is the physical properties of the material. Some fluoride crystals have low thermal conductivity, such as CaF$_2$ and SrF$_2$. The PbF$_2$ crystal has high thermal conductivity (28 W/m/K) and stable mechanical and chemical properties [36,37]. Consequently, with these favorable characteristics, the PbF$_2$ crystal may be selected as a promising host material.

In this paper, Er: PbF$_2$, Tm: PbF$_2$, Er/Tm: PbF$_2$ crystals were successfully prepared by the Bridgman technique. The spectroscopic properties of prepared crystals were analyzed based on absorption spectra, emission spectra, and fluorescence decay curves. Compared with the Er: PbF$_2$ crystal, the Er/Tm co-doped PbF$_2$ crystal presents a larger 2.78 µm fluorescence emission intensity and higher fluorescence branching ratio. Moreover, theoretical calculations were performed to discover that the co-doping of the Tm$^{3+}$ ion can make the Er$^{3+}$ and Tm$^{3+}$ ions more evenly distributed in PbF$_2$ crystals, which can effectively break the local clusters of the Er$^{3+}$ in Er: PbF$_2$ crystal, thus ensuring efficient energy transfer between Er$^{3+}$ and Tm$^{3+}$ ions, and resulting in the enhancement of 2.78 µm MIR fluorescence emission.

2. Experimental Section

The 1.0 at.% Er: PbF$_2$, 0.5 at.% Tm: PbF$_2$, and 1.0 at.% Er/0.5 at.% Tm: PbF$_2$ crystals were grown by the conventional Bridgman method in an atmosphere of N$_2$ with intermediate molybdenum heating. The fluoride powders of the PbF$_2$ (99.999%), ErF$_3$ (99.999%), and TmF$_3$ (99.999%) were all raw materials. The raw materials were weighed and thoroughly mixed. The process of crystal growth was similar to our previous work [37]. The melt was homogenized in a covered graphite crucible in a high-temperature zone at 1000 °C for 8 h, and the crystal growth process was driven by lowering the graphite crucible at a speed of 0.5 mm/h. After the growth process was completed, the cooling rate of the crystal was 30 °C/cm–40 °C/h. The actual concentration of Er$^{3+}$ and Tm$^{3+}$ ions in the grown samples were measured utilizing inductively coupled plasma atomic emission
spectrum (ICP-AES). The concentrations of Er$^{3+}$ and Tm$^{3+}$ ions in dual-doped Er/Tm: PbF$_2$ crystal were 1.15 at.%, and 0.58 at.%, respectively. The concentration of Er$^{3+}$ ion in the Er: PbF$_2$ crystal was 1.15 at.%, and the concentration of Tm$^{3+}$ ion in the Tm: PbF$_2$ crystal was 0.59 at.%.  

The crystalline structure of as-grown samples was observed utilizing D/max2550 X-ray diffraction (XRD) with Cu K$_{\alpha}$ radiation. The Perkin–Elmer UV-VIS-NIR spectrometer (Lambda 900) with a resolution of 1 nm was used to detect the absorption spectra of prepared samples in the range of 400–2200 nm. The emission spectra, up-conversion fluorescence spectra, and fluorescence decay curves were detected and recorded using the Edinburgh Instruments FLS920 and FSP920 spectrophotometers. The repetition frequency of the excitation pulse for measuring the fluorescence decay curves was set to 20 Hz, and the duration of the excitation pulses was 30s. All the measurements were performed at room temperature.

3. Calculation Method

In the framework of density functional theory, VASP codes and the plane-wave basis set method were used for calculation [38,39]. The mutual interactions were described by the projector augmented-wave pseudopotential with an exchange-correlation function (Perdew–Burke–Ernzerhof form) [40,41]. The cut-off was set at 550 eV and a $1 \times 1 \times 1$ Gamma k-grid was used to guarantee the relaxation accuracy of $10^{-5}$ eV and 0.01 eVÅ$^{-1}$ within a $2 \times 2 \times 2$ supercell, respectively. The spin polarization was included in the calculations. According to the method reported previously [42], the formation energy ($\Delta E$) and cluster symbols were obtained. It is pointed that the energy correction of the PbF$_2$ crystal was different from that of CaF$_2$, SrF$_2$, and BaF$_2$ crystals. For a $2 \times 2 \times 2$ supercell with a net charge, the calculated value in PbF$_2$ crystal was 0.069 eV.

4. Results and Discussion

4.1. Crystal Structure Analysis

Figure 1 shows the XRD patterns and refined XRD patterns of the Er: PbF$_2$, Tm: PbF$_2$, Er/Tm: PbF$_2$ crystals, and the JCPDS standard card of the PbF$_2$ crystal (nos. 06-2051) [37]. The residuals of refinements (fit profiles shown in Figure 1) of Er: PbF$_2$, Tm: PbF$_2$, Er/Tm: PbF$_2$ crystals were 9.61%, 7.71%, 10.17%, respectively. It is obvious that no clear shift in the phase diffraction peaks was observed and all XRD curves were well matched with the standard card of the $\beta$-PbF$_2$ crystalline phase (nos. 06-2051). The results demonstrate successful co-doping of Er$^{3+}$ and Tm$^{3+}$ ions in PbF$_2$ crystal without phase transitions.

Figure 1. XRD patterns and refined XRD patterns of the Er/Tm: PbF$_2$, Er: PbF$_2$, Tm: PbF$_2$ crystals and PbF$_2$ crystal standard card.
4.2. First-Principles Calculations

Based on the first-principal calculations, the cluster structure of Tm$^{3+}$ and Er$^{3+}$ ions were simulated to research the change of local structures of doping ions in PbF$_2$ crystal. The possible thermodynamically stable Er$^{3+}$ and Tm$^{3+}$ centers in PbF$_2$ crystals are shown in Figure 2a,b. It is clear to see that there are 9 different types of centers in each Tm: PbF$_2$ and Er: PbF$_2$ crystals. In particular, only the 3$_1$ 10 16 13,-1 center in the Tm: PbF$_2$ crystal varies from the 2$_1$ 10 16 13,-1 center in the Er: PbF$_2$ crystal, and the other eight different types of centers in the Tm: PbF$_2$ crystal are the same as the Er: PbF$_2$ crystal. Moreover, Figure 2c shows the formation energy of Er$^{3+}$ and Tm$^{3+}$ versus the number of Er$^{3+}$ and Tm$^{3+}$ ions within a cluster, respectively. It can be seen that the slope of Er$^{3+}$ clusters in PbF$_2$ crystal is −0.988 eV, which is almost the same as the slope of Tm$^{3+}$ clusters in the PbF$_2$ crystal (−1.003 eV). These results indicate that the clustering characteristics of Er$^{3+}$ and Tm$^{3+}$ ions in PbF$_2$ crystal are almost consistent. This phenomenon agreed well with the approximately equal segregator coefficients of Er$^{3+}$ (1.15) and Tm$^{3+}$ (1.16) in the Er/Tm: PbF$_2$ crystal mentioned above, which may be owing to the slightly different ion radii between Er$^{3+}$ (88.1 pm) and Tm$^{3+}$ (86.9 pm) ions. That is to say, it can be considered that the Er$^{3+}$ and Tm$^{3+}$ ions replace Pb$^{2+}$ ions with equal probability when they are co-doped in PbF$_2$ crystal, which makes the Er$^{3+}$ and Tm$^{3+}$ ions more evenly distributed in the PbF$_2$ crystal. The results suggest that the efficient energy transfer between Er$^{3+}$ and Tm$^{3+}$ ions can be guaranteed due to the uniform distribution of Er$^{3+}$ and Tm$^{3+}$ ions, and result in the enhancing of 2.78 µM MIR fluorescence emission in the ensuing discussion.

Figure 2. (a) Thermodynamically stable Er$^{3+}$ centers in PbF$_2$ crystal; (b) Thermodynamically stable Tm$^{3+}$ centers in PbF$_2$ crystal; (c) Formation energy of Er$^{3+}$ and Tm$^{3+}$ versus the number of rare-earth ions within a cluster.

4.3. Absorption Spectroscopy

The illustrations in Figure 3 shows the photos of Er/Tm: PbF$_2$, Er: PbF$_2$, Tm: PbF$_2$ crystals and their cut and polished crystal pieces; their sizes are also marked, respectively. It can be seen that all the crystal pieces are transparent and have no inclusions. Figure 3 illustrates the room temperature absorption spectra of Er: PbF$_2$, Tm: PbF$_2$, and Er/Tm: PbF$_2$ crystals ranging from 400 nm to 2200 nm. Clearly, the typical absorption bands centered at approximately 417, 451, 486, 521, 541, 650, 802, 975, and 1509 nm in the Er: PbF$_2$ crystal originated from the transitions from the ground state $^4$I$_{15/2}$ level to upper-lying $^2$H$_{9/2}$, $^4$I$_{5/2}$, $^4$F$_{7/2}$, $^2$H$_{11/2}$, $^4$S$_{3/2}$, $^4$F$_{9/2}$, $^4$I$_{9/2}$, $^4$I$_{11/2}$ and $^4$I$_{13/2}$ levels of Er$^{3+}$ ion, respectively [37]. While in the Tm: PbF$_2$ crystal mainly five absorption bands of Tm$^{3+}$ ions are labeled, the absorption peaks centered at round 464, 680, 792, 1211, and 1618 nm are in accord with the transitions from ground state $^3$H$_6$ level to upper-lying $^4$F$_{4}$, $^3$F$_{2}$, $^3$F$_{4}$, $^3$H$_{5}$ and $^3$F$_{3}$ levels, respectively. Obviously, the huge absorption band centered at around 792 nm in the range of 750–830 nm corresponding to Tm$^{3+}$: $^3$H$_6$ → $^3$H$_4$ transition well coincides with the wavelength of 808 nm AlGaAs LD pumping. The absorption bands in the Er/Tm: PbF$_2$ crystal are altogether composed of the transitions of Er$^{3+}$ and Tm$^{3+}$ ions discussed above, indicating the successful introduction of both Er$^{3+}$ and Tm$^{3+}$ ions within a cluster, respectively.
ions. Strong overlap between the Tm\(^{3+}\): \(^3\)H\(_6\) \(\rightarrow\) \(^3\)H\(_4\) absorption transition and the Er\(^{3+}\): \(^4\)I\(_{15/2}\) \(\rightarrow\) \(^4\)I\(_{9/2}\) absorption transition can be seen in the Er/Tm: PbF\(_2\) crystal. The absorption overlap indicates that a possible nonradiative energy transfer process Tm\(^{3+}\): \(^3\)H\(_4\) \(\rightarrow\) Er\(^{3+}\): \(^4\)I\(_{9/2}\) would effectively occur for enhancing the absorption efficiency of Er\(^{3+}\) ion \(\sim\)800 nm. Therefore, benefiting from the broad absorption band of Tm\(^{3+}\) ion centered at around LD pump wavelength and the possibility for energy transfer, the Tm\(^{3+}\) ion can act as a suitable sensitizer for Er\(^{3+}\) ion in the Er/Tm dual-doped PbF\(_2\) crystal.

For demonstrating the sensitization effect of Tm\(^{3+}\) ion for Er\(^{3+}\) ion via the Tm\(^{3+}\): \(^3\)H\(_4\) \(\rightarrow\) Er\(^{3+}\): \(^4\)I\(_{9/2}\) energy transfer transition, the lifetimes of Tm\(^{3+}\): \(^3\)H\(_4\) level in the Tm\(^{3+}\) single-doped and Er/Tm dual-doped PbF\(_2\) crystals were measured and shown in Figure 4a,b, respectively. The decay curves were measured under the condition of 1.47 \(\mu\)m emission (Tm\(^{3+}\): \(^3\)H\(_4\) \(\rightarrow\) \(^3\)F\(_4\)) and 800 nm excitation (Tm\(^{3+}\): \(^3\)H\(_6\) \(\rightarrow\) \(^3\)H\(_4\)) and were all well fitted by single-exponential behavior. As shown in Figure 4a, the measured lifetime of the Tm\(^{3+}\): \(^3\)H\(_4\) manifold is 1.67 ms in the Tm: PbF\(_2\) crystal, while the lifetime is 0.54 ms in the Er/Tm: PbF\(_2\) crystal shown in Figure 4b. The remarkable decreasing lifetime in the Er/Tm: PbF\(_2\) crystal indicates the effective sensitization effect of the Tm\(^{3+}\) ion. The energy transfer efficiency from Tm\(^{3+}\): \(^3\)H\(_4\) to Er\(^{3+}\): \(^4\)I\(_{9/2}\) level can be calculated by the following equation:

\[
\eta_{ET} = 1 - \tau_{ET}/\tau_T,
\]

where \(\tau_{ET}\) and \(\tau_T\) are the lifetimes of Tm\(^{3+}\): \(^3\)H\(_4\) level in Tm: PbF\(_2\), Er/Tm: PbF\(_2\) crystals, respectively. The high value of \(\eta_{ET}\) (67.66\%) confirms that the Tm\(^{3+}\) ion has a significant influence on Er\(^{3+}\): \(^4\)I\(_{9/2}\) level in PbF\(_2\) crystal, and can effectively act as a sensitizer for Er\(^{3+}\) ion for enhancing \(\sim\)2.7 \(\mu\)m MIR emission.

![Absorption spectra of Tm: PbF\(_2\), Er: PbF\(_2\), and Er/Tm: PbF\(_2\) crystals ranging from 400 to 2200 nm at room temperature. (Illustration: the photos of Er/Tm: PbF\(_2\), Er: PbF\(_2\), Tm: PbF\(_2\) crystals and their cut and polished crystal pieces, respectively.)](image)
4.4. Emission Spectra and Emission Cross-Sections

For further clarifying the energy transfer mechanism between Tm\(^{3+}\) and Er\(^{3+}\) ions, the emission spectra of Er/Tm: PbF\(_2\), Er: PbF\(_2\) samples in the range of 1400–1700 nm, and Er/Tm: PbF\(_2\), Tm: PbF\(_2\) samples in the 1700–2200 nm region are shown in Figure 5a,b, respectively. The test parameters of the luminescence performance of the prepared samples, such as pump power and slits, are uniformed. As shown in Figure 5a, compared with the Er: PbF\(_2\) crystal the emission intensity centered at around 1.55 \(\mu\)m corresponding to the Er\(^{3+}\): 4I\(_{15/2}\) → 4I\(_{13/2}\) transition in the Er/Tm: PbF\(_2\) crystal weakened sharply, at almost ten times lower. The result shows that the introduction of Tm\(^{3+}\) ion would significantly reduce the population of the Er\(^{3+}\): 4I\(_{13/2}\) energy level, thereby enhancing the ~2.7 \(\mu\)m mid-infrared emission and reversely weakening the 1.55 \(\mu\)m infrared emission. This depopulation of Er\(^{3+}\): 4I\(_{13/2}\) energy level is mainly attributed to the deactivation effect of Tm\(^{3+}\) ions via energy transfer process: Er\(^{3+}\): 4I\(_{13/2}\) → Tm\(^{3+}\): 3F\(_{4}\) in Er/Tm: PbF\(_2\) crystal. As the deactivation energy transfer process occurs, the population on the Tm\(^{3+}\): 3F\(_{4}\) level would increase, thereby enhancing the 1.91 \(\mu\)m emission (Tm\(^{3+}\): 3F\(_{4}\) → 3H\(_{6}\) transition) in the Er/Tm: PbF\(_2\) crystal, but it is actually weakened (shown in Figure 5b). The 1.91 \(\mu\)m emission intensity of the Tm\(^{3+}\) ion in Er/Tm: PbF\(_2\) crystal is nearly three times lower than that in the Tm\(^{3+}\) single doped PbF\(_2\) crystal. This result is mainly assigned to the cross-relaxation (CR) process between Tm\(^{3+}\) and Er\(^{3+}\) ions (Tm\(^{3+}\): 3F\(_{4}\) + Er\(^{3+}\): 4I\(_{13/2}\) → Tm\(^{3+}\): 3H\(_{4}\) + Er\(^{3+}\): 4I\(_{15/2}\)), bringing about the depopulation of the Tm\(^{3+}\): 3F\(_{4}\) level and Er\(^{3+}\): 4I\(_{13/2}\) level. Therefore, the reduced emission intensity of 1.55 \(\mu\)m of Er\(^{3+}\) ion and 1.91 \(\mu\)m of Tm\(^{3+}\) ion both would depopulate the ions on the Er\(^{3+}\): 4I\(_{13/2}\) level, which is beneficial to enhance ~2.7 \(\mu\)m MIR emission. More importantly, as shown in Figure 6, the emission intensity of the Er/Tm: PbF\(_2\) crystal centered at around 2.7 \(\mu\)m in the 2500–3100 nm region is remarkably larger than that of the Er: PbF\(_2\) crystal, confirming that the efficient enhanced ~2.7 \(\mu\)m emission is achieved in the Er/Tm: PbF\(_2\) designed crystal. To further confirm the prospects of Er: PbF\(_2\), Er/Tm: PbF\(_2\) crystals as the mid-infrared luminescent material in laser applications, the 2.78 \(\mu\)m emission cross-sections are subsequently calculated according to the Fuchtbauere–Ladenburg theory [43]:

\[
\sigma_{em}(\lambda) = \frac{A\beta A^5 I(\lambda)}{8\pi cn^2 \int \lambda I(\lambda) d\lambda}
\]  

where \(\lambda\) denotes the wavelength of fluorescence spectrum, \(I(\lambda)\) is the intensity of emission spectrum at \(\lambda\), \(I(\lambda)/\int \lambda I(\lambda) d\lambda\) is the normalized line shape function of the emission spectrum of prepared crystal, \(n\) is the refractive index of PbF\(_2\) crystal, \(c\) is the speed of light in a vacuum, \(\beta\) is the fluorescence branching ratio of 4I\(_{11/2}\) → 4I\(_{13/2}\) transition, and \(A\) is
the spontaneous emission probability. The value of $\beta$ for ~2.7 µm mid-infrared emission in Er: PbF$_2$ is calculated to be 14.9%, and in the Er/Tm: PbF$_2$ crystal is calculated to be 20.24%. The maximum emission cross-section of the Er/Tm: PbF$_2$ crystal is calculated to be 0.63 $\times$ 10$^{-20}$ cm$^2$ at 2780 nm, which is almost twice that of the Er: PbF$_2$ crystal (0.32 $\times$ 10$^{-20}$ cm$^2$). Moreover, as shown in Table 1, this higher stimulated emission cross-section in the Er/Tm: PbF$_2$ crystal possibly coincides well with the higher fluorescence branching ratio $\beta$ (20.24%) of the Er$^{3+}$: $4I_{11/2} \rightarrow 4I_{13/2}$ transition. A higher emission cross-section is more favorable in achieving high performance of MIR laser operation. These results are related to the more uniform distribution of Er$^{3+}$ and Tm$^{3+}$ ions in PbF$_2$ crystal after the co-doping of Tm$^{3+}$ ions, which is consistent with the theoretical calculation results. Furthermore, it is pointed out that the enhancing of 2.78 $\mu$m MIR fluorescence emission is more dependent on the efficient energy transfer between Er$^{3+}$ and Tm$^{3+}$ ions, which comes from the uniform distribution of doped ions.

![Figure 5](image1.png)

**Figure 5.** (a) Emission spectra of the Er: PbF$_2$, Er/Tm: PbF$_2$ crystals in the range of 1400–1700 nm ($\lambda_{ex} = 800$ nm); (b) emission spectra of Tm: PbF$_2$, Er/Tm: PbF$_2$ crystals in the range of 1700–2200 nm ($\lambda_{ex} = 800$ nm).

![Figure 6](image2.png)

**Figure 6.** Emission spectra of the Er: PbF$_2$, Er/Tm: PbF$_2$ crystals in the range of 2500–3100 nm ($\lambda_{ex} = 800$ nm).
Table 1. MIR emission cross-sections $\sigma_{em}$, and lifetimes of $^4I_{11/2}, ^4I_{13/2}$ levels of Er/Tm: PbF$_2$, Er: PbF$_2$ crystals compared with other Er$^{3+}$-doped crystals.

| Crystal               | $\sigma_{em}$ ($10^{-20}$ cm$^2$) | $\tau(^{4}I_{11/2})$ (ms) | $\tau(^{4}I_{13/2})$ (ms) | $\tau(^{4}I_{11/2})/\tau(^{4}I_{13/2})$ (%) | Ref.          |
|-----------------------|-----------------------------------|-----------------------------|-----------------------------|-----------------------------------------------|--------------|
| 1.0 at.% /0.5 at.% Er/Tm: PbF$_2$ | 0.630@2780nm | 6.91 ± 0.01 | 3.14 ± 0.01 | 220.06 | [This work] |
| 1 at.% Er: PbF$_2$    | 0.320@2780nm | 6.03 ± 0.01 | 12.06 ± 0.05 | 50.00 | [This work] |
| 10 at.% Er:CaLaGa$_3$O$_7$ | 7.34@2714nm | 0.72 | 7.99 | 9.01 | [44] |
| 10 at.% Er:CaLaGa$_3$O$_7$ | 17.9@2702nm | 0.77 | 8.41 | 9.16 | [45] |
| 8 at.% Er:LuAl$_3$(BO$_3$)$_4$ | 8.60@3170nm | 2.10 | 2.54 | 82.68 | [46] |
| 7 at.% Er:Y$_2$O$_3$  | 1.41@2723nm | 2.95 | 17.57 | 16.79 | [47] |
| 10 at.% Er:Er:GdScO$_3$ | 1.30@2.7µm | 1.10 | 4.48 | 24.55 | [24] |
| 5 at.% Er:YAP         | 9.00@2792nm | 0.85 | 7.30 | 11.64 | [13] |
| 7 at.% Er:Lu$_2$O$_3$ | 1.10@2730nm | 1.10 | 4.30 | 25.58 | [14] |
| 5 at.% Er:GdScO$_3$   | 0.93@2720nm | 2.24 | 4.57 | 49.02 | [15] |
| 4 at.% Er:Er:YAP      | 0.78@2727nm | 9.56 | 15.06 | 63.48 | [16] |
| 4 at.% Er:CaF$_2$     | 0.65@2720nm | 5.98 | 9.94 | 60.16 | [16] |

4.5. Energy Transfer Mechanism between Tm$^{3+}$ and Er$^{3+}$ Ions

Based on spectroscopic results discussed above, the simplified energy level scheme and electron transitions of the Er$^{3+}$/Tm$^{3+}$ co-doped PbF$_2$ crystal are presented in Figure 7. The cyclic related processes of the Tm$^{3+}$ and Er$^{3+}$ ions in the crystal under optical excitation are as follows: cross-relaxation, energy transfer between Tm$^{3+}$ and Er$^{3+}$ ions, and multiphonon relaxation. The main two ET (namely ET1, ET2) and three CR (namely CR1, CR2, CR3) processes are listed as follows:

ET 1: Tm$^{3+}$: $^3H_4$ + Er$^{3+}$: $^4I_{15/2}$ $\rightarrow$ Tm$^{3+}$: $^3H_6$ + Er$^{3+}$: $^4I_{9/2}$;
ET 2: Er$^{3+}$: $^4I_{13/2}$ + Tm$^{3+}$: $^3H_6$ $\rightarrow$ Er$^{3+}$: $^4I_{15/2}$ + Tm$^{3+}$: $^3F_4$;
CR 1: Tm$^{3+}$: $^3F_4$ + Er$^{3+}$: $^4I_{13/2}$ $\rightarrow$ Tm$^{3+}$: $^3H_4$ + Er$^{3+}$: $^4I_{9/2}$;
CR 2: Tm$^{3+}$: $^3F_4$ + Er$^{3+}$: $^4I_{13/2}$ $\rightarrow$ Tm$^{3+}$: $^3H_4$ + Er$^{3+}$: $^4I_{15/2}$;
CR 3: 2Er$^{3+}$: $^4I_{13/2}$ $\rightarrow$ Er$^{3+}$: $^4I_{15/2}$ + Er$^{3+}$: $^4I_{9/2}$.

Figure 7. Simplified energy level scheme and electron transitions of Er$^{3+}$/Tm$^{3+}$ co-doped system.

As discussed, the Tm$^{3+}$: $^3H_4$ $\rightarrow$ $^3H_6$ transition is resonant with the Er$^{3+}$: $^4I_{15/2}$ $\rightarrow$ $^4I_{9/2}$ transition in the Er/Tm: PbF$_2$ crystal. Therefore, after the crystal is excited to the Tm$^{3+}$: $^3H_4$ level by a pump of 800 nm LD, ET1 process Tm$^{3+}$: $^3H_4$ $\rightarrow$ Er$^{3+}$: $^4I_{9/2}$ would occur. Ions in the Er$^{3+}$: $^4I_{9/2}$ level decay non-radiatively to the lower Er$^{3+}$: $^4I_{11/2}$ level, and then decay radiatively to the Er$^{3+}$: $^4I_{13/2}$ level and emit 2.78 µm mid-infrared light. Ions in the Er$^{3+}$:
4I_{13/2} level continue to decay radiatively to the ground state Er^{3+}: 4I_{15/2} level and emit 1.55 µm infrared light. Similarly, the Er^{3+}: 4I_{13/2} → 4I_{15/2} transition is resonant with the Tm^{3+}: 3H_6 → 3F_4 transition, and the ET2 process from Er^{3+}: 4I_{13/2} to Tm^{3+}: 3F_4 level takes place. The ET2 process would reduce the population of the lower level of Er^{3+}: 4I_{13/2}, thereby enhancing the 2.78 µm emission and weakening the 1.55 µm emission, as shown in Figures 5a and 6. Meantime, the energy transfer up-conversion (UC) CR3 process (Er^{3+}: 2^{4}I_{13/2} → 4^{1}I_{15/2} + ^{4}I_{9/2}) in the crystal can also populate the Er^{3+}: 4^{1}I_{11/2} level and depopulate the Er^{3+}: 4I_{13/2} level. Additionally, ions in the Tm^{3+}: 3F_4 level decay radiatively to the 3H_6 level and emit 1.91 µm emission. The subsequent CR1 populates the Er^{3+}: 4I_{9/2} level, and then the Er^{3+}: 4I_{11/2} level is populated through the nonradiative decay from the 4I_{9/2} level to the 4I_{11/2} level, increasing the population ratio of 4I_{11/2}/4I_{13/2} levels. Moreover, the ions in the Tm^{3+}: 3F_4 energy level will also absorb energy and jump to the upper Tm^{3+}: 3H_4 energy level due to Stark level splitting, and then the CR2 process described above occurs. The CR2 process can simultaneously reduce the population Er^{3+}: 4I_{13/2}, Tm^{3+}: 3F_4 levels, to achieve 2.78 µm emission enhancement and 1.91 µm emission reduction, as shown in Figures 5b and 6. The CR2 process also brings about the increasing population of the Tm^{3+}: 3H_4 level. Besides emitting 1.47 µm light via the Tm^{3+}: 3H_4 → 3F_4 transition, ions in the Tm^{3+}: 3H_4 level can populate the Er^{3+}: 4I_{9/2} level via ET1 process, resulting in further enhancement of the sensitization effect. To prove the CR2 process, the UC emission spectra of Er: PbF_2 and Er/Tm: PbF_2 crystals are shown in Figure 8 under 980 nm excitation. Clearly, as shown in Figure 7, under 980 nm NIR light excitation, the electrons in the ground level 4I_{15/2} can be excited to the intermediate level 4I_{11/2}, and the electrons in the 4I_{11/2} level sequentially populate the 4F_7/2 level (4I_{15/2} → 4I_{11/2} → 4F_7/2). Additionally, then, the multiple nonradiative multi-phonon relaxation in the 4F_7/2 state in turn populate the lower 2H_{11/2}, 4S_{3/2}, 4F_{9/2}, and 4I_{9/2} levels, which would produce 800 nm light via the process: 4I_{9/2} → 4I_{15/2}. It is clear to see that the UC emission intensity of the Er/Tm: PbF_2 crystal is at least two times larger than that of the Er: PbF_2 crystal at around 800 nm. Obviously, Tm^{3+} ions have no absorption band matching the 980 nm excitation (shown in Figure 3). This enhancing UC emissions phenomenon is possibly assigned to the CR2 and ET1 mechanism processes illustrated in Figure 7. To summarize, the ET1, ET2, CR1, CR2, CR3 processes all have significant effects on narrowing the lifetime gap of upper-lying Er^{3+}: 4I_{11/2} and lower-lying Er^{3+}: 4I_{13/2} levels or even achieving population conversion of these two levels, thereby obtaining efficient enhanced 2.78 µm emission.

![Up-conversion emissions of Er: PbF_2, and Er/Tm: PbF_2 crystals in the range of 760–860 nm (λ_{ex} = 980nm).](image-url)
4.6. Fluorescence Decay Curves and Fluorescence Lifetimes

For further demonstrating the energy interaction mechanism between Er$^{3+}$ and Tm$^{3+}$ ions, the time-resolved decay curves of the Er$^{3+}$ ion 2.78 μm (4I$_{11/2}$ → 4I$_{13/2}$) and 1.55 μm (4I$_{13/2}$ → 4I$_{15/2}$) fluorescence emission for the Er/Tm: PbF$_2$ and Er: PbF$_2$ crystals were measured and shown in Figure 9. The lifetimes of 4I$_{13/2}$ levels were measured under the conditions of 1.55 μm emission (4I$_{13/2}$ → 4I$_{15/2}$) and 1.49 μm excitation (4I$_{15/2}$ → 4I$_{13/2}$). The decay curves of the Er$^{3+}$: 4I$_{11/2}$ and Er$^{3+}$: 4I$_{13/2}$ levels are well fitted with single-exponential behavior. As shown in Figure 9a,b, the measured lifetime of the upper-lying 4I$_{11/2}$ level in the Er/Tm: PbF$_2$ crystal (6.91 ms) is 14.6% longer compared with the Er: PbF$_2$ crystal (6.03 ms), which is assigned to the sensitization effect of the Tm$^{3+}$ ion on the upper-lying Er$^{3+}$: 4I$_{11/2}$ level. Moreover, as shown in Figure 9c,d, the measured lifetime of the lower-lying 4I$_{13/2}$ level in the Er/Tm: PbF$_2$ crystal is 3.14 ms, which is 73.96% shorter compared with the Er: PbF$_2$ crystal (12.06 ms). This remarkable decrease of the lifetime of lower-lying 4I$_{13/2}$ level denotes that Tm$^{3+}$ ions can dramatically depopulate the Er$^{3+}$: 4I$_{13/2}$ level via ET2, CR1, CR2, CR3 processes, thereby enhancing the 2.78 μm emission in PbF$_2$ crystals. The ET2, CR1, CR2, CR3 processes all have significant effects on narrowing the lifetime gap of upper-lying Er$^{3+}$: 4I$_{11/2}$ and lower-lying Er$^{3+}$: 4I$_{13/2}$ levels or even achieving population conversion of these two levels. Besides, the energy transfer efficiency η$_{ET2}$ was calculated to be 73.96%, confirming the efficient deactivation effect of the Tm$^{3+}$ ion for the Er$^{3+}$ ion. Furthermore, Table 1 shows the lifetimes of 4I$_{11/2}$, 4I$_{13/2}$ levels of Er/Tm: PbF$_2$, Er: PbF$_2$ crystals, and other Er$^{3+}$ doped laser crystals. The shorter fluorescence lifetime of 4I$_{13/2}$ lower level induces the longer fluorescence lifetime ratio $\tau$(4I$_{11/2}$)/$\tau$(4I$_{13/2}$). The fluorescence lifetime ratio $\tau$(4I$_{11/2}$)/$\tau$(4I$_{13/2}$) in Er/Tm: PbF$_2$ crystal is 220.06%, which is dramatically larger than that of the Er: PbF$_2$ crystal (50.00%) and other Er$^{3+}$ doped crystals. The remarkably enhanced $\tau$(4I$_{11/2}$)/$\tau$(4I$_{13/2}$) ratio in Er/Tm: PbF$_2$ crystal is favorable for achieving efficient laser operation ~2.7 μm. As a consequence, the introduction of Tm$^{3+}$ ions can simultaneously act as sensitization and deactivation ions for the Er$^{3+}$ ion, thereby enhancing 2.78 μm mid-infrared emission and reducing the laser threshold of 2.78 μm luminescence.

![Fluorescence decay curves](image_url)

**Figure 9.** (a) Fluorescence decay curves of the Er$^{3+}$: 4I$_{11/2}$ energy level of Er: PbF$_2$ crystal ($\lambda_{ex} = 800$ nm, $\lambda_{em} = 2780$ nm); (b) Er$^{3+}$: 4I$_{11/2}$ energy level of Er/Tm: PbF$_2$ crystal ($\lambda_{ex} = 800$ nm, $\lambda_{em} = 2780$ nm); (c) Er$^{3+}$: 4I$_{13/2}$ energy level of Er: PbF$_2$ crystal ($\lambda_{ex} = 1490$ nm, $\lambda_{em} = 1550$ nm); (d) Er$^{3+}$: 4I$_{13/2}$ energy level of Er/Tm: PbF$_2$ crystal ($\lambda_{ex} = 1490$ nm, $\lambda_{em} = 1550$ nm).
5. Conclusions

In summary, Er$^{3+}$: PbF$_2$, Tm$^{3+}$: PbF$_2$, and Er$^{3+}$/Tm$^{3+}$: PbF$_2$ crystals were prepared successfully by the Bridgman technique. An efficient enhanced 2.78 µm emission was obtained in the Er/Tm: PbF$_2$ crystal for the first time, and the proposed energy transfer mechanism of the Er/Tm: PbF$_2$ crystal was systematically investigated. The theoretical calculations were performed to discover that the co-doping of Tm$^{3+}$ ions can make the Er$^{3+}$ and Tm$^{3+}$ ions more evenly distributed in PbF$_2$ crystals, which can effectively break the local clusters of Er$^{3+}$ in Er: PbF$_2$ crystal, thus ensuring efficient energy transfer between Er$^{3+}$ and Tm$^{3+}$ ions, and resulting in the enhancing of 2.78 µm MIR fluorescence emission. The cyclic energy transfer mechanism contains several energy transfer processes and cross-relaxation processes, which all have significant effects on narrowing the lifetime gap of upper-lying Er$^{3+}$: $^4I_{11/2}$ and lower-lying Er$^{3+}$: $^4I_{13/2}$ levels or even achieving population conversion of these two levels. As proved, the Tm$^{3+}$ ion can simultaneously act as an appropriate sensitized and deactivated ion for the Er$^{3+}$ ion in the PbF$_2$ crystal. Compared with the Er$^{3+}$ single-doped crystal, the Er$^{3+}$/Tm$^{3+}$ co-doped PbF$_2$ crystal has the larger 2.78 µm mid-infrared fluorescence emission intensity, higher fluorescence branching ratio (20.24%), and higher stimulated emission cross-section ($0.63 \times 10^{-20}$ cm$^2$), corresponding to Er$^{3+}$: $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition. Therefore, the introduction of Tm$^{3+}$ ions is favorable for achieving efficient enhanced 2.78 µm emission in the Er/Tm: PbF$_2$ crystal, which can become a promising material for low threshold, and high-efficiency mid-infrared laser applications under the pump of a conventional 800 nm LD.

Author Contributions: Conceptualization, P.Z.; methodology, J.L. and Q.C.; software, F.M.; validation, Y.H.; formal analysis, S.Z.; investigation, J.L., H.T. and Q.Y.; resources, Y.H.; and Z.L.; data curation, J.L. and Q.C.; writing—original draft preparation, J.L. and X.N.; writing—review and editing, P.Z.; visualization, Q.C.; supervision, Z.C.; project administration, Z.C.; funding acquisition, Y.H. and Z.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (NSFC) (51972149, 51872307, 51702124); Key-Area Research and Development Program of Guangdong Province (2020B090922006); Guangdong Project of Science and Technology Grants (2018B0303230 17, 2018B010114002); Guangzhou science and technology project (201904010385, 201903010042); The Fundamental Research Funds for the Central Universities (21620445).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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