Phase Transformation and Intense 2.7 μm Emission from Er³⁺ Doped YF₃/YOF Submicron-crystals

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Yttrium fluoride YF₃:Er³⁺ and yttrium oxyfluoride YOF:Er³⁺ submicron-crystals with mid-infrared fluorescent emissions were synthesized for the first time. The rhombohedral phase YOF submicron-crystals were synthesized by the crystalline phase transformation from pure orthorhombic YF₃ submicron-crystals, which were prepared by co-precipitation method. The composition and morphology were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM), which showed that submicron-crystals were quasi-spherical with the particle size of ~400 nm. A novel formation mechanism of YOF submicron-crystals was proposed. Photoluminescence (PL) spectra indicated the 2.7 μm emission of Er³⁺ has remarkably enhanced with the increase of Er³⁺ doping concentration, and a novel dynamic circulatory energy transfer mechanism was proposed. Fourier transform infrared spectra (FTIR) were used to demonstrate the change of hydroxyl content. These oxyfluoride submicron-crystals provide a new material for nano/submicron-crystals-glass composites, and open a brand new field for the realization of mid-infrared micro/nano-lasers.

In recent years, solid state lasers operating around 2.7 μm have attracted more and more attention due to their potential applications in various fields, such as remote sensing, atmosphere pollution monitoring, and military, etc. However, during the research process of mid-infrared lasers, there are many kinds of problems which restrict their development, such as the luminous efficiency of rare-earth ions, the stability of host materials, etc. Thus, it is extremely important to search for a new solid state material to solve these problems. Nano/submicron-crystals, as the candidate hosts for mid-infrared fluorescence and laser, have attracted great attention due to their superior characteristics compared with conventional glass and glass ceramics materials, such as higher luminous efficiency, smaller particle size, higher chemical stability and more mature synthesis methods, etc. Thus, rare-earth ions doped nano/submicron-crystals, which can be combined with glass matrixes to form nano/submicron-crystals-glass composites for fiber-drawing, open a brand new field for the realization of mid-infrared micro/nano-lasers.

Up to now, mid-infrared fluorescence can be achieved in many kinds of rare-earth ions and get intensive study, such as Er³⁺, Ho³⁺, Dy³⁺, etc. Among all the rare-earth ions, Er³⁺ fluorescence emitting at 2.7 μm, due to the I₁/₂→ I₃/₂ transition, plays a key role in the investigations and has been achieved in many kinds of glasses, glass ceramics and single-crystals hosts. However, many kinds of factors must be considered in order to obtain high mid-infrared luminescent efficiency. Among them, a minimal absorption coefficient in the typical H₂O absorption band around 3 μm and lower phonon energy of the host materials are the extremely important influencing factors. This is because that the mid-infrared fluorescence can be absorbed by the hydroxyl groups (OH⁻) and undetected. Moreover, the higher phonon energy of host materials could result in the increase of the nonradiative transition between the two energy levels of Er³⁺ ions, and subsequently decrease the radiative transition of 2.7 μm emission. Therefore, choosing a right material as mid-infrared luminous host materials is especially important in this research.

Oxide and fluoride nano/submicron-crystals as two major kinds of micro/nano-materials have been extensive studied in many fields. The results confirm that, oxide nano/submicron-crystals have better mechanical strength and chemical stability, but higher phonon energy (larger than 500 cm⁻¹), and fluoride nano/submicron-crystals have lower phonon energy, but chemically and thermally unstable. However, oxyfluorides nano/submicron-crystals combine the advantages of both fluoride and oxide nano/submicron-crystals, such as they can show better chemical and thermal stability than fluorides, and lower phonon energy than oxides, so that it will be
desired as ideal mid-infrared host materials. Yttrium fluoride (YF$_3$) is one of most promising materials as a kind of the down/up conversion materials, due to their wider optical transmission window and the minimization of the excited state quenching of rare-earth ions, especially it has lower phonon energy ($\sim$350 cm$^{-1}$). Yttrium oxyfluoride (YOF) as a typical oxyfluoride with a phonon energy of $\sim$400 cm$^{-1}$, not only contains the advantages of YF$_3$, but also has other unique advantages, such as excellent chemical and thermal stability than YF$_3$. Thus, YOF nano/submicron-crystals are chosen as an ideal matrix material for mid-infrared fluorescence in this study. Furthermore, due to much OH$^-$ exist in the structure of nano/submicron-crystals, which is unavoidable in the chemical synthesis process, there have been no any reports about the mid-infrared fluorescence emissions from fluoride or oxyfluorides nano/submicron-crystals so far. Thus, search a novel routine to solve the OH$^-$ absorption problem (dehydration) is extremely important for the mid-infrared fluorescence emissions of crystal particles in this study.

At present, there are many wet chemical methods to synthesize YF$_3$ and YOF nano/submicron-crystals, including microemulsion, co-precipitation, sol-gels and hydrothermal method. And all these chemical processes achieve homogeneous mixing of activator cations on the atomic level, leading to an increase in reaction rate and lowering synthesis temperature. Among these synthesis methods, co-precipitation method has more superiority, because it is a more milder and mature chemical reaction, as well as higher repeatability and larger production. Moreover, it uses ammonium hydrogen fluoride (NH$_4$HF$_2$) as the precipitator, so that during the process of temperature rise, the OH$^-$ in the structure of crystal particles can be removed effectively by the hydroscopic property of fluoride and instability of YF$_3$. Thus, co-precipitation method is chosen as the synthesis method in this study, which is also beneficial to the preparation of nano/submicron-crystals-glass composites in the future.

Herein, the preparation of YOF:Er$^{3+}$ submicron-crystals with mid-infrared fluorescence is reported for the first time. The YOF: Er$^{3+}$ submicron-crystals were synthesized on the basis of the YF$_3$: Er$^{3+}$ submicron-crystals with good morphology by co-precipitation method and continuous calcining method. During the calcining process, utilized the hydroscopic property of fluoride and instability of YF$_3$:Er$^{3+}$ submicron-crystals, YF$_3$:Er$^{3+}$ submicron-crystals were transformed into YOF:Er$^{3+}$ submicron-crystals free of OH$^-$. The possible formation mechanism has been discussed in detail. Based on the luminescence characteristics of submicron-crystals with different Er$^{3+}$ doping concentrations, as well as the change of Er$^{3+}$: $^{4}I_{13/2}$ and $^{4}I_{15/2}$ levels lifetime, a novel dynamic circulatory energy transfer mechanism of Er$^{3+}$ in YOF submicron-crystals has been tentatively proposed.

### Results

#### Structural and phase investigations of YF$_3$:Er$^{3+}$ and YOF:Er$^{3+}$ submicron-crystals

Fig. 1 shows XRD patterns of 4 mol% Er$^{3+}$ doped fluoride precursor powders calcined at different temperatures and several diffraction peaks are observed. From the patterns, when the temperature is 400°C and 600°C, almost all the diffraction peaks are in agreement with the standard card of the orthorhombic phase YF$_3$ (JCPDF: 74-0911). With the increase of temperature, an obvious phase transformation has occurred, and when the temperature reaches 1100°C, the products present the pure rhombohedral phase YOF (JCPDF: 71-2100). It illustrates that YF$_3$ submicron-crystals have successfully transformed into YOF submicron-crystals with the increase of temperature. But further increase of temperature will result in the occurrence of a little impure phase, Y$_2$O$_3$ (JCPDF: 20-1412). This is because that with the increase of temperature, fluoride become so instability that F ions in YF$_3$ crystal lattice can be oxidized gradually due to the oxygen in the environment, which is beneficial for oxygen atoms replacing fluoride atoms and entering into crystals lattice. And the content of oxygen atoms in crystals lattice has a remarkable increase with the increase of temperature, which results in the formation of Y$_2$O$_3$, as shown in Fig. 1. Thus, the increase of temperature from 600°C to 1200°C resulted in a substantial decrease in the YF$_3$ phase and the appearance of a new phase, YOF, to the detriment of Y$_2$O$_3$. Moreover, with the increase of temperature, the diffraction peaks grow stronger and the full width at half maximum (FWHM) of the peaks become narrower, indicating the growth of crystalline particles with better crystallinity. Therefore, we choose precursor powders

![Figure 1](https://www.nature.com/scientificreports/)  
**Figure 1** | XRD patterns of 4 mol% Er$^{3+}$ doped fluoride precursor powders calcined at different temperatures for 2 h.

![Figure 2](https://www.nature.com/scientificreports/)  
**Figure 2** | XRD patterns of YF$_3$ submicron-crystals (calcined at 600°C for 2 h) doped with different Er$^{3+}$ concentrations.
calcined at 600°C and 1100°C for 2 h to form pure YF₃:Er³⁺ and YOF:Er³⁺ submicron-crystals as the typical synthesis condition in the following text.

Fig. 2 and Fig. 3 show XRD patterns of different concentration of Er³⁺ doped YF₃ and YOF submicron-crystals, respectively. In Fig. 2, when the temperature is 600°C, all the diffraction peaks can be assigned to the orthorhombic phase YF₃ (JCPDF: 74-0911) and the addition of Er³⁺ almost has no effect on the phase of submicron-crystals products. Similarly, when the temperature is 1100°C, all the diffraction peaks can be assigned to the rhombohedral phase YOF (JCPDF: 71-2100) and no other impurity phase is detected, as shown in Fig. 3. Besides, with the increase of Er³⁺ doping concentration, the diffraction peaks have a little shifting to higher 2θ region, which indicates that Er³⁺ with smaller iron radius have replaced Y³⁺ and entered into YF₃ and YOF crystals lattice, respectively. It is worth mentioning that, in this study, the doping concentration of rare-earth ions in all samples is only titular concentration.

Morphology of YF₃:Er³⁺ and YOF:Er³⁺ submicron-crystals. The SEM images of 4 mol% Er³⁺ doped fluoride precursor powders calcined at different temperatures are shown in Fig. 4a–f. During the process of temperature rise, the morphology has an obvious change, along with crystalline phase transformed from pure orthorhombic YF₃ phase into pure rhombohedral YOF phase. A schematic illustration of the transformation process is shown in Fig. 4g and the possible formation mechanism is proposed as follows. When the temperature is rose from 400°C to 600°C, the average size of YF₃ submicron-crystals with better dispersity is grown to about 300–400 nm and presents quasi-spherical morphology (Fig. 4b), as the process of “(1) Growing”. When the temperature reaches 800°C, due to oxygen atoms join in the crystal formation and growth, the crystalline phase is forced to be transformed from fluoride into oxyfluoride. But this temperature is still lower and cannot provide enough energy for the formation of pure YOF crystal nucleus, so that only an agglomerate and self-assemble process happens under the effect of oxygen atoms, and the average size reaches up to 1–2 μm (Fig. 4c), as the process of “(2) Self-assemble”. However, when the temperature is 1000°C or 1100°C, there are enough energy and oxygen atoms for the formation and growth of YOF crystal nucleus, and this formation process can be rationally explained by a dissolution-recrystallization mechanism. Herein, under this higher temperature, sufficient oxygen atoms enter into crystal lattices and result in the formation and growth of YOF crystal nucleus (Fig. 4d). Finally, pure rhombohedral YOF phase have formed at 1100°C, and the average size of YOF submicron–crystals is about 400 nm (Fig. 4e), as the process of “(3) Dissolution-Recrystallization”. Then, with the future increase of temperature to...

**Figure 3** | XRD patterns of YOF submicron-crystals (calcined at 1100°C for 2 h) doped with different Er³⁺ concentrations.

**Figure 4** | SEM images of 4 mol% Er³⁺ doped fluoride precursor powders calcined at different temperatures for 2 h. (a) 400°C, (b) 600°C, (c) 800°C, (d) 1000°C, (e) 1100°C and (f) 1200°C. All of the scale bars are 2 μm. (g) Schematic illustration for the formation process of YOF submicron-crystals.
1200°C, interfacial boundary diffusion is occurred and grain size grow slightly (Fig. 4f), as the process of “(4) Growing”.

In order to further prove the “phase transformation” between the YF₃ and YOF crystalline phase, the thermogravimetry-differential scanning calorimetry (TG-DSC) curves of the fluoride precursor powders in air atmosphere with a heating rate of 10°C/min are shown in Fig. 5. The DSC curve exhibits two endothermic peaks around 366.4°C and 409.0°C which is due to the formation of the YF₃ crystalline phase, and this result agrees well with the XRD result that YF₃ crystalline begin to form at ~400°C (as the XRD pattern shown in Fig. 1). At the same time, during this process, the weight has lost about 10.27% due to the dehydration and vaporization of many kinds of fluoride by-products and residual organics. Moreover, there is also an intense endothermic peak at 1068.7°C due to the formation of YOF crystalline phase which is in accordance with the XRD result that YOF crystalline begin to form at ~1000°C and complete the phase transformation process at ~1100°C (as the XRD patterns shown in Fig. 1). And during this process, the weight of the sample has lost about 2.03% due to the dehydroxylation and dehydration of the sample, which can promote the phase transformation process. From the above results, it is surprising that the TG-DSC results agree well with the XRD results, which confirm the formation and phase transformation of YF₃, YOF and Y₂O₃ crystalline. It is worth mentioning that, due to the rapid heating rate (10°C/min) and short holding time during TG-DSC measurement, a slight error is found between the formation and phase transformation temperature in TG-DSC curves and XRD patterns.

Fig. 6a–d shows SEM images of different concentrations of Er³⁺ doped YF₃ submicron-crystals synthesized by co-precipitation method at 600°C for 2 h. With the increase of Er³⁺ doping concentration, the morphology almost have no obvious change and the average size of YF₃ submicron-crystals is maintained as 300~400 nm. Therefore, it can be deduced that the increase of Er³⁺ doping concentration have no obvious effect on the average size and morphology of YF₃ submicron-crystals. And the similar results are also confirmed in different Er³⁺ concentrations doped YOF submicron-crystals synthesized at 1100°C for 2 h (not illustrated).

Fig. 7a shows the HR-TEM image of YF₃:Er³⁺ submicron-crystals. The crystal lattice fringes with some different spacing d values of ~0.166 nm and ~0.288 nm can be measured directly, which corresponds to the (321) and (210) crystal facets of the orthorhombic phase YF₃, respectively. The selected area electron diffraction (SAED) pattern corresponding to the individual YF₃:Er³⁺ submicron-crystals is shown in Fig. 7b, which indicates the individual YF₃:Er³⁺ submicron-crystals exhibit a single crystalline character. The EDS spectrum of YF₃:Er³⁺ submicron-crystals is also illustrated in Fig. 7c. In the picture, the peaks assigned to designed elements (i.e. Y, F and Er) are clearly observed. Besides the Si peak from the silicon wafer used to pick up the sample in the course of EDS measurement, no other impurity is detected. Thus, the result indicates that the YF₃:Er³⁺ submicron-crystals are mainly consisted of Y, F and Er elements.

Fig. 8a shows the HR-TEM image of YOF:Er³⁺ submicron-crystals, which includes a series of crystals facets. Four kinds of crystal lattice fringes with the spacing d values of ~0.248 nm, ~0.310 nm, ~0.323 nm and ~0.269 nm are observed, which corresponds to the (015), (012), (101) and (104) crystal facets of the...
Figure 7 | (a) HR-TEM image and (b) SAED pattern of the YF$_3$:Er$^{3+}$ submicron-crystals, and the scale bar is 2 nm and 5 1/nm, respectively. (c) EDS spectrum of the YF$_3$:Er$^{3+}$ submicron-crystals. The presence of the Si peak results from the silicon wafer used to pick up the sample in the course of EDS measurement.

Figure 8 | (a) HR-TEM image and (b) SAED pattern of the YOF:Er$^{3+}$ submicron-crystals, and the scale bar is 2 nm and 5 1/nm, respectively. (c) EDS spectrum of the YOF:Er$^{3+}$ submicron-crystals. The presence of the Si peak results from the silicon wafer used to pick up the sample in the course of EDS measurement.
most major reason. Therefore, these three major factors result in that the luminous efficiency of YOF submicron-crystals prepared at 1100°C for 2 h is far better than that of YF₃ submicron-crystals prepared at 600°C for 2 h.

To investigate the luminescence mechanism of 2.7 μm emission, we also investigated the 1.5 μm near-infrared and up-conversion visible emissions of different Er³⁺ doping concentrations in YOF submicron-crystals. With the increase of Er³⁺ doping concentration in YOF submicron-crystals, an emission at 1.5 μm due to the Er³⁺: ⁴I₁₁/₂→⁴I₁₃/₂ transition significantly decreases, as shown in Fig. 12. The up-conversion emissions of YOF:Er³⁺ submicron-crystals are shown in Fig. 13a. The green emissions at 520 nm and 540 nm are attributed to the Er³⁺: ⁴H₁₁/₂→⁴I₁₃/₂ and Er³⁺: ⁴S₅/₂→⁴I₁₃/₂ transitions, the red emissions at 640 nm and 800 nm are attributed to the Er³⁺: ⁴F₉/₂→⁴I₁₃/₂ and Er³⁺: ⁴I₉/₂→⁴I₁₃/₂ transitions. Ratios of the intensity of green emission (540 nm) to red emission (640 nm), G/R are illustrated in Fig. 13b. From this figure, we can find that the value of G/R decreases monotonously with the Er³⁺ doping concentration changing from 2 to 8 mol%. And with the increase of Er³⁺ doping concentration, the intensity of the 800 nm emission has a remarkable increase (Fig. 13c). Thus, these results indicate that the increase of Er³⁺ doping concentration in YOF submicron-crystals results in the decrease of the up-conversion and 1.5 μm emissions, but increases the 2.7 μm and 800 nm emissions.

The 2.7 μm emission of Er³⁺ is due to the ⁴I₁₁/₂→⁴I₃/₂ transition, so the fluorescence decay curves of the ⁴I₃/₂ (1.5 μm emission) and ⁴I₁₁/₂ (2.7 μm emission) levels, as well as the fluorescence lifetime of the two levels, have been measured in Fig. 14 and Fig. 15. With the increase of Er³⁺ doping concentration, both the fluorescence lifetime

Figure 9 | The FTIR spectra of 4 mol% Er³⁺ doped fluoride precursor powders calcined at different temperatures for 2 h.

Figure 10 | The 2.7 μm emission of xEr³⁺ (x = 0, 2, 4, 6, 8 mol%) doped YOF submicron-crystals (calcined at 1100°C for 2 h).Inset: Er³⁺ concentration dependence of the peak intensity of the 2.7 μm emission.

Figure 11 | The 2.7 μm emission of 4 mol% Er³⁺ doped fluoride precursor powders calcined at different temperatures for 2 h. Inset: the enlarged image of the curves of YF₃:Er³⁺ submicron-crystals (calcined at 400°C and 600°C for 2 h) in range from 2400 nm to 3000 nm, respectively.
of the $^{4}I_{11/2}$ and $^{4}I_{13/2}$ levels have remarkable decrease. The fluorescence lifetime of the lower level ($^{4}I_{13/2}$) is decreased from 10.28 ms to 4.14 ms, while that of the upper level ($^{4}I_{11/2}$) is decreased from 3.0 ms to 1.67 ms. Therefore, on these basis, it can be deduced that there should be several energy transfer processes between adjacent Er$^{3+}$ ions, during the process of Er$^{3+}$ doping concentration increasing.

**Discussion**

Obviously, with the increase of Er$^{3+}$ doping concentration, the distance between Er$^{3+}$ ions in YOF crystalline lattices is remarkably decreased and this is benefit for electrons transition and energy recycling between adjacent Er$^{3+}$ ions. Fig. 16 shows the energy levels diagram and possible energy transfer processes between two adjacent Er$^{3+}$ ions. And a novel dynamic circulatory energy transfer mechanism is founded systematically as follows. Electrons in the Er$^{3+}$:$^{4}I_{15/2}$ level are excited to the $^{4}I_{11/2}$ level by the ground state absorption (GSA) process when sample is pumped by 976 nm LD. On one hand, some electrons in the $^{4}I_{11/2}$ level can undergo the excited state absorption (ESA1) and cross relaxation (CR3) processes to make the $^{4}F_{7/2}$ level populated. The excited electrons populated nonradiatively relax to the $^{4}H_{11/2}$, $^{4}S_{3/2}$ and $^{4}F_{9/2}$ levels, and generate the green and red emissions by radiatively relaxation. On the other hand, some electrons in the $^{4}I_{11/2}$ level can nonradiatively or radiatively relax to the $^{4}I_{13/2}$ level, and the radiation relaxation generates the 2.7 μm emission. Subsequently, the majority of electrons in the $^{4}I_{13/2}$ level can radiatively relax to generate the 1.5 μm emission. Moreover, some electrons in the $^{4}I_{13/2}$ level can undergo the ESA2 process to make a contribution to the green and red emissions, or transfer to the $^{4}I_{9/2}$ level by the CR1 process, which generate the 800 nm and 2.7 μm emissions. Moreover, the CR2 process can also change the status of the $^{4}I_{9/2}$ and $^{4}I_{13/2}$ levels. Based on the results discussed above, with the increase of Er$^{3+}$ doping concentration, the possible energy transfer (ET) processes between the same energy levels of two adjacent Er$^{3+}$ ions are more obvious and other energy transfer processes are more active. The ET1, ET2 and CR1 processes can compose a dynamic circulatory energy transfer process. During this process, the CR1 process is crucial importance, which well achieves the population inversion between the $^{4}I_{11/2}$ and $^{4}I_{13/2}$ levels, and makes the energy transfer between adjacent Er$^{3+}$ ions more active, as well as increases the 2.7 μm emission between the two levels (Fig. 10). Meanwhile, due to the CR1 process, the intensity of the 800 nm emission increases (Fig. 13c), while that of the 1.5 μm emission decreases (Fig. 12). Moreover, due to the ET1, ET2 and CR1 processes, the transfer of electrons in the $^{4}I_{13/2}$ and $^{4}I_{11/2}$ levels between two adjacent Er$^{3+}$ ions become an unusual active dynamic processes, so that the fluorescent lifetime of the two levels have a remarkable decrease (Fig. 14 and Fig. 15). And with the increase of Er$^{3+}$ doping concentration.

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**Figure 12** | The 1.5 μm emission of xEr$^{3+}$ (x = 2, 4, 6, 8 mol%) doped YOF submicron-crystals (calcined at 1100°C for 2 h). Inset: Er$^{3+}$ concentration dependence of the peak intensity of the 1.5 μm emission.

**Figure 13** | (a) The up-conversion emissions of xEr$^{3+}$ (x = 2, 4, 6, 8 mol%) doped YOF submicron-crystals (calcined at 1100°C for 2 h). Inset: the enlarged image of the curves in range from 750 nm to 900 nm. (b) Ratio of the intensity of green emission (540 nm) to red emission (640 nm), G/R versus Er$^{3+}$ concentration. (c) The peak intensity of the 800 nm emission versus Er$^{3+}$ concentration.
concentration, the value of \( G/R \) has a larger decrease (Fig. 13b), this is because that the ET processes between the same energy levels of adjacent \( \text{Er}^{3+} \) ions can subsequently suppress the population in excited levels of \( ^2\text{H}_{11/2} \) and \( ^4\text{S}_{3/2} \), resulting in the decrease of green emissions. And during this process, the \( ^4\text{F}_{9/2} \) level has more advantage, resulting in the increase of red emissions, with the increase of \( \text{Er}^{3+} \) doping concentration. At the same time, the CR1 and CR2 processes can also decrease the value of \( G/R \). Therefore, with the increase of \( \text{Er}^{3+} \) doping concentration, the ET1, ET2 and CR1 processes compose the dynamic circulatory energy transfer process occurred between adjacent \( \text{Er}^{3+} \) ions and become ever more active, so that the fluorescent lifetime of \( ^4\text{I}_{15/2} \) and \( ^4\text{I}_{11/2} \) levels have a remarkable decrease. Due to this kind of energy cycle process, although the fluorescent lifetime of upper level \( ^4\text{I}_{11/2} \) is shorter than that of lower level \( ^4\text{I}_{15/2} \), the population inversion between the two levels is well achieved and the 2.7 \( \mu \)m emission can be obtained and enhanced, with the increase of \( \text{Er}^{3+} \) doping concentration.

In conclusion, \( \text{Er}^{3+} \) doped pure rhombohedral phase YOF submicron-crystals were synthesized by the crystalline phase transformed from pure orthorhombic YF\(_3\) submicron-crystals, which were prepared by co-precipitation method and continuous calcining method. And the formation process of YOF submicron-crystals with quasi-spherical morphology mainly contains four steps, “growing”, “self-assemble”, “dissolution-recrystallization” and “growing” processes. Meanwhile, during the process of chemical synthesis, utilized the hydroscopic property of \( \text{NH}_4\text{HF}_2 \) to remove the OH\(^-\) in the structure of crystal particles, and the content of OH\(^-\) was obviously decrease, as confirmed by FTIR spectra. Moreover, with the \( \text{Er}^{3+} \) concentration increasing from 2 to 4 mol\%, the 2.7 \( \mu \)m and 800 nm emissions

**Figure 14** | The fluorescence decay curves of the \( \text{Er}^{3+}:^4\text{I}_{13/2} \) level (1.5 \( \mu \)m emission) in \( \times \text{Er}^{3+} \) (\( x = 2, 4, 6, 8 \) mol\%) doped YOF submicron-crystals (calcined at 1100°C for 2 h).

**Figure 15** | The fluorescence decay curves of the \( \text{Er}^{3+}:^4\text{I}_{11/2} \) level (2.7 \( \mu \)m emission) in \( \times \text{Er}^{3+} \) (\( x = 2, 4, 6, 8 \) mol\%) doped YOF submicron-crystals (calcined at 1100°C for 2 h).

**Figure 16** | The energy levels of \( \text{Er}^{3+} \) with relative transitions and the energy transfer processes between adjacent \( \text{Er}^{3+} \) ions.
were remarkably enhanced, as well as the decrease of 1.5 μm emission and value of G/R. And the fluorescent lifetime of the \( I_{11/2} \) and \( I_{13/2} \) levels obviously decreased with the increase of Er\(^{3+} \) doping concentration, due to the crucial dynamic circulatory energy transfer process (Er\(^{3+} \): \( I_{13/2} \) – Er\(^{3+} \):\( I_{11/2} \) → Er\(^{3+} \):\( I_{13/2} \)). The population inversion is well achieved for the first time. Through the combination with glass matrixes to form nanocrystals/submicron-crystals-glass composites\(^1\), it is expected to open a brand new field for the realization of mid-infrared micro/nano-lasers.

**Methods**

The aqueous solutions of Yb\(^{3+} \) and Er\(^{3+} \) were mixed together to yield the desired stoichiometry of the final submicro-crystals (Yb\(^{3+} \)-Er\(^{3+} \)) with x = 0.02, 0.04, 0.06, 0.08 (in mol). This mixed aqueous solution was added dropwise into an aqueous solution of NH\(_4\)H\(_2\)O (analytical grade) under magnetic stirring at room temperature and the dropping rate was kept at about 2 mL/min. During titration process, ammonium hydroxide (NH\(_4\)H\(_2\)O, analytical grade) was used to adjust the pH value of the mixed solution and the final pH was in the range of 4–5. Then, the mixed solution was aging for 3 h at room temperature. The fluoride precursor nanoparticles were centrifuged and washed with water and ethanol several times to remove residual ammonia and nitric ions. After dried at 80°C for 12 h, the fluoride precursor powders were crushed and calcined in air muffle furnace with a heating rate of 3°C/min and holden at different temperatures for 2 h. Finally, the corresponding submicro-crystals were obtained.

The crystalline structures of YF\(_3\) and YOF submicro-crystals were observed using X-ray diffraction (XRD) on a D8 advance X-ray diffractometer (Bruker, Switzerland) with Cu Ka radiation (λ = 1.54056 Å) and a scanning speed of 0.2°/min. The morphology and size distribution of the powders were observed by field emission-scanning electron microscopy (FE-SEM, Nova NanoSEM430, FEI, Netherlands) equipped with an energy-dispersive X-ray spectrometer (EDS) and high-resolution transmission electron microscopy (HR-TEM, 2100F, JEOL, Japan). Thermal analysis of the precursor powders were conducted using simultaneous thermal analyzer (STA, STA449C/3/MFC/GIPUTIET, NETZSCH, Germany). A heating rate of 10°C/min was adopted. The contents of OH\(^-\) in the crystal particles were estimated from Fourier transform-infrared spectroscopy (FTIR, FTIR-33, Bruker, Switzerland). The phosphorescence lifetime spectra were measured on a Triax 320 spectrometer (Jobin-Yvon Co., France) with a resolution of 0.5 nm, which were estimated from Fourier transform-infrared spectroscopy (FTIR, Vector-33, Bruker, Switzerland). The photoluminescence spectra were measured on a Triax 320 spectrometer (TDS3012C, Tektronix, America) equipped on the Triax 320 spectrometer. All the measurements were carried out at room temperature.

1. Sanamyan, T., Kanskar, M., Xiao, Y., Kedlaya, D. & Dubinskii, M. Er\(^{3+} \)-Y\(^{3+} \) doped Y\(_2\)O\(_3\)-Er\(^{3+} \) doped CaF\(_2\) doped rare-earth doped fluorescence were observed for the first time. Through the combination with glass matrixes to form nanocrystals/submicron-crystals-glass composites\(^1\), it is expected to open a brand new field for the realization of mid-infrared micro/nano-lasers.
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Author contributions
G.P.D. proposed and guided the overall project. G.Q.C performed all experiments and analyzed the result. All the authors discussed the results. G.Q.C. and G.P.D. wrote the manuscript, with comments from J.R.Q., Q.Y.Z. and Z.M.Y.

Additional information
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