Simultaneous morphology evolution and upconversion emission tuning of single Y-based fluoride microcrystal induced by Sc^{3+} co-doping

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ABSTRACT

Upconversion phosphors composed of both gray-white and gray-black microcrystals were synthesized using a facile hydrothermal route. The microcrystals with different contrast in the SEM images were confirmed to be Y-based and Sc-based microcrystals by SEM, XRD, EDX and elemental mapping. The morphology evolution of Y-based microcrystal induced by Sc^{3+} co-doping can be ascribed to the variation of anisotropic growth for different crystal planes. We studied the dependence of fluorescence intensity on pump power and investigated the variation of fluorescence decay dynamics for the different compositions. It was found that an increase of the energy transfer rate from Yb^{3+} to Er^{3+} , Ho^{3+} , Eu^{3+} and Tm^{3+} , and a decrease of the phonon energy by Sc^{3+} co-doping were responsible for the observed fluorescence tuning. Such a simultaneous morphology evolution and upconversion fluorescence tuning of single Y-based fluoride microcrystal with low phonon energy will show a great potential in microlaser, photovoltaics, and photo-communication.

Keywords: A. Optical materials; A. Inorganic compounds; B. Crystal growth; D. Luminescence; D. Phosphors

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1. Introduction

Rare Earth (RE) activated luminescent materials have drawn continued attention in various fields [1-5], due to their unique optical properties arising from their rich energy level structure, narrow excitation/emission bands, long excited state lifetimes, weak background fluorescence, etc [6-11]. Recently, most of the attention is focused on nanocrystals for a variety of potential applications especially as luminescent nano-bioprobes [12-14]. In comparison with doped nanocrystals, RE-doped microcrystals usually show higher luminescence quantum yields due to the smaller surface-to-volume ratio and less surface defects that act as quenching centers. As a result, a rich variety of morphologies and particle sizes can give rise to variations in emission strengths for different emission lines and this is particularly important for RE-doped microcrystals, and their potential application in solar cells, solid state lasers, displays, and optical telecommunication [15-18].

Ion co-doping has been regarded as an efficient strategy for the luminescence tuning and morphology manipulation of RE-doped microcrystals. Recently, remarkable upconversion fluorescence enhancements was accomplished by morphology evolution in β -NaYF₄:Yb³⁺, Er³⁺ microcrystals by K⁺ and Cr³⁺ co-doping [19,20]. The influence of Li⁺ co-doping on the upconversion emission of β -NaLuF₄:Yb³⁺, Ln³⁺ (Ln=Tm, Ho) microcrystals has also been discussed [21]. The luminescence tuning and morphology evolution by non-RE ion co-doping were ascribed to the modification of local crystal field. It is found that co-doping optically active RE ions in microcrystal usually plays a role by acting as a sensitizer for upconversion [22-23]. Obvious upconversion

emission tuning has been realized in single LiYF_4 : Yb^{3+} , Ho^{3+} microcrystal by Ce^{3+} co-doping, but the morphology of microcrystal keeps unchanged, which limits its application [24]. Among various RE-doped microcrystals, Sc^{3+} -codoped microcrystal has been reported rarely [25]. Sc^{3+} is a fluorophilic ion with the smallest RE ion radius, and a distinct ionic electron configuration. Sc^{3+} co-doping can induce some novel spectroscopic properties [26,27]. To the best of our knowledge, simultaneous luminescence tuning and morphology evolution of microcrystalline material induced by Sc^{3+} co-doping have not been reported to date.

Here we present a facile hydrothermal method to synthesize Y-based fluoride microcrystals co-existing with Sc-based analogs by Sc^{3+} co-doping at high temperature in hydrothermal synthesis method. By simply tuning the nominal co-doping concentration of Sc^{3+} , we obtained regular Y-based polyhedron microcrystals with different morphologies, and the formation mechanism will be discussed. More importantly, we also explored the upconversion luminescence tuning of single phase Y-based polyhedron microcrystals and discuss the tuning mechanism. As far as we know, it is the first time report in which variation of the morphology evolution and tuning of the upconversion emission have been realized in single phase Y-based microcrystals by Sc^{3+} co-doping.

2. Experimental details

2.1. Chemicals

All of the chemicals were analytical grade and were used as received without any further purification. NaF (98.0%) and HNO_3 (65.0-68.0%) were provided by

Sinopharm Chemical Reagent Co., Ltd. EDTA (ethylenediaminetetraacetic acid, 99.5%) was purchased from Tianjing Shentong Chemical Reagent Co., Ltd. Ln_2O_3 ($\text{Ln}=\text{Y}$, Yb , Gd , Sc , Er , Tm , Ho , Eu , Sigma-Aldrich, 99.99%) were separately dissolved in nitric acid at elevated temperature followed by evaporating the excess HNO_3 , resulting in the formation of an aqueous solution of the corresponding $\text{Ln}(\text{NO}_3)_3$.

2.2. Preparation

All the samples were synthesized by a facile hydrothermal method. The corresponding details were presented in Table 1. In a typical procedure for the synthesis of sample Er4, an aqueous solution containing $\text{Y}(\text{NO}_3)_3$ (0.5 M, 0.24 mL), $\text{Yb}(\text{NO}_3)_3$ (0.25 M, 0.16 mL), $\text{Gd}(\text{NO}_3)_3$ (0.5 M, 0.08 mL), $\text{Sc}(\text{NO}_3)_3$ (0.5 M, 1.56 mL) and $\text{Er}(\text{NO}_3)_3$ (0.5 M, 0.04 mL) was mixed with deionized water (30 mL) and EDTA (0.2937 g) under vigorous stirring for 30 min to form a chelating complex solution. Subsequently, 0.3 g NaF was added to the solution to form a colloidal suspension and kept under constant stirring for another 30 min. Finally, the obtained solution was slowly transferred into a 40 mL Teflon-lined autoclave and kept at $225\text{ }^{\circ}\text{C}$ for 48 h. The final products were washed with deionized water and anhydrous ethanol several times, then dried at $90\text{ }^{\circ}\text{C}$ for 24 h.

2.3. Characterization

X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/Max2550 diffractometer at a scanning rate of $4^{\circ}\text{ min}^{-1}$, using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda=0.15406\text{ nm}$). The morphology and elemental analysis were carried on a

scanning electron microscope (SEM, Quanta 200, accelerating voltage: 200 kV) equipped with an energy-dispersive X-ray analysis (EDX, Genesis XM, spot scanning mode), and a JEM-2100F field emission transmission electron microscope (TEM, accelerating voltage: 200 kV). A Ti sapphire femtosecond laser (Mira-900) was employed as excitation source. A SP 2750i monochromator (ACTON, spectral resolution: 0.008 nm) equipped with a PIXIS 100 charge coupled device (CCD, ACTON) was used for spectrum acquisition. Laser confocal microscopy was realized by an OLYMPUS BX51 optical microscope. A 980 nm diode laser (Changchun New Industries Optoelectronics Technology Co., Ltd.) and a boxcar (SRS) were used for upconversion fluorescence decay profile collection. Proper notch filters were placed in front of the monochromator to block the scattering light.

3. Results and discussion

3.1. Crystal structure

SEM images of sample Er0-4 were shown in Fig. 1. As shown in Fig. 1(a), except for a few thin microrods, the Sc^{3+} -free sample (Er0) was almost entirely composed of short hexagonal prisms with an average size of 7 μm in length and 5 μm in diameter. Two kinds of morphologies have been observed in the 18% Sc^{3+} -doped sample (Er1). One is small octadecahedron with cracked ends, and the other is big hexagonal prism with a number of discrete tips (Fig. 1(b)). By doping with higher Sc^{3+} concentrations (38-78%, Fig. 1(c)-(e)), the number of irregular octadecahedrons decreased, and the average size of irregular octadecahedrons in sample Er4 (78% Sc^{3+}) was significantly smaller than those included in sample Er2-3. Additionally, a distinct

amorphous gray-black crystal with increased Sc content was also present in sample Er2-4.

XRD patterns were recorded to investigate the crystal structure of as-prepared samples. As shown in Fig. 2, all the diffraction peaks of Sc^{3+} -free sample can be well indexed with hexagonal NaYF_4 (JCPDS 16-0334), which gives evidence for the formation of a single phase crystalline material. When the Sc^{3+} concentration varies in the range of 18-58%, several additional peaks at $\sim 22^\circ$ and 45° appear and are ascribed to monoclinic Na_3ScF_6 (JCPDS 47-1221), and their intensities keep increasing with the increasing content of Sc^{3+} . It is suggested that hexagonal NaYF_4 and monoclinic Na_3ScF_6 coexist in sample Er1-3. Apart from the dominant strong peaks that belong to hexagonal NaYF_4 , three other weak peaks belonging to monoclinic Na_3ScF_6 and two peaks belonging to hexagonal NaScF_4 (JCPDS 20-1152) emerged for sample Er4 (78% Sc^{3+}). We suggest that the microcrystals with a different contrast in SEM (gray-white and gray-black microcrystals, Fig. 1) are Y-based (hexagonal NaYF_4) and Sc-based (monoclinic Na_3ScF_6 and/or hexagonal NaScF_4) microcrystals, respectively. Additionally, the peaks around 22° and 45° that belong to monoclinic Na_3ScF_6 disappeared in sample Er4, which can be ascribed to the higher Sc^{3+} concentration of precursor solution (78%). The symmetry of hexagonal NaScF_4 is higher than that for monoclinic Na_3ScF_6 , and needs the higher binding energy. The higher Sc^{3+} concentration means the smaller interionic distance, and it's beneficial to provide a high binding energy.

To verify the identification and to determine the elemental composition of the two

kinds of microcrystals, EDX spectra were collected in the spot scanning mode. The scanning spots labeled as red and blue solid circles in the insets of Fig. 3 correspond to Y- and Sc-based microcrystals suggested above, respectively. The EDX spectra confirmed the presence of Na, F, Y, Yb, Gd, Er elements in all the samples, and additional Sc in Sc^{3+} -doped samples. Furthermore, the Sc content in blue region was much higher than that in red region (Fig. 3(b) and (c)), which agrees well with the XRD and SEM results. Although the amount of Sc^{3+} that really entered into the Y- or Sc-based crystal lattices increased with the increasing of the added Sc^{3+} , the actual amount, especially for the Y-based microcrystals, was clearly smaller than the nominal concentration, which can be ascribed to the large difference in ionic radius between Sc^{3+} and other RE ions. As shown in Fig. 2, the diffraction peaks associated with the hexagonal NaYF_4 phase shift slightly to the larger angle when the actual Sc^{3+} content increases. Combining with Bragg's Law, we can find it was caused by the decrease of crystalline interplanar spacing, which was induced by the introduction of a small amount of Sc^{3+} (with the smallest RE ionic radius) into the lattices.

As shown in Fig. 4, F, Na, Sc, Y, Gd, Yb and Er elements appear in sample Er4, simultaneously. Figs. 4(b) and (c) show clearly that F and Na elements distribute homogeneously in the Y- and Sc-based microcrystals. More importantly, the Sc element mainly distributes in the Sc-based microcrystals (Fig. 4(d)), and the Y, Gd, Yb and Er elements mainly distributed in the Y-based microcrystals (Fig. 4(e)-(h)). It agrees well with the XRD and EDX results which also suggest the formation of two types of microcrystals with different composition and crystal structure.

3.2. Morphology evolution

To understand the morphology evolution mechanism of Y-based microcrystals, the influence of hydrothermal synthesis temperature and time were studied and used to obtain insight in the intermediate products. The SEM pictures of obtained intermediate samples corresponding to sample Er0-4 are shown in Figs. 5 and 6, respectively. It can be clearly seen that the Sc^{3+} -free sample (Er01) was composed of a large number of nanocrystals (around 200 nm, Fig. 5(a)). Before the hydrothermal action, the complexation between RE ions and EDTA molecules was strong. The obtained intermediate nanocrystals (sample Er01) for low reaction temperature and short reaction times can be well indexed with the metastable cubic $\text{Na}_5\text{Y}_9\text{F}_{32}$ structure (JCPDS No. 27-1428, not shown). It has been reported that the radius of doped ion plays a vital role for the crystal stability of NaYF_4 , in which the smaller radius ions favor formation of the cubic phase while the bigger ions are inclined to form the hexagonal phase [28,29]. On the other hand, the number of Y-based microcrystals increased gradually with the increasing of the doped Sc^{3+} (Fig. 5(b)-(e)), and the number of nanocrystals attached on their surfaces decreased simultaneously. When the nominal concentration of Sc^{3+} reaches 78%, a complete phase transformation of Y-based microcrystals from cubic to hexagonal has been realized (Fig. 5(e)). It indicates that the small radius Sc^{3+} favored the formation of hexagonal NaYF_4 . Meanwhile, the growth of the six crystal planes belonging to the $\{10\bar{1}0\}$ family and the two belonging to the $\{0001\}$ family have been restrained, and those for the 12 crystal planes of $\{20\bar{2}1\}$ family have been accelerated (Fig. 5(b)-(e)). A part of

microcrystals with a morphology of dodecahedron has also been found (Fig. 5(e)), which was induced by the oriented growth of Y-based microcrystal. When the reaction time decreased to 2 h, only a few microcrystals with a size of 1-2 μm were found in the samples doped 38%, 58% and 78% Sc^{3+} (Fig. 6).

All the results discussed above confirm that the introduction of Sc^{3+} causes a faster growth of Y-based microcrystal. It induced the accelerated growth of $\{20\bar{2}1\}$ crystal planes, and the decelerated growth of $\{10\bar{1}0\}$ and $\{0001\}$ crystal planes, respectively. The observed morphology evolution of octahedron→icosahedron→octadecahedron (Fig. 5(c)-(e)) can be ascribed to the anisotropic growth of different crystal planes. It should be noted that the actual number of Sc^{3+} ions that entered into the crystal lattices of Y-based microcrystals was very low. A large part of Sc^{3+} was used to form monoclinic/hexagonal Sc-based microcrystals under hydrothermal atmosphere at high temperature and long reaction time. As the radius of non- Sc^{3+} RE ion (Y^{3+} , Gd^{3+} , Er^{3+} and Yb^{3+}) is much bigger than that of Sc^{3+} , these ions are not easily incorporated into the Sc-based microcrystals (Fig. 4). The rest of Sc^{3+} probably served as the separant of the Y-based crystal seeds, and helped them to grow to the critical size for the transformation of cubic to hexagonal.

3.2. Upconversion emission tuning

Normalized upconversion emission spectra and photographs of single luminescent Y-based microcrystal are presented in Fig. 7. The corresponding upconversion mechanisms are shown in Fig. 8. A series of typical upconversion emission intensity vs pump power plots for sample Er0-4 is also presented in Fig. 9. All the obtained

slopes were close to 2, which is consistent with the suggested upconversion mechanisms in suggested in Fig. 8. In the Er^{3+} , Ho^{3+} and Eu^{3+} doped samples, the relative intensity of green emission band (Fig. 8(a)-(c): $^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (Er^{3+}), $^5\text{F}_4/^5\text{S}_2 \rightarrow ^5\text{I}_8$ (Ho^{3+}), $^5\text{D}_1 \rightarrow ^7\text{F}_{1,2}$ (Eu^{3+})) to the red counterpart (Fig. 8(a)-(c): $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (Er^{3+}), $^5\text{F}_5 \rightarrow ^5\text{I}_8$ (Ho^{3+}), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (Eu^{3+})) increased with the increasing of co-doping of Sc^{3+} (Fig. 7(a)-(c)). On the contrary, for Tm^{3+} the intensity ratio of blue emission band ($^1\text{D}_2 \rightarrow ^3\text{F}_4$) to the near-infrared emission band ($^3\text{H}_4 \rightarrow ^3\text{H}_6$) decreased with an increase of Sc^{3+} of co-doping in the Tm^{3+} doped sample (Fig. 7(d)). Obvious upconversion fluorescence enhancement has been realized in Yb^{3+} , Er^{3+} and Sc^{3+} triply-doped NaYF_4 microcrystal, which was ascribed to the decrease of local symmetry proposed by Huang et al [25]. In the current system, the fluorescence intensity ratio of the forced electric dipole transition of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to the magnetic dipole transition of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ shows no significant change in each of Eu^{3+} containing samples (the inset of Fig. 7(c)), which indicates that the local symmetry around luminescent ion has not changed significantly by Sc^{3+} co-doping. We can argue that the upconversion emission tuning was probably not induced by the variation of local symmetry.

However, the line shapes of some emission bands (such as $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ of Er^{3+} , $^5\text{D}_0 \rightarrow ^7\text{F}_3$ of Eu^{3+} , and $^3\text{H}_4 \rightarrow ^3\text{H}_6$ of Tm^{3+}) change obviously with Sc^{3+} content, (Fig. 7). As the $4f$ electrons of trivalent RE ions are shielded by the outer $5s^25p^6$ electrons, the electron-phonon coupling is very weak, and its influence on the line shape can be ignored. The RE ion energy level of $^{2S+1}\text{L}_J$ (S, L, and J are spin, angular, and total quantum numbers, respectively) has a degeneracy of $2J+1$, and can be splitted into at

most $2J+1$ Stark energy levels by crystal field. The sub-emission peaks associated with a same emission band in Fig. 7 can be ascribed to the transitions from different Stark energy levels of excited state to the ground state counterparts. For the emission bands mentioned above, the peak positions of these sub-transitions keeps unchanged for different Sc^{3+} -doped samples, but the relative emission intensities change obviously. As the energy gap between $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ of Er^{3+} is very small, the emission intensity ratio of $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ can be employed to measure the local temperatures around luminescent centers [30,31], and the higher ratio means the higher local temperature. We calculate the ratio for different samples, and find the ratio varies obviously with the variation of Sc^{3+} -doped concentration, which means the local temperatures changed obviously. It induces different populations for the Stark energy levels that belong to a same excited/ground state, thus giving different sub-transition intensities for different Sc^{3+} -doped samples.

From the EDX measurements (Fig. 3), we can conclude that the most of RE ions were incorporated in the Y-based microcrystals, except for Sc^{3+} . From sample Er0 to Er4, the actual Er^{3+} concentrations of the Y-based microcrystals were 1.41%, 1.43%, 1.39%, 1.37% and 1.43%, respectively. All the relative errors were less than 3%. For the actual Yb^{3+} concentration, the same result has been obtained, apart from a maximum relative error of 2.8%. Additionally, we have also found the upconversion emission intensity of Sc-based microcrystals was much weaker than that in Y-based counterpart. All these suggest that the upconversion emission tuning was probably not caused by the variations of the activator or sensitizer ion concentrations, and their

ratio.

The diameter of laser beam used in current system can only be focused to 1 μm , which is much smaller than the average size of Y-based microcrystal. We focused the excitation light spot on the different positions of single microcrystal, and no significant variation of relative intensity was found. It indicates that the upconversion emission tuning was not caused by a variation in the position of the excitation beam. For single Y-based microcrystals with different morphologies, the relative intensity of different emission bands stays nearly unchanged, which shows that the influence of morphology on the fluorescence tuning can also be ignored.

The observed upconversion emission tuning in Fig. 7(a)-(c) indicates that the relative population between the emitting energy levels for green and red emission has been changed strongly by Sc^{3+} co-doping. As shown in Fig. 8(c), the upconversion emission of Eu^{3+} is realized by a cooperative energy transfer process that involves two excited Yb^{3+} ions [32]. It suggests that the employed excitation power was high enough to bridge the initial state ($^2\text{F}_{7/2}$) and the emission states ($^5\text{D}_{0,1}$). The distance R between luminescent ion (Er^{3+} , Ho^{3+} and Eu^{3+}) and sensitizer ion (Yb^{3+}) will be shortened after the Sc^{3+} (the smallest radius RE ion) enters into the crystal lattice. The energy transfer from the sensitizer ion to the luminescent ion involves dipole-dipole interaction, in which case the transfer rate is proportional to R^{-6} [33,34]. In the current system, the higher transfer rate can be induced by Sc^{3+} co-doping. As the excitation power is sufficiently high, the higher energy level of green fluorescence (Fig. 8(a)-(c): $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ (Er^{3+}), $^5\text{F}_4/^5\text{S}_2$ (Ho^{3+}), $^5\text{D}_1$ (Eu^{3+})) can be populated much easier than that

for the red counterpart.

On the other hand, as the maximum phonon energy of NaLnF₄ (Ln=RE element) decreased gradually by reducing the atomic weight of RE element [35], the maximum phonon energy will be reduced by Sc³⁺ codoping as Sc is the lightest RE element, and the fact that Sc³⁺ radius is the smallest among trivalent RE ions. The multi-phonon relaxation rate for various processes (Fig. 8(a)-(c): $^4S_{3/2} \rightarrow ^4F_{9/2}$, $^4I_{11/2} \rightarrow ^4I_{13/2}$ (Er³⁺); $^5S_2/^5F_4 \rightarrow ^5F_5$, $^5I_6 \rightarrow ^5I_7$ (Ho³⁺); $^5D_1 \rightarrow ^5D_0$ (Eu³⁺)) will be decreased by reducing the phonon energy, which reduces the relative population for the emitted energy level of red fluorescence (Fig. 8(a)-(c)) and increases the relative population of the green counterpart, simultaneously. For Tm³⁺-contained Y-based microcrystal, the reduction of the maximum phonon energy can render the population of $^1D_2$ state more difficult than $^3H_4$ state as a three-photon process and a cross relaxation process ($(^1G_4, ^3H_4) \rightarrow (^1D_2, ^3F_4)$) have been involved in the $^1D_2 \rightarrow ^3F_4$ transition (Fig. 7(d)), which induced the relative intensity tuning as shown in Fig. 7(d).

Typical normalized upconversion fluorescence decay profiles of sample Er0-4 (for $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions) are presented in Fig. 10. By fitting these decay curves with bio-exponential functions, the rise and decay times were extracted, as shown in Table 2, in which the ratio denotes the ratio of rise or decay time for sample Er0 to that for sample Eri (i=0,1, ... , 4). It can be seen clearly that the rise time decreased gradually with increasing of Sc³⁺ concentration for both transitions. Furthermore, it decreased slower for the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition than for the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition, which was induced by the stiffer competition between the

increase of the energy transfer rate and the decrease of the multi-phonon relaxation rate, as there are two multi-phonon relaxation processes have been involved the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition and only one for $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition (Fig. 8). Simultaneously, we have found the decay time increased gradually with increasing of Sc^{3+} concentration for both transitions, and the rate of increase is faster for the red transition than that for the green transition, which gives a clear evidence of the increase of maximum phonon energy. For the $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission band, we have also found that the obtained slope by linear fitting increased gradually with the increasing of Sc^{3+} concentration, as opposed to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ emission band (Fig. 9), which proves the previous discussion about the adjustment of relative populations by decreasing the maximum phonon energy to be reasonable.

Additionally, with a tripling in the Yb^{3+} doped concentration of sample Er0-4 (Table 1), the similar morphology evolution has also been observed in Fig. 11. More significantly, the upconversion emission tuning turns to be more distinct and can be discerned by naked eye (Fig. 12), which provides further powerful evidence for the increase of the energy transfer rate by Sc^{3+} codoping. As a result, the increase of energy transfer rate to different degrees for these main upconversion transitions, and the decrease of maximum phonon energy by Sc^{3+} codoping should be mainly responsible for the observed upconversion emission tuning.

More recently, simultaneous quasi-one-dimensional propagation and tuning of upconversion luminescence in a single β - $NaYF_4:Yb^{3+}, Er^{3+}$ microtube has been realized by Gao et al [36], which indicates the upconversion emission in microcrystal

with regular morphology could be confined to a micro-scale. Analogously, if the upconversion emission is confined to the current octadecahedron microcrystal, it can be acted as a micro laser resonator, which can eliminate excitation energy losses by the two sharp tips of octadecahedron.

4. Conclusion

In conclusion, with Sc^{3+} co-doping, a simultaneous morphology evolution and the upconversion emission tuning in single microcrystallites has been realized by a facile hydrothermal synthesis strategy. Regular Y-based microcrystals with various polyhedron morphologies accompanied with Sc-based counterpart of a different morphology can be synthesized and controlled via the Sc^{3+} concentration. Based on the crystal phases identified and morphology evolution observed, a mechanism for the formation of the Y-based microcrystal has been presented. Upconversion emission tuning of main emission bands for single Y-based microcrystal which contained luminescent ions (Er^{3+} , Ho^{3+} , Eu^{3+} , Tm^{3+}) has been significantly improved by Sc^{3+} co-doping. The spectroscopic results indicated that the change of relative population for various emitting excited states is induced by the variation of the energy transfer rate, and that the maximum phonon energy were the main reasons for the observed upconversion emission tuning. The current study provides a simple and new strategy for simultaneous morphology evolution and upconversion emission tuning of single RE-doped microcrystals, which be important for the development of new luminescent materials in the fields of microlaser, photovoltaics, and photo-communication.

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References

- [1] H.H. Gorris, O.S. Wolfbeis, *Angew. Chem. Int. Ed.* 52 (2013) 3584-3600.
- [2] M. Xin, D.T. Tu, H.M. Zhu, W.Q. Luo, Z.G. Liu, P. Huang, R.F. Li, Y.G. Cao, X.Y. Chen, *J. Mater. Chem. C* 3 (2015) 7286-7293.
- [3] S.W. Hao, L.M. Yang, H.L. Qiu, R.W. Fan, C.H. Yang, G.Y. Chen, *Nanoscale* 7 (2015) 10775-10780.
- [4] R. Cheng, Y.R. Chen, Z.Q. Li, X.H. Chen, P.X. Yang, H.B. Zhu, Y.L. Huang, Z. Sun, S.M. Huang, *J. Mater. Sci-Mater. El.* 25 (2014) 4066-4073.
- [5] X.H. He, B. Yan, *CrystEngComm*, 17 (2015) 621-627.
- [6] B.R. Judd, *Phys. Rev.* 127 (1962) 750-761.
- [7] G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511-520.
- [8] X.Y. Huang, Q.Y. Zhang, *J. Appl. Phys.* 107 (2010) 063505.

- [9] S. Sarkar, B. Meesaragandla, C. Hazra, V. Mahalingam, *Adv. Mater.* 25 (2013) 856-860.
- [10] R. Kolesov, K. Xia, R. Reuter, R. Stöhr, A. Zappe, J. Meijer, P.R. Hemmer, J. Wrachtrup, *Nat. Commun.* 3 (2012) 1029.
- [11] W. Zheng, P. Huang, D.T. Tu, E. Ma, H.M. Zhu, X. Y. Chen, *Chem. Soc. Rev.* 44 (2015) 1379-1415.
- [12] S. Lu, D.T. Tu, P. Hu, J. Xu, R.F. Li, M. Wang, Z. Chen, X.Y. Chen, *Angew. Chem. Int. Ed.* 54 (2015) 7915-7919.
- [13] S. Majeed, M. Bashir, S.A. Shivashankar, *J. Nanopart. Res.* 17 (2015) 309.
- [14] T.S. Yang, Y. Sun, Q. Liu, W. Feng, P.Y. Yang, F.Y. Li, *Biomaterials*, 33 (2012) 3733-3742.
- [15] G.E. Arnaoutakis, J. Marques-Huesoa, A. Ivaturi, S. Fischer, J.C. Goldschmidt, K.W. Krämer, B.S. Richards, *Sol. Energ. Mat. Sol. C.* 140 (2015) 217-223.
- [16] F. Wang, X.G. Liu, *Chem. Soc. Rev.* 38 (2009) 976-989.
- [17] E. Downing, L. Hesselink, J. Ralston, R. Macfarlane, *Science* 273 (1996) 1185-1189.
- [18] G. Rumbles, *Nature*, 409 (2001) 572-573.
- [19] M.Y. Ding, D.Q. Chen, S.L. Yin, Z.G. Ji, J.S. Zhong, Y.R. Ni, C.H. Lu, Z.Z. Xu, *Sci. Rep-UK* 5 (2015) 12745.
- [20] C.Y. Wang, X.H. Cheng, *J. Alloy. Compd.* 649 (2015) 196-203.
- [21] H. Lin, D.K. Xu, D.D. Teng, S.H. Yang, Y.L. Zhang, *New J. Chem.* 39 (2015) 2565-2572.

- [22] L.L. Wang, M. Lan, Z.Y. Liu, G.S. Qin, C.F. Wu, X. Wang, W.P. Qin, W. Huang, L. Huang, *J. Mater. Chem. C* 1 (2013) 2485-2490.
- [23] G.F. Wang, W.P. Qin, L.L. Wang, G.D. Wei, P.F. Zhu, R. Kim, *Opt. Express* 16 (2008) 11907-11914.
- [24] W. Gao, R.B. Wang, Q.Y. Han, J. Dong, L.X. Yan, H.R. Zheng, *J. Phys. Chem. C* 119 (2015) 2349-2355.
- [25] Q.M. Huang, J.C. Yu, En Ma, K.M. Lin, *J. Phys. Chem. C* 114 (2010) 4719-4724.
- [26] X.H. He, B. Yan, *Cryst. Growth Des.* 14 (2014) 3257-3263.
- [27] X. Teng, Y.H. Zhu, W. Wei, S.C. Wang, J.F. Huang, R. Naccache, W.B. Hu, A.I.Y. Tok, Y. Han, Q.C. Zhang, Q.L. Fan, W. Huang, J.A. Capobianco, L. Huang, *J. Am. Chem. Soc.* 134 (2012) 8340-8343.
- [28] Q.Q. Dou, Y. Zhang, *Langmuir* 27 (2011) 13236-13241.
- [29] D.L. Gao, X.Z. Zhang, W. Gao, *ACS Appl. Mater. Interfaces* 5 (2013) 9732-9739.
- [30] L. Aigouy, G. Tessier, M. Mortier, B. Charlot, *Appl. Phys. Lett.* 87 (2005) 184105.
- [31] F. Auzel, *Chem. Rev.* 104 (2004) 139-174.
- [32] Y. Dwivedi, S.N. Thakur, S.B. Rai, *Appl. Phys. B* 89 (2007) 45-51.
- [33] A. Chalzel, *J. Chem. Phys.* 67 (1977) 4735.
- [34] S. Saini, H. Singh, B. Bangchi, *J. Chem. Sci.* 118 (2006) 23-35.
- [35] M.M. Lage, R.L. Moreira, F.M. Matinaga, J.Y. Gesland, *Chem. Mater.* 17 (2005)

4523-4529.

[36] D.L. Gao, D.P. Tian, X.Y. Zhang, W. Gao, Sci. Rep. 6 (2016) 22433.

Table 1 Details of as-prepared samples.

Name	Nominal molar content of RE ion (%)								Hydrothermal condition	
	Sc ³⁺	Yb ³⁺	Y ³⁺	Gd ³⁺	Er ³⁺	Ho ³⁺	Eu ³⁺	Tm ³⁺	Temperature (°C)	Time (h)
Er0	0	19.6	58.8	19.6	2	0	0	0	225	48
Er1	18	16	48	16	2	0	0	0		
Er2	38	12	36	12	2	0	0	0		
Er3	58	8	24	8	2	0	0	0		
Er4	78	4	12	4	2	0	0	0		
Er5	0	58.8	19.6	19.6	2	0	0	0	225	48
Er6	18	48	16	16	2	0	0	0		
Er7	38	36	12	12	2	0	0	0		
Er8	58	24	8	8	2	0	0	0		
Er9	78	12	4	4	2	0	0	0		
Er01	0	19.6	58.8	19.6	2	0	0	0	180	12
Er11	18	16	48	16	2	0	0	0		
Er21	38	12	36	12	2	0	0	0		
Er31	58	8	24	8	2	0	0	0		
Er41	78	4	12	4	2	0	0	0		
Er02	0	19.6	58.8	19.6	2	0	0	0	180	2
Er12	18	16	48	16	2	0	0	0		
Er22	38	12	36	12	2	0	0	0		
Er32	58	8	24	8	2	0	0	0		
Er42	78	4	12	4	2	0	0	0		
Ho0	0	19.6	58.8	19.6	0	2	0	0	225	48
Ho1	18	16	48	16	0	2	0	0		
Ho2	38	12	36	12	0	2	0	0		
Ho3	58	8	24	8	0	2	0	0		
Ho4	78	4	12	4	0	2	0	0		
Eu0	0	19.6	58.8	19.6	0	0	2	0	225	48
Eu1	18	16	48	16	0	0	2	0		
Eu2	38	12	36	12	0	0	2	0		
Eu3	58	8	24	8	0	0	2	0		
Eu4	78	4	12	4	0	0	2	0		
Tm0	0	19.6	58.8	19.6	0	0	0	2	225	48
Tm1	18	16	48	16	0	0	0	2		
Tm2	38	12	36	12	0	0	0	2		
Tm3	58	8	24	8	0	0	0	2		
Tm4	78	4	12	4	0	0	0	2		

Table 2 Rise and decay times of sample Er0-4 for the transitions $^4S_{3/2} \rightarrow ^4I_{15/2}$ (monitored wavelength: 538.34 nm) and $^4F_{9/2} \rightarrow ^4I_{15/2}$ (monitored wavelength: 653.11 nm) obtained by fitting with bio-exponential functions (ratio denotes the ratio of rise or decay time for sample Er0 to that for sample Eri (i=0,1, ... , 4)).

Name	$^4S_{3/2} \rightarrow ^4I_{15/2}$ (538.34 nm)				$^4F_{9/2} \rightarrow ^4I_{15/2}$ (653.11 nm)			
	Rise (μ s)	Ratio	Decay (μ s)	Ratio	Rise (μ s)	Ratio	Decay (μ s)	Ratio
Er0	66.44	1.00	100.18	1.00	34.50	1.00	160.99	1.00
Er1	50.82	0.76	111.01	1.11	29.43	0.85	169.19	1.05
Er2	44.91	0.68	123.47	1.23	25.58	0.74	177.34	1.10
Er3	35.96	0.54	135.66	1.35	20.88	0.61	182.38	1.13
Er4	21.75	0.33	145.62	1.45	19.52	0.57	188.70	1.17

Figure captions

Fig. 1. SEM images of sample (a) Er0, (b) Er1, (c) Er2, (d) Er3 and (e) Er4 (scaling factor: 30 μ m).

Fig. 2. XRD patterns of sample Er0-4.

Fig. 3. EDX spectra of sample (a) Er0, (b) Er2 and (c) Er4 (inset: the SEM image for the corresponding sample, red and blue spots indicate the locations of scanning spots).

Fig. 4. (a) SEM picture of sample Er4 and corresponding element mappings for (b) F, (c) Na, (d) Sc, (e) Y, (f) Gd, (g) Yb and (h) Er elements (Collect condition: Res, 512x400; Dwell, 200 μ s; ROIs, 2; Frames, 64).

Fig. 5. SEM pictures of sample (a) Er01, (b) Er11, (c) Er21, (d) Er31 and (e) Er41 (scaling factor: 20 μ m), and the TEM pictures of small nanocrystals for the corresponding samples (the scaling factor of inset: 200 nm).

Fig. 6. SEM pictures of sample (a) Er02, (b) Er12, (c) Er22, (d) Er32 and (e) Er42

(scaling factor: 20 μm).

Fig. 7. Upconversion emission spectra of single Y-based microcrystal for (a) Er^{3+} (normalized to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$), (b) Ho^{3+} (normalized to $^5\text{F}_5 \rightarrow ^5\text{I}_8$, except for sample Ho4), (c) Eu^{3+} (normalized to $^5\text{D}_0 \rightarrow ^7\text{F}_3$, inset: the amplification of 585-625 nm spectral region) and (d) Tm^{3+} (normalized to $^3\text{H}_4 \rightarrow ^3\text{H}_6$) contained samples ($\lambda_{\text{exc}}=980$ nm, inset: luminescent photographs for single microcrystal).

Fig. 8. Schematic energy level diagrams with proposed upconversion mechanisms for Yb^{3+} and (a) Er^{3+} , (b) Ho^{3+} , (c) Eu^{3+} and (d) Tm^{3+} codoped Y-based microcrystals ($\lambda_{\text{exc}}=980$ nm).

Fig. 9. Integrated intensity of upconversion fluorescence emission band of (a) $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and (b) $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ vs pump power for sample Er0-4 (scattered point: measured data, solid line: linear fitting).

Fig. 10. Normalized upconversion fluorescence decay profiles of sample Er0-4 for the transitions of (a) $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (monitored wavelength: 538.34 nm) and (b) $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (monitored wavelength: 653.11 nm).

Fig. 11. SEM pictures of sample (a) Er5, (b) Er6, (c) Er7, (d) Er8 and (e) Er9 (scaling factor: 30 μm).

Fig. 12. Upconversion emission spectra (normalized to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) of single Y-based microcrystal for sample Er5-9 ($\lambda_{\text{exc}}=980$ nm, inset: luminescent photographs for single microcrystal).

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12