Morphology evolution and pure red upconversion mechanism of \(\beta\)-NaLuF\(_4\) crystals

Hao Lin, Dekang Xu, Anming Li, Dongdong Teng, Shenghong Yang & Yueli Zhang

A series of \(\beta\)-NaLuF\(_4\) crystals were synthesized via a hydrothermal method. Hexagonal phase microdisks, microprisms, and microtubes were achieved by simply changing the amount of citric acid in the initial reaction solution. Pure red upconversion (UC) luminescence can be observed in \(\beta\)-NaLuF\(_4\):Yb\(^{3+}\), Tm\(^{3+}\), Er\(^{3+}\) and Li\(^+\) doped \(\beta\)-NaLuF\(_4\):20\% Yb\(^{3+}\), 1\% Tm\(^{3+}\), 20\% Er\(^{3+}\). Based on the rate equations, we report the theoretical model about the pure red UC mechanism in Yb\(^{3+}/\)Tm\(^{3+}\)/Er\(^{3+}\) doped system. It is proposed that the pure red UC luminescence is mainly ascribed to the energy transfer UC from Tm\(^{3+}\):F\(_{4}\) \(\rightarrow\) H\(_2\) to Er\(^{3+}\):I\(_{11/2}\) \(\rightarrow\) F\(_{9/2}\) and the cross-relaxation (CR) effect [Er\(^{3+}\):S\(_{11/2}\) + I\(_{11/2}\) \(\rightarrow\) I\(_{9/2}\) + F\(_{9/2}\)] rather than the long-accepted mechanism (CR process among Er\(^{3+}\):F\(_{7/2}\) + I\(_{11/2}\) \(\rightarrow\) F\(_{9/2}\) + F\(_{9/2}\)). In addition, compared to the Li\(^+\)-free counterpart, the pure red UC luminescence in \(\beta\)-NaLuF\(_4\):20\% Yb\(^{3+}\), 1\% Tm\(^{3+}\), 20\% Er\(^{3+}\) with 15 mol\% Li\(^+\) doping is enhanced by 13.7 times. This study provides a general and effective approach to obtain intense pure red UC luminescence, which can be applied to other synthetic strategies.

Recently, lanthanide (Ln) doped upconversion (UC) materials have aroused extensive attention because of their potential applications in fields such as flat-panel displays, therapeutics, photovoltaics, and biological imaging\(^{1-9}\). Their advantages include long luminescence lifetimes, low toxicity and high photochemical stability\(^{10-14}\), which make them more desirable than conventional fluorescent materials. As an important fluoride, \(\beta\)-NaLuF\(_4\) has excellent UC luminescence due to its high refractive index, low phonon energy, and high thermal stability, which has attracted significant interest\(^{15-18}\). In contrast to green and blue light, red light (600–700 nm) can deeply penetrate biotissues owing to the lack of efficient endogenous absorbers\(^{19-21}\). Consequently, a strategy to achieve high purity of red UC luminescence will be useful for UC applications, especially for biological imaging. As is known, UC materials usually display multiplex emissions due to Ln ions have more than one metastable excited state\(^{19}\). Thus, avoiding the blue and green emissions and boosting the red emission are needed to obtain high pure red UC luminescence. For instance, Tan et al. reported the pure red UC emission in NaYbF\(_4\) nanocrystals doping with Tm\(^{3+}\)/Er\(^{3+}\) codoped system. The first CR effect is the long-accepted and most popular mechanism\(^{22-24}\). According to Capobianco et al.’s report\(^{25}\), the enhanced red UC emission was obtained owing to a CR process [Er\(^{3+}\):F\(_{7/2}\) + I\(_{11/2}\) \(\rightarrow\) F\(_{9/2}\) + F\(_{9/2}\)]. In addition, compared to the Li\(^+\)-free counterpart, the pure red UC luminescence in NaYbF\(_4\):1\% Tm\(^{3+}\), 20\% Er\(^{3+}\) with 15 mol\% Li\(^+\) doping is enhanced by 13.7 times. This study provides a general and effective approach to obtain intense pure red UC luminescence, which can be applied to other synthetic strategies.

State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China. Correspondence and requests for materials should be addressed to Y.Z. (email: stszyl@mail.sysu.edu.cn)
The hollow structure of the tubes is generated owing to the growth rate at the center is lower than that at the edges. And (c) chelating agent has a great impact on the kinetics of crystal growth. Citric acid plays a critical role in the morphology evolution of the final products due to its high thermal stability and ability to form complexes with other metal ions.

In this article, a series of \( \beta \)-NaLuF\(_4\) crystals were prepared via a hydrothermal method using citric acid as a chelating agent, and their pure red UC luminescence were studied. Hexagonal phase microdisks, microprisms, and microtubes were achieved by simply changing the amount of citric acid in the initial reaction solution. Importantly, pure red UC luminescence can be observed in \( \beta \)-NaLuF\(_4\); \( \text{Yb}^{3+}, \text{Tm}^{3+}, \text{Er}^{3+} \) and \( \text{Li}^{+} \) doped \( \beta \)-NaLuF\(_4\); 20% \( \text{Yb}^{3+} \), 1% \( \text{Tm}^{3+} \), 20% \( \text{Er}^{3+} \). Based on the rate equations, the theoretical model about the pure red UC mechanism in \( \text{Yb}^{3+}\)/\( \text{Tm}^{3+}\)/\( \text{Er}^{3+} \) doped system is presented. The red UC emission of 660 nm in \( \text{Li}^{+} \) doped \( \beta \)-NaLuF\(_4\); 20% \( \text{Yb}^{3+} \), 1% \( \text{Tm}^{3+} \), 20% \( \text{Er}^{3+} \) is greatly increased compared to the \( \text{Li}^{+} \) –free sample under 980 nm excitation at room temperature.

Results and Discussion

Morphology evolution of \( \beta \)-NaLuF\(_4\) crystals. Citric acid has been regarded as one of the most effective chelating agents because of its ability to regulate the morphology and dimension of the samples in the hydrothermal process. In the present system, citric acid also plays a critical role in the morphology evolution of \( \beta \)-NaLuF\(_4\) crystals. Figure 1 shows the XRD patterns of the as-prepared \( \beta \)-NaLuF\(_4\) samples with different citric acid contents from 2 to 8 mmol. As can be seen, all the diffraction peaks can be well indexed to pure \( \beta \)-NaLuF\(_4\), which is consistent with the standard card (JCPDS 27-0726). No other impurity peaks are detected, indicating the high purity of \( \beta \)-NaLuF\(_4\) samples. It is worth to note that the relative intensities of (100), (110), (101) and (201) peaks display some differences from each other, implying the existence of oriented growth under different \( \text{Cit}^{3-} \) contents. The above XRD results are supported by the corresponding SEM images, as exhibited in Fig. 2. When the adding citric acid is 2 mmol (Fig. 2a), regular hexagonal phase microdisks with an average size of 0.79 \( \mu \)m are obtained. As the citric acid content increases to 3 mmol (Fig. 2b), short hexagonal phase microtubes with hollow structure are presented in Fig. 2c. The tubes have an average height of 9.47 \( \mu \)m and an average diameter of 1.88 \( \mu \)m. The ratios of height to diameter (H/D ratios) are calculated to be about 0.10, 0.25, and 5.04 when the adding citric acid is 2, 3, and 8 mmol. From the above analysis, it can be concluded that the H/D ratio is increased as the citric acid content increases from 2 to 8 mmol. Based on the high anisotropic structure of \( \beta \)-NaLuF\(_4\), when the adding citric acid increases from 2 to 8 mmol, \( \text{Cit}^{3-} \) absorbs onto the \{0001\} facets more strongly than the \{10\overline{1}0\} facets. Thus, the growth rate along \{0001\} direction is faster than that along \{10\overline{1}0\} direction, resulting in the morphology evolution from disks to tubes and the enhancement of H/D ratio. The hollow structure of the tubes is generated owing to the growth rate at the center is lower than that at the edges. The corresponding schematic diagrams of \( \beta \)-NaLuF\(_4\) crystals under different citric acid contents are displayed in Fig. 2(d–f).

Pure red UC mechanism of \( \beta \)-NaLuF\(_4\); \( \text{Yb}^{3+}, \text{Tm}^{3+}, \text{Er}^{3+} \) crystals. A series of \( \beta \)-NaLuF\(_4\); \( \text{Yb}^{3+}, \text{Tm}^{3+}, \text{Er}^{3+} \) crystals were synthesized by adding 3 mmol citric acid. Figure 3 shows the UC emission spectra (normalized to \( \text{Er}^{3+} \) 540 nm emission) of (a) \( \beta \)-NaLuF\(_4\); 20% \( \text{Yb}^{3+}/\text{Er}^{3+} \), (b) \( \beta \)-NaLuF\(_4\); 20% \( \text{Yb}^{3+}/0.5\% \text{Tm}^{3+}/\text{Er}^{3+} \), and (c) \( \beta \)-NaLuF\(_4\); 20% \( \text{Yb}^{3+}/1\% \text{Tm}^{3+}/\text{Er}^{3+} \) under 980 nm excitation at room temperature.
Green emissions at around 520/540 nm correspond to the transitions of Er$^{3+}$:2$^4H_{11/2}^1S_{3/2}$ → $^4I_{15/2}$. Red emissions at approximately 660 nm and 696 nm are attributed to the transition of Er$^{3+}$:4$^2F_{9/2}$ → $^4I_{15/2}$ and the transition of...
Tm\(^{3+}\):\(^4\)F\(_{7/2}\) \(\rightarrow\) \(^3\)H\(_{6}\), respectively. As can be seen, compared with Tm\(^{3+}\)-free group [Fig. 3(a)], the RGR is greatly increased in 0.5% Tm\(^{3+}\)-group [Fig. 3(b)] and 1% Tm\(^{3+}\)-group [Fig. 3(c)]. The maximum RGR is observed in 0.5% Tm\(^{3+}\) and 1% Tm\(^{3+}\)-groups doped with 20 mol% Er\(^{3+}\). From the insets of Fig. 3(a–c) and Table 1, it can be clearly seen that the RGR is almost unchanged in Tm\(^{3+}\)-free group while dramatically enhanced in 0.5% Tm\(^{3+}\) and 1% Tm\(^{3+}\)-groups with the increase of Er\(^{3+}\) dopant content. The RGR in 0.5% Tm\(^{3+}\) (R/G = 43.7) and 1% Tm\(^{3+}\) (R/G = 49.3)-groups with 20% Er\(^{3+}\) doping are increased by 26 and 19 times compared to their 0.5% Er\(^{3+}\) doping (R/G = 1.66, 2.57). Consequently, low-content doping of Tm\(^{3+}\) and high-content doping of Er\(^{3+}\) induce great enhancement in the RGR. Figure 4 shows the pump power dependence of green and red UC emissions in 0.5% Tm\(^{3+}\) and 1% Tm\(^{3+}\)-groups with 0.5%, 5% and 20% Er\(^{3+}\) doping under 980 nm excitation. According to the formula\(^{45}\): 

\[ I_{uc} \propto P^n, \]

where \(I_{uc}\) is the output UC emission intensity, \(P\) is the infrared excitation power, \(n\) is the absorbed laser photon number when emitting an UC photon. As shown in Fig. 4(a,c), the slopes of green emission (Er\(^{3+}\):\(^4\)F\(_{9/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\)) are 1.23, 1.40, and 1.72 in \(\beta\)-NaLuF\(_4\):20% Yb/0.5% Tm/xEr; 1.15, 1.53, and 1.61 in \(\beta\)-NaLuF\(_4\):20% Yb/1% Tm/xEr (x = 0.5, 5, 20%). The slopes of red emission (Er\(^{3+}\):\(^4\)S\(_{3/2}\) \(\rightarrow\) \(^4\)I\(_{15/2}\)) are 1.22, 1.10, and 0.64 in 0.5% Tm\(^{3+}\)-group; 1.27, 1.16, and 1.08 in 1% Tm\(^{3+}\)-group with 0.5%, 5% and 20% Er\(^{3+}\) doping. On the basis of the above analysis, it can be concluded that green emission varies from one-photon process to two-photon processes, and red emission (660 nm) keeps one-photon process in 0.5% Tm\(^{3+}\) and 1% Tm\(^{3+}\)-groups.

In this paper, we built a theoretical model to have a deep understanding of the ET process in Yb\(^{3+}\)/Tm\(^{3+}\)/Er\(^{3+}\) doped system. We supposed \(^4\)F\(_{7/2}\), \(^2\)H\(_{11/2}\), and \(^4\)S\(_{3/2}\) energy levels as a same level. When the Yb\(^{3+}\)/Tm\(^{3+}\)/Er\(^{3+}\) system
doped with low Er\(^{3+}\) content, CR effect between Er\(^{3+}\) can be neglected. The corresponding rate equations are as follows:

\[
\frac{dN_i}{dt} = \omega_{ji} N_j - \omega_{ij} N_i + \rho N_i - \lambda_i N_i
\]

where \(\omega_{ji}\), \(\omega_{ij}\), and \(\rho\) correspond to the ET rates of \(i\rightarrow j\) (ET1), \(i\rightarrow j\rightarrow i\) (ET2), \(i\rightarrow j\rightarrow k\rightarrow i\) (ET3), \(i\rightarrow j\rightarrow k\rightarrow l\rightarrow i\) (ET4), and \(i\rightarrow j\rightarrow k\rightarrow l\rightarrow m\rightarrow i\) (ET5), respectively. \(\lambda_i\) are the spontaneous relaxation (MPR) rates from \(i\rightarrow j\rightarrow k\rightarrow l\rightarrow m\rightarrow i\) and \(i\rightarrow j\rightarrow k\rightarrow l\rightarrow m\) levels, respectively. As presented in Fig. 5, the Er\(^{3+}\) F\(_{9/2}\) level is populated through the ET1 + ET3 processes. Then green UC emission is generated by the MPR processes of \(\text{Er}^{3+}\rightarrow \text{Tm}^{3+}\rightarrow \text{Yb}^{3+}\rightarrow \text{Tm}^{3+}\rightarrow \text{Yb}^{3+}\rightarrow \text{Tm}^{3+}\rightarrow \text{Yb}^{3+}\). In consideration of the high Yb\(^{3+}\) content, many radiative and nonradiative processes can be ignored, such as the back ET process from Er\(^{3+}\) to Er\(^{3+}\). Under steady-state condition, the rate equations can be acquired as follows:

\[
\omega_{j1} N_j - \omega_{1j} N_{1j} = 0
\]

\[
\omega_{ji} N_j - \omega_{ij} N_i + \rho N_i - \lambda_i N_i = 0
\]

The population density of Yb\(^{3+}\) F\(_{5/2}\) can be described as follows:

\[
\frac{dN_{yb}}{dt} = \sigma \rho N_{yb} - \sum_i \omega_{i1} N_i N_{yb} - A_i N_{yb} N_{yb}
\]

where \(\sigma\) is the absorption cross-section of Yb\(^{3+}\) F\(_{5/2}\) level, \(\rho\) is the pump rate of near-infrared (NIR) laser. Under steady-state condition, we get

\[
N_{yb} = \sigma \rho N_{yb} \left( A_{yb} + \sum_i \omega_i N_i \right) \propto \rho
\]

By solving the above equations, we have

\[
N_j = N_0 N_{yb} \omega_{yb} / [A_j (\omega_{j1} + M_j \omega_j) + M_j \omega_j + M_j \omega_j] + (N_0 \omega_{j1} / [A_j (M_j \omega_j + M_j \omega_j)] / [N_j (\omega_{j1} + M_j \omega_j)] + (N_{yb} \omega_{j1} + \omega_{j1} + M_j \omega_j)] \propto \rho
\]

(1)
As can be seen from Equations (1) and (2), both red-emitting manifold \( N_3 \) and green-emitting manifold \( N_4 \) have linear relationships with pump power at low Er\(^{3+}\) dose, which are in good agreement with the experimental results shown in Fig. 4. When the Yb\(^{3+}\)/Tm\(^{3+}\)/Er\(^{3+}\) system doped with high Er\(^{3+}\) content, pure red UC luminescence can be obtained. As is known, CR is dependent on the distance among activators. The average distance between Er\(^{3+}\) reduces with the increase of Er\(^{3+}\) dopant dose, which would result in the enhancement of CR effect. Thus, the CR process among Er\(^{3+}\) plays an important role in the achievement of pure red UC luminescence. There are generally three CR processes between Er\(^{3+}\) that account for the increase of RGR (has been described in the section of “Introduction”), as displayed in Fig. 6. Additionally, the ET, ET5 processes between Tm\(^{3+}\) and Er\(^{3+}\) also make a significant contribution to the high RGR. In the following sections, the above three CR effects are discussed systematically. As the Yb\(^{3+}\)/Tm\(^{3+}\)/Er\(^{3+}\) system doped with high Er\(^{3+}\) content, green UC emission can be neglected, and red UC emission (660 nm) mainly comes from two ways: (a) the CR effect among Er\(^{3+}\); (b) the ET from Tm\(^{3+}\) to Er\(^{3+}\).

**Theoretical model for the first CR effect.** The corresponding rate equations are as follows:

\[
\begin{align*}
N_j &= N_0 N_{Yb} \omega_{j} / \{M_0 \omega_{j} (\omega_{2j} + M_0 \omega_{j}) + A_4 (N_{Yb} \omega_{j} + \omega_{2j} + M_0 \omega_{j}) \\
&+ (N_{Yb} \omega_{j} + \omega_{2j} + M_0 \omega_{j}) \omega_{j} \} \propto \rho \\
N_j / N &= [A_4 (\omega_{2j} + M_0 \omega_{j}) + M_0 \omega_{j} (\omega_{2j} + M_0 \omega_{j}) \\
&+ (N_{Yb} \omega_{j} + \omega_{2j} + M_0 \omega_{j}) \omega_{j}] / (A_4 N_{Yb} \omega_{j}) \tag{3}
\end{align*}
\]

As can be seen from Equation (5), the green-emitting level \( N_4 \) does not have quasi-quadratic relationship with pump power, which is not corresponding to Fig. 4(a,c) where \( n \) are 1.72 and 1.61 in 0.5% Tm\(^{3+}\) and 1% Figure 6. Proposed ET mechanism of red UC emission in β-NaLuF\(_4\):Yb\(^{3+}\), Tm\(^{3+}\), Er\(^{3+}\) (with high Er\(^{3+}\) content). The mechanism involves the CR effects among Er\(^{3+}\),26-28 and ET from Tm\(^{3+}\) to Er\(^{3+}\),23.
Tm\(^{3+}\)-groups at high content (20 mol%) of Er\(^{3+}\) doping, indicating CR1 is not suitable for explaining the experimental results. Consequently, CR1 has nothing to do with the increase of red emission (660 nm) at high Er\(^{3+}\) content in Yb\(^{3+}\)/Tm\(^{3+}\)/Er\(^{3+}\) doped system.

Theoretical model for the second CR effect. The corresponding rate equations are as follows:

\[
\frac{dN_i}{dt} = \omega_i N_0 - \omega_i N_j N_l
\]

\[
\frac{dN_j}{dt} = \omega_j N_0 N_0 + \omega_j N_i N_l - \omega_j N_j N_l - \omega_j N_i N_0 - \omega_j N_j N_0
\]

\[
\frac{dN_l}{dt} = \omega_l N_0 N_0 - \omega_l N_i N_j - \omega_l N_j N_i
\]

\[
\omega_{C_2} = \text{CR rate for } [\text{Er}^{3+}:4S_{3/2} + 4I_{13/2} \rightarrow 4F_{9/2} + 4I_{11/2} (CR2)]
\]

By solving the equations under steady-state condition, we have

\[
N_i = N_0 N_0 \omega_j / A_j \propto \rho
\]

\[
N_j = N_0 N_0 \omega_j (N_{0j} \omega_j - \omega_{2j}) / [M_0 \omega_j (\omega_{2j} + M_i \omega_i)] \propto \rho^2
\]

\[
N_i / N_j = M_0 \omega_j (\omega_{2j} + M_i \omega_i) / [A_j (N_{0j} \omega_j - \omega_{2j})] \propto \rho^{-1}
\]

As can be seen from Equations (7) and (8), red-emitting manifold \(N_i\) and green-emitting manifold \(N_j\) have linear and quasi-quadratic relationships with pump power at high Er\(^{3+}\) content, which correspond to the relevant results in Fig. 4. The power dependence of RGR for \(\beta\)-NaLuF\(_4\):20% Yb/1% Tm/20% Er is exhibited in Fig. 7(a). It can be clearly seen that the RGR is decreased with the increase of pump power. The ratio of \(N_i\) to \(N_j\) shows the inverse proportional relationship to pump power [Equation (9)], which is in accordance with the result in Fig. 7(a). From the above analysis, it can be deduced that CR2 maybe makes a contribution to the high RGR when the Yb\(^{3+}\)/Tm\(^{3+}\)/Er\(^{3+}\) system doped with high Er\(^{3+}\) dose.

Theoretical model for the third CR effect. The corresponding rate equations are as follows:

\[
\frac{dN_j}{dt} = \omega_j N_0 N_0 + \omega_j N_i N_l - \omega_j N_j N_l - \omega_j N_i N_0 - \omega_j N_j N_0
\]

\[
\omega_{C_3} = \text{CR rate for } [\text{Er}^{3+}:4S_{3/2} + 4I_{13/2} \rightarrow 4F_{9/2} + 4I_{11/2} (CR3)]
\]

and red UC emission (660 nm) is obtained by the subsequent ETU process \([4F_{9/2} (\text{Er}^{3+}) + 4F_{5/2} (\text{Yb}^{3+}) \rightarrow 4F_{7/2} (\text{Er}^{3+}) + 2F_{7/2} (\text{Yb}^{3+})]\). By solving the equations under steady-state condition, we get

\[
N_3 = N_0 N_0 \omega_j / A_3 + N_0^2 \omega_j^2 \omega_{C_3} / [A_3 M_3 \omega_3 (\omega_{23} + N_0 \omega_{C_3})] \propto a \rho + b \rho^2
\]
As can be seen from Equation (10), red-emitting level \(4_{13/2} \rightarrow 4_{15/2}\) can be used to explain the experimental results. With pump power, which are in good agreement with the results shown in Figs 4(a,c) and 7(a), respectively. Thus, CR3 can be used to explain the experimental results.

On the basis of the above analysis, it can be concluded that both CR2 and CR3 maybe are the appropriate ET mechanisms for the achievement of pure red UC luminescence at high Er\(^{3+}\) content in Yb\(^{3+}/\)Tm\(^{3+}/\)Er\(^{3+}\) doped system. According to our experimental results, there are three reasons to prove that CR3 (Er\(^{3+}:\)4\(^{15/2} \rightarrow \)4\(^{13/2}\)) is the main CR effect for the population process of \(^4\)F\(_{9/2}\) manifold. First, the ratio of NIR to green (NIR) is enhanced with the increase of Er\(^{3+}\) content in \(\beta\)-NaLuF\(_4\):20% Yb/1% Tm/\(\beta\)-NaLuF\(_4\) (NIR emission corresponds to the \(^4\)I\(_{15/2}\) → \(^4\)I\(_{13/2}\) transition of Er\(^{3+}\)) as presented in Fig. 7(b). The increasing NGR indicates that the population of Er\(^{3+}\) \(^4\)I\(_{15/2}\) level becomes larger and larger compared to Er\(^{3+}\) \(^4\)S\(_{3/2}\)/\(^4\)H\(_{13/2}\) levels. As is known, the probability of MPR from \(^{4}\)I\(_{11/2}\) to \(^{4}\)I\(_{13/2}\) is quite low due to the low phonon energy in our system. Thus, the increasing NGR is mainly ascribed to CR3. Second, the decay curves of the \(^4\)I\(_{15/2}\) → \(^4\)I\(_{13/2}\) transition of Er\(^{3+}\) in \(\beta\)-NaLuF\(_4\):20% Yb/1% Tm/0.5% Er and \(\beta\)-NaLuF\(_4\):20% Yb/1% Tm/20% Er are shown in Fig. 8. The decay lifetime was calculated based on the function: 

\[
\tau = \int_{t_0}^{t} \frac{1}{I(t)} dt
\]

where \(I(t)\) is the emission intensity at time \(t\), and \(I_p\) is the peak intensity in the decay curve. The calculation results show that \(\tau_{0.5\%\text{Er}} = 1.40\) ms and \(\tau_{20\%\text{Er}} = 0.55\) ms. The energy transfer efficiency (ETE) can be evaluated by the following expression: 

\[
\eta_{\text{ETE}} = \frac{\tau_{0.5\%\text{Er}}}{\tau_{20\%\text{Er}}}
\]

The calculation result shows that \(\eta_{\text{ETE}} = 60.71\%\). With the increase of Er\(^{3+}\) dose, the enhanced red UC emission (660 nm) mainly comes from the increasing NGR is mainly ascribed to CR3. Therefore, the CR3 process is required before the CR2 process, resulting in the leading role of CR3 in the CR effects.

It can be concluded that the pure red UC luminescence is mainly ascribed to the ETU from \(^{4}\)F\(_{9/2}\) to \(^{4}\)I\(_{11/2}\) to \(^{4}\)I\(_{13/2}\) and the CR effect \([\text{Er}^{3+}:\)\(^4\)S\(_{3/2}\) + \(^4\)I\(_{15/2}\) → \(^4\)F\(_{9/2}\) + \(^4\)I\(_{13/2}\)\] rather than the long-accepted and most popular mechanism (CR1 process among \(\text{Er}^{3+}:\)\(^4\)F\(_{9/2}\) + \(^4\)I\(_{15/2}\) → \(^4\)I\(_{13/2}\) + \(^4\)I\(_{15/2}\)).

**Li\(^+\) doped \(\beta\)-NaLuF\(_4\):20% Yb\(^{3+}\), 1% Tm\(^{3+}\), 20% Er\(^{3+}\) crystals.** A series of Li\(^+\) doped \(\beta\)-NaLuF\(_4\):20% Yb\(^{3+}\), 1% Tm\(^{3+}\), 20% Er\(^{3+}\) crystals were synthesized by adding 3 mmol citric acid. Figure 9 presents the XRD patterns (a) and the main diffraction peak (b) of different Li\(^+\) doped \(\beta\)-NaLuF\(_4\):20% Yb\(^{3+}\), 1% Tm\(^{3+}\), 20% Er\(^{3+}\) crystals. As shown in Fig. 9(a), all the diffraction peaks of the products can be indexed as pure \(\beta\)-NaLuF\(_4\) (JCPDS 27-0726) even the Li\(^+\) concentration increases up to 20 mol\%, indicating that Li\(^+\) doping has no influence on the crystal structure of the products. The corresponding UC emission spectra of the products under 980 nm excitation are shown in Fig. 10. As can be seen, the pure red UC luminescence is greatly enhanced after Li\(^+\) doping. Compared to the Li\(^+\)-free sample, the pure red UC luminescence in \(\beta\)-NaLuF\(_4\):20% Yb\(^{3+}\), 1% Tm\(^{3+}\), 20% Er\(^{3+}\) with 15 mol% Li\(^+\) doping is increased by 13.7 times. This phenomenon is mainly caused by the asymmetric surrounding environment around Ln ions after Li\(^+\) doping. Figure 9(b) exhibits that the main diffraction peak moves to the larger angles when the Li\(^+\) concentration is from 0 to 15 mol\%, whereas shifts in reverse as the Li\(^+\) concentration increases up to 20 mol\%. According to Bragg’s law \(2d\sin \theta = n\lambda\), where \(d\) represents the interplanar distance, \(\theta\) represents the diffraction angle, and \(\lambda\) represents the diffraction wavelength. When \(d\) decreases, \(\theta\)
increases; when $d$ increases, $\theta$ decreases. As is displayed in Fig. 11(a), Na$^{+}$ and Ln$^{3+}$ occupy the same lattice site in $\beta$-NaLuF$_4$ lattice. When the Li$^{+}$ is introduced into the host lattice, it can replace Na$^{+}$ ($d$ decreases, $\theta$ increases, 0 < Li$^{+}$ concentration \leq 15 mol%) [Fig. 11(b)] or occupy the interstitial site ($d$ increases, $\theta$ decreases, 15 < Li$^{+}$ concentration \leq 20 mol%) [Fig. 11(c)] due to its small ionic radius, leading to the contraction or expansion of unit cell. Both the contraction and expansion of unit cell would reduce the symmetry of crystal field around Ln ions, inducing the sharp increase of pure red UC luminescence intensity$^{29-31}$. The strongest UC luminescence intensity is acquired in $\beta$-NaLuF$_4$:20% Yb$^{3+}$, 1% Tm$^{3+}$, 20% Er$^{3+}$ with 15 mol% Li$^{+}$ doping, which is attributed to the most asymmetric surrounding environment around Ln ions, as shown in Fig. 9(b).

Conclusion
In summary, hexagonal phase microdisks, microprisms, and microtubes were achieved by simply changing the amount of citric acid in the initial reaction solution. Pure red UC luminescence can be observed in $\beta$-NaLuF$_4$:Yb$^{3+}$, Tm$^{3+}$, Er$^{3+}$ and Li$^{+}$ doped $\beta$-NaLuF$_4$:20% Yb$^{3+}$, 1% Tm$^{3+}$, 20% Er$^{3+}$. We prove that the low-content doping of Tm$^{3+}$ and high-content doping of Er$^{3+}$ induce great enhancement in the RGR. The RGR in 0.5% Tm$^{3+}$ (R/G = 43.7) and 1% Tm$^{3+}$ (R/G = 49.3)-groups with 20% Er$^{3+}$ doping are increased by 26 and 19 times compared to their 0.5% Er$^{3+}$ doping (R/G = 1.66, 2.57). Green emission varies from one-photon process to two-photon processes, and red emission (660 nm) keeps one-photon process in 0.5% Tm$^{3+}$ and 1% Tm$^{3+}$-groups. Based on the rate equations, we report the theoretical model about the pure red UC mechanism in Yb$^{3+}$/Tm$^{3+}$/Er$^{3+}$ doped system. It is proposed that the pure red UC luminescence is mainly ascribed to the ETU from Tm$^{3+}$:4F$_{9/2}$ to Er$^{3+}$:4I$_{11/2}$ to Er$^{3+}$:4F$_{9/2}$ and the CR effect [Er$^{3+}$:4F$_{9/2}$ + 4I$_{15/2}$ \rightarrow 4I$_{11/2}$ + 4F$_{9/2}$ (CR3)]. Additionally, compared to the Li$^{+}$-free sample, the pure red UC luminescence in $\beta$-NaLuF$_4$:20% Yb$^{3+}$, 1% Tm$^{3+}$, 20% Er$^{3+}$ with 15 mol% Li$^{+}$ doping is enhanced by 13.7 times. The results suggest that the enhanced pure red UC luminescence in Li$^{+}$ doped $\beta$-NaLuF$_4$:20% Yb$^{3+}$, 1% Tm$^{3+}$, 20% Er$^{3+}$ may have potential applications in flat-panel displays, solid-state lasers and light-emitting diodes. Besides, this study provides a general and effective approach to obtain...
intense pure red UC luminescence, which can be applied to other synthetic strategies to prepare many types of nanocrystals with high purity of red UC luminescence, making it suitable for the future bioapplications.

**Methods**

**Chemicals.** All of the chemicals are of analytical grade and used as received without further purification. 1 M of Lu(NO$_3$)$_3$, 0.5 M of Yb(NO$_3$)$_3$, 0.1 M of Er(NO$_3$)$_3$, and 0.1 M of Tm(NO$_3$)$_3$ stock solutions were prepared by dissolving the corresponding rare earth oxide (99.99%) in dilute nitric acid (30%) at elevated temperature.

**Preparation.** A series of $\beta$-NaLuF$_4$ crystals with different morphologies were synthesized via a hydrothermal method using citric acid as a chelating agent. In a typical procedure, (2 mmol/3 mmol/8 mmol) of citric acid (2 M, 1 mL/1.5 mL/4 mL), 5 mmol of NaOH (4 M, 1.25 mL) and 10 mL of deionized water were mixed and stirred for 10 min. Then 1 mmol of Ln(NO$_3$)$_3$ [1 mmol of Lu(NO$_3$)$_3$ (1 M, 1 mL)] was added to the above mixture and then stirred for 30 min to form the RE-Cit$_3^{3-}$ complex. Subsequently, an aqueous solution containing 8 mmol of NaF (1 M, 8 mL) and (9 mL/8.5 mL/6 mL) of deionized water was added into the chelated RE-Cit$_3^{3-}$ complex to form a colloidal suspension and kept stirring for another 30 min. Finally, the suspension was transferred into a 50 mL-Teflon vessel, sealed in an autoclave and maintained at 200 °C for 10 h before cooling down naturally. The final products were separated by centrifugation, washed several times with ethanol and deionized water, then dried in air at 60 °C for 12 h. $\beta$-NaLuF$_4$: 20% Yb$^{3+}$, (0%/0.5%/1%)Tm$^{3+}$, (0.5%/2%/5%/10%/20%)Er$^{3+}$ crystals and (8%/15%/20%)Li$^{+}$ doped $\beta$-NaLuF$_4$:20% Yb$^{3+}$, 1% Tm$^{3+}$, 20% Er$^{3+}$ crystals were prepared by a similar process (Cit$^{3-}$ = 3 mmol) under the same experimental conditions. In particular, as for (8%/15%/20%)Li$^{+}$ doped $\beta$-NaLuF$_4$:20% Yb$^{3+}$, 1% Tm$^{3+}$, 20% Er$^{3+}$ crystals, after the formation of RE-Cit$_3^{3-}$ complex, a mixture containing (0.64 mmol/1.2 mmol/1.6 mmol) of LiNO$_3$ (1 M, 0.64 mL/1.2 mL/1.6 mL), (7.36 mmol/6.8 mmol/6.4 mmol) of NaF (1 M, 7.36 mL/6.8 mL/6.4 mL), (0.32 mmol/0.6 mmol/0.8 mmol) of NH$_4$HF$_2$ (1 M, 0.32 mL/0.6 mL/0.8 mL) and (6 mL/5.5 mL/5.5 mL) of deionized water were added into the chelated RE-Cit$_3^{3-}$ complex to form the colloidal suspension.

**Characterization.** The phase and structure of the as-prepared products were confirmed by powder X-ray diffraction (XRD) patterns using the D-Max 2200VPC XRD from Rigaku Company. Morphologies and grain sizes were verified by using an Oxford Quanta 400F Thermal Field Emission environmental Scanning Electronic Microscope (SEM). UC photoluminescence spectra were acquired on the Edinburgh Instrument FLSP920 steady-state fluorescence spectrometer equipped with a 2 W 980 nm laser diode. The spot size of the 980 nm laser on the samples is about 0.05 cm$^2$.

**References**

1. Shalav, A., Richards, B. S., Trupke, T., Krämer, K. W & Güdel, H. U. Application of NaYF$_4$:Er$^{3+}$ up-converting phosphors for enhanced near-infrared silicon solar cell response. Appl Phys Lett 86, 013505–3 (2005).
2. Das, G. K. et al. Gadolinium oxide ultra-narrow nanorods as multimodal contrast agents for optical and magnetic resonance imaging. Langmuir 26, 8959–8965 (2010).
3. Wang, F. & Liu, X. G. Recent advances in the chemistry of lanthanide-doped upconversion nanocrystals. Chem Soc Rev 38, 976–989 (2009).
4. Idris, N. M. et al. Tracking transplanted cells in live animal using upconversion fluorescent nanoparticles. Biomaterials 30, 5104–5113 (2009).
5. Ding, M. et al. Simultaneous morphology manipulation and upconversion luminescence enhancement of $\beta$-NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ microcrystals by simply tuning the KF dosage. Sci Rep 5, 12745, doi: 10.1038/srep12745 (2015).
6. Wang, C. Y. & Cheng, X. H. Controlled hydrothermal growth and tunable luminescence properties of $\beta$-NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ microcrystals. J Alloys Compd 617, 807–815 (2014).
11. Zhang, F. & Wong, S. S. Ambient large-scale template-mediated synthesis of high-aspect ratio single-crystalline, chemically doped rare-earth phosphate nanowires for bioimaging. ACS Nano 4, 99–112 (2010).

12. Li, Z. Q. & Zhang, Y. Monodisperse silica-coated polyvinylpyrrolidone/NaYF$_4$ nanocrystals with multicolor upconversion fluorescence emission. Angew Chem Int Ed 45, 7732–7735 (2006).

13. Cheng, L. et al. Facile preparation of multifunctional upconversion nanoprobes for multimodal imaging and dual-targeted photothermal therapy. Angew Chem 123, 7523–7528 (2011).

14. Yi, G. S. & Chow, G. M. Water-soluble NaYF$_4$:Yb, Er(Tm)/NaYF$_4$/polymer core/shell/shell nanoparticles with significant enhancement of upconversion fluorescence. Chem Mater 19, 341–343 (2007).

15. Niu, N. et al. Hierarchical bundles structure of β-β-NaLuF$_4$ facile synthesis, shape evolution, and luminescence properties. RSC Adv 2, 10337–10344 (2012).

16. He, F. et al. Morphology-controllable synthesis and enhanced luminescence properties of β-β-NaLuF$_4$: Ln (Ln = Eu, Tb and Ce/Tb) microcrystals by solvothermal process. J Mater Chem C 2, 7569–7577 (2012).

17. Desiraju, G. R. Polymorphism: the same and not quite the same. Cryst Growth Des 8, 3–5 (2008).

18. Gao, Y., Zhao, Q., Xu, Z. H. & Sun, Y. Y. Hydrothermally derived NaLaF$_4$:Yb$^{3+}$, Ln$^{3+}$ (Ln$^{3+} = $ Er$^{3+}$, Tm$^{3+}$ and Ho$^{3+}$) microstructures with controllable synthesis, morphology evolution and multicolor luminescence properties. New J Chem 38, 2629–2638 (2014).

19. Wang, J., Wang, F., Wang, C., Liu, Z. & Liu, X. G. Single-band upconversion emission in lanthanide-doped KMN$_2$F$_4$ nanocrystals. Angew Chem Int Ed 50, 10369–10372 (2011).

20. Tian, G. et al. Mn$^{2+}$ dopant-controlled synthesis of NaYF$_4$:Yb/Er upconversion nanofibers for in vivo imaging and drug delivery. Adv Mater 24, 1226–1231 (2012).

21. Zeng, S. J. et al. Simultaneous realization of phase/size manipulation, upconversion luminescence enhancement, and blood vessel imaging in multifunctional nanoprobes through transition metal Mn$^{2+}$ doping. Adv Funct Mater 24, 4051–4059 (2014).

22. Wei, W. et al. Cross relaxation induced pure red upconversion in activator- and sensitizer-rich lanthanide nanophosphors. Chem Mater 26, 3183–3186 (2014).

23. Chan, E. M., Gargas, D. J., Schuck, P. J. & Milliron, D. J. Concentrating and recycling energy in lanthanide codopants for efficient and spectrally pure emission: the case of NaYF$_4$:Er$^{3+}$/Tm$^{3+}$ upconverting nanocrystals. J Phys Chem B 116, 10561–10570 (2012).

24. Su, I. et al. Phonon-assisted mechanisms and concentration dependence of Tm$^{3+}$ blue upconversion luminescence in codoped NaY(WO$_4$)$_2$ crystals. J Phys D: Appl Phys 39, 2094–2099 (2006).

25. Wang, H. R., Yi, Z. G., Rao, L., Liu, H. R. & Zeng, S. J. High quality multi-functional NaErF$_4$ nanocrystals: structure-controlled synthesis, phase-induced multi-color emissions and tunable magnetic properties. J Mater Chem C 1, S529–S526 (2013).

26. Vetrone, F., Boyer, J. C., Capobianco, J. A., Speghini, A. & Bettinelli, M. Significance of Yb$^{3+}$ concentration on the upconversion mechanisms in codoped Y$_2$O$_3$: Er$^{3+}$, Yb$^{3+}$ nanocrystals. J Appl Phys 96, 661–667 (2004).

27. Gao, D., Zhang, X., Zheng, H., Gao, W. & He, E. Yb$^{3+}$/Er$^{3+}$ codoped β-β-NaYF$_4$ microrods: synthesis and tuning of multicolor upconversion. J Alloys Compd 554, 395–399 (2013).

28. Salas, P. et al. Synthesis, characterization and luminescence properties of ZrO$_2$: Yb$^{3+}$/Er$^{3+}$ nanophosphor. Opt Mater 27, 1295–1300 (2005).

29. Zhao, C. Z. et al. Li$^{+}$ ion doping: an approach for improving the crystallinity and upconversion emissions of NaYF$_4$: Yb$^{3+}$, Tm$^{3+}$ nanocrystals. Nanoscale 5, 8084–8089 (2013).

30. Yin, W. et al. Enhanced red emission from GdF$_3$: Yb$^{3+}$, Er$^{3+}$ upconversion nanocrystals by Li$^{+}$ doping and their application for bioimaging. Chem Eur J 18, 9239–9245 (2012).

31. Cheng, Q., Sui, J. H. & Cai, W. Enhanced upconversion emission in Yb$^{3+}$ and Er$^{3+}$ codoped NaGdF$_4$ nanocrystals by introducing Li$^{+}$ ions. Nanoscale 4, 779–784 (2012).

32. Li, C. X. et al. Different microstructures of β-β-NaYF$_4$, fabricated by hydrothermal process: effects of pH values and fluoride sources. Chem Mater 19, 4933–4942 (2007).

33. Li, C. X. et al. Shape-Controllable Synthesis and upconversion properties of lutetium fluoride (doped with Yb$^{3+}$/Er$^{3+}$/Rh$^{3+}$/Er$^{3+}$) microcrystals by hydrothermal process. J Phys Chem C 112, 13395–13404 (2008).

34. Lin, H. et al. Tuning of structure and enhancement of upconversion luminescence in NaLuF$_4$:Yb$^{3+}$, Ho$^{3+}$ crystals. Phys Chem Chem Phys 17, 19515–19526 (2015).

35. Lin, H. et al. Simultaneous realization of structure manipulation and emission enhancement in NaLuF$_4$ upconversion crystals. J Mater Chem C 3, 11754–11765 (2015).

36. Lin, H. et al. Shape-controllable synthesis and enhanced upconversion luminescence of Li$^{+}$ doped β-β-NaLuF$_4$:Yb$^{3+}$, Ln$^{3+}$ (Ln = Tm, Ho) microcrystals. New J Chem 39, 2565–2572 (2015).

37. Sun, Y. G. & Xia, Y. N. Large-scale synthesis of uniform silver nanowires through a soft, self-seeding, polyol process. Adv Mater 14, 833–837 (2002).

38. Jiang, D. L. et al. Shape-controlled synthesis of F-substituted hydroxyapatite microcrystals in the presence of Na$_2$EDTA and citric acid. J Colloid Interface Sci 350, 30–38 (2010).

39. Sun, Y. J., Liu, H. J., Wang, X., Kong, X. G. & Zhang, H. Optical spectroscopy and visible upconversion studies of YVO$_4$:Er$^{3+}$ nanocrystals synthesized by a hydrothermal process. Chem Mater 18, 2726–2732 (2006).

40. Hao, Q., Xu, L. Q., Li, G. D. & Qian, Y. T. Hydrothermal synthesis of microscaled Cu$_2$CO$_3$ polyhedral composites and their sensitivity to convergent electron beams. Langmuir 25, 6363–6367 (2009).

41. Kim, T. U., Kim, J. A., Pawar, S. M., Moon, J. H. & Kim, J. H. Creation of nanoscale two-dimensional patterns of ZnO nanorods using laser interference lithography followed by hydrothermal synthesis at 90 °C. Cryst Growth Des 10, 4256–4261 (2010).

42. Chen, S. et al. Chelation-controlled compound transition of luminescent fluoride crystals. Mater Lett 106, 326–331 (2013).

43. Niu, N. et al. Tunable multicolor and bright white emission of one-dimensional NaLu$_2$F$_6$:Yb$^{3+}$, Ln$^{3+}$ (Ln = Er, Tm, Ho, Er/Tm, Tm/ Ho) microstructures. J Mater Chem C 2, 10889–10899 (2012).

44. Wang, Y., Gai, S. L., Niu, N., He, F. & Yang, P. P. Synthesis of NaYF$_4$ microcrystals with different morphologies and enhanced upconversion luminescence properties. Phys Chem Chem Phys 15, 16795–16805 (2013).

45. Wang, F. X. et al. Upconversion and pump saturation mechanisms in Er$^{3+}$/Yb$^{3+}$ co-doped Y$_2$Ti$_2$O$_7$ nanocrystals. J Appl Phys 115, 134310–7 (2014).

46. Xu, D. K., Liu, C. E., Yan, J. W., Yang, S. H. & Zhang, Y. L. Understanding energy transfer mechanisms for tunable emission of Yb$^{3+}$/Er$^{3+}$ codoped CdF$_2$ nanoparticles: concentration-dependent luminescence by near-infrared and violet excitation. J Phys Chem C 119, 6862–6868 (2015).
Acknowledgements
This work was supported by the National Natural Science Foundation of China under Grant No. 61176010 and No. 61172027, Guangdong Natural Science Foundation under Grant No. 2014A030311049, and the Research Foundation of IARC-SYSU under Grant No. IARC 2014-09.

Author Contributions
H.L. performed the experiments and wrote the manuscript; H.L. carried out the optical and structural characterizations of the as-synthesized samples; D.X. participated in experiment design and helpful recommendations; D.X., A.L., S.Y. and Y.Z. participated in the analysis of experimental data; All authors reviewed the manuscript.

Additional Information
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Lin, H. et al. Morphology evolution and pure red upconversion mechanism of β-NaLuF₄ crystals. Sci. Rep. 6, 28051; doi: 10.1038/srep28051 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/