The influence of the introduction of Li\(^+\) ions on the upconversion (UC) properties of KLu\(_2\)F\(_7\):Yb\(^{3+}\), Er\(^{3+}\) nanocrystalline has been investigated in detail. It is found that the UC emission intensity of 10 mol\% Li\(^+\) ions doped KLu\(_2\)F\(_7\):Yb\(^{3+}\), Er\(^{3+}\) nanocrystalline is enhanced about 13 times in comparison with that of Li\(^+\)-free sample. Under the excitation of 980 nm laser diode (LD), a significant improvement of the green to red emission ratio (GRR) in the 10 mol\% Li\(^+\)-doped sample is observed by increasing pump power density. Li\(^+\) ions could occupy the cationic sites or the interstitial sites in the KLu\(_2\)F\(_7\) host matrix, which probably eliminate the defect states via the charge compensation and tailor of the crystal field, leading to the promotion of the UC emission efficiency. Additionally, the explanation for the power density dependence of the UC color is given. With Li\(^+\) ions doped, the elimination of the traps in the NPs as well as the tailoring of the crystal field around Er\(^{3+}\) ions play vital roles in the UC properties, which will be a meaningful research direction.

Experimental

The Li\(^+\) ions doped KLu\(_2\)F\(_7\):Yb\(^{3+}\), Er\(^{3+}\) NPs were prepared by a hydrothermal method. In a typical experiment, 0.77 mmol Lu\(_2\)O\(_3\) (99.99%, Aladdin, China), 0.16 mmol Yb\(_2\)O\(_3\) (99.99%, Aladdin, China) and 0.02 mmol Er\(_2\)O\(_3\) (99.99%, Aladdin, China) powder were dissolved in dilute nitrate solution and the residual nitrate was removed by heating and evaporation, resulting in the formation of clear solution of [Ln(NO\(_3\))]\(_3\) (Ln = Lu, Yb, Er). Then, 0.05 mmol LiNO\(_3\) (99.99%, Aladdin, China) water solution was added into the above mixture. The products (KLu\(_2\)F\(_7\):16%Yb\(^{3+}\), 2%Er\(^{3+}\), 5%Li\(^+\)) were obtained as a kind of white powder after drying at 80 °C in a baking oven. The other concentration (0%, 10%, 15% and 20%) Li\(^+\)-doped KLu\(_2\)F\(_7\):16%Yb\(^{3+}\), 2%Er\(^{3+}\) samples were synthesized by a similar procedure except that different moles of LiNO\(_3\) involved in the reaction.

X-ray powder diffraction (XRD) was performed using a D8 Focus diffractometer (Bruker) with Cu-K\(_\alpha\) radiation (\(\lambda = 0.15405\) nm) in the 20 range from 10° to 80°. The particle morphology and size were studied by the Scanning Electronic Microscopy (SEM) with FEI-Quanta 600. The UC photoluminescence spectra of the samples under a 980 nm infrared laser excitation were recorded by HITACHI-F-7000 spectrophotometer at room temperature. The thermoluminescence (TL) curves were measured with a Fujita TL meter (Beijing Nuclear Instrument Factory). Weight of the measured samples was constant (0.002 g). Prior to the TL measurement, the samples were first exposed to the radiation from ultraviolet (UV) light (365 and 254 nm) for about 20 min, then heated from room temperature to 550 K with a rate of 1 K/s. The photoluminescence decay curves were measured by FS980 fluorescence spectrophotometer.

The preparation of UC nanoparticles (NPs) that exhibits anti-Stokes emission is important for applications in fields as diverse as solar cells, photovoltaics, biological imaging, and photocatalysis. In particular, lanthanide-doped fluorides have some distinct advantages superior to oxide-based UC materials due to their low phonon energy, high signal-to-noise ratio and excellent chemical stability. However, the applications of lanthanide-doped fluorides are still constrained because of the low UC efficiency and the restricted tunability of the luminescence color output. Various attempts have been devoted to improving these aspects, including both internal adjustments and external approaches, as varying the crystal phase or morphology of the NPs, adjusting the concentration of the doped rare earth, introducing a co-dopant sensitizer, surface coating or adopting of a core-shell structure. The excitation and relaxation dynamics of energy levels involved in UC process can be manipulated to vary the relative luminescence intensity in different UC bands of a lanthanide ion or to realize a combination of UC emission bands from other lanthanide ions. To improve the UC emission efficiency and adjust the relatively color, a core-shell structure or a combination of activators is selected, which are aimed at reducing the surface defects. However, the synthesis of NPs featuring controllable color with high chromatic purity remains a formidable challenge, as lanthanide ions generally have more than one metastable excited state and the defects are unavoidable in NPs. Nowadays, a new class of KLu\(_2\)F\(_7\) NPs with orthorhombic crystallographic structure has drawn a widespread interest, in which the lanthanide ions are distributed in arrays of tetrad crystals. This unique arrangement enables the preservation of excitation energy within the sub-lattice domain and effectively minimizing the migration of excitation energy to defects. Based on this, the adjustment of UC emission color and the unusual four-photon violet UC is selected, which are aimed at reducing the surface defects. Based on this, the mechanism of the enhanced UC emission intensity of the as-synthesized KLu\(_2\)F\(_7\):Yb\(^{3+}\), Er\(^{3+}\) NPs with Li\(^+\) ions doped under the excitation of 980 nm LD is investigated. Additionally, the explanation for the power density dependence of the UC color is given. With Li\(^+\) ions doped, the elimination of the traps in the NPs as well as the tailoring of the crystal field around Er\(^{3+}\) ions play vital roles in the UC properties, which will be a meaningful research direction.
Results and Discussion

Fig. 1a shows the XRD patterns of 0, 5, 10, 15 and 20 mol% Li⁺ ions doped KLu₂F₇:Yb³⁺/Er³⁺ NPs. All samples are orthorhombic structure according to the standard card of KYb₂F₇ (JCPDF 27–0459). No impurity peaks are observed, indicating that these KLu₂F₇:Yb³⁺/Er³⁺ samples synthesized with different amounts of Li⁺ ions doped are of high purity. The positions of the diffraction peaks shift slightly when Li⁺ ions are introduced. Fig. 1b shows the main diffraction peak shift toward larger angle gradually from 27.86° to 28.14° as the concentration of Li⁺ ions increases in the range of 0–15 mol%. It indicates that the lattice shrinks when Li⁺ ions doped in the lattice serve as a controller for the morphology.

UC photoluminescence properties of a series of KLu₂F₇:16%Yb³⁺, 2%Er³⁺, x%Li⁺ (x = 0, 5, 10, 15 and 20) excited by 980 nm LD with the power of 50 W/cm² at room temperature are depicted in Fig. 3. The position of the emission peaks of Er³⁺ is not affected by introducing Li⁺ ions. The dominant green emissions of 525 and 543 nm are assigned to the transitions of 2⁵H₁₁₂→4¹S₅₂ and ²⁵S₅₂→4¹S₅₂ of Er³⁺ ions, respectively, and the red emission of 688 nm is attributed to the ²⁵F₅₄→4¹S₅₂ transition. With an increasing concentration of Li⁺ ions, the integrated emission intensities increase firstly and then decrease. The UC luminescence intensity reaches its maximum in 10 mol% Li⁺ ions doped sample, which is 13 times than that of Li⁺-free sample. The UC intensity decreases when the concentration of Li⁺ ions reaches to 20 mol%. These phenomena may derive from the contributions that the introduction of Li⁺ ions could tailor Er³⁺ ions’ local environment, decrease the defect states. A small fraction of Li⁺ ions substituted in the lattice could induce the asymmetric environment around Er³⁺ ions, which promotes the fast energy transfer from Yb³⁺ to Er³⁺ ions. Furthermore, defects are unavoidably formed during the synthesis process, indicating that the introduction of Li⁺ ions is expected to influence the UC properties by changing defect states as well.

Thermoluminescence (TL) spectra are presented to reveal the change of defect states caused by Li⁺ ions. As shown in Fig. 4, two TL peaks located around 325 and 387 K can be identified in Li⁺-free sample. However, the TL peaks located around 325 and 387 K are insignificant when Li⁺ ions are doped, indicating the traps are eliminated. During the synthesis process under high temperature and pressure, the substitution of K⁺ ions with Yb³⁺ and Er³⁺ ions is unavoidable, though the replacement of Lu³⁺ ions is dominant. Therefore, the introduction of the vacancy defects (Vₓ⁺), which cannot be avoided because of the charge balance principle. Moreover, the surface defects are inevitable in nanoparticles. Both of these defects contribute to the observation of the traps. It could be expected that the introduction of Li⁺ ions eliminates the traps efficiently, since the substituting of Lu⁺ ions with Li⁺ ions producing the vacancy of F⁻ (Li⁺₀⁺₂⁺ + 2F⁻) accomplishes the charge compensation. Thus, the introduction of Li⁺ ions could improve the UC emission efficiency significantly.

The thermoluminescence decay curves of S₁₁₂→4¹S₅₂ (543 nm) and F₁₁₂→4¹S₅₂ (668 nm) of KLu₂F₇:16%Yb³⁺, 2%Er³⁺, x%Li⁺ (x = 0, 5, 10, 15 and 20) NPs are recorded as shown in Fig. 5. All the decay curves of the samples could be well fitted to a single exponential function:

\[ I(t) = I₀ + A exp(-t/\tau) \]

Table I. Cell parameters and volume of KLu₂F₇:16%Yb³⁺, 2%Er³⁺, x%Li⁺.

| sample | a/Å  | b/Å  | c/Å  | cell volume/Å³ |
|--------|------|------|------|----------------|
| x = 0  | 11.6125 | 13.4990 | 7.6572 | 1200.32 |
| x = 1  | 11.6130 | 13.4950 | 7.6577 | 1200.10 |
| x = 3  | 11.6149 | 13.4901 | 7.6570 | 1199.75 |
| x = 5  | 11.6172 | 13.4872 | 7.6561 | 1199.58 |
| x = 7  | 11.6220 | 13.4754 | 7.6527 | 1198.50 |
| x = 10 | 11.6277 | 13.4623 | 7.6442 | 1196.07 |
| x = 15 | 11.6614 | 12.9858 | 7.4952 | 1135.02 |
| x = 20 | 10.9075 | 13.1652 | 8.0773 | 1159.70 |
Figure 2. SEM images of the KLu$_2$F$_7$:16%Yb$^{3+}$, 2%Er$^{3+}$, x%Li$^+$ NPs x = 0 (a), x = 5 (b), x = 10 (c) and x = 20 (d). The insets show the histograms of the average particle size distribution of these samples.

Where I is the photoluminescence intensity of Er$^{3+}$ ions, A$_1$ is constant; t is time; and $\tau_1$ is the decay time for the exponential component. As shown in Fig. 5, the introduction of Li$^+$ ions prolongs the decay time of $^4S_{3/2}$ and $^4F_{9/2}$ levels in Er$^{3+}$ ions indicating that the local environment around Er$^{3+}$ ions are tailored with the Li$^+$ ions doped. With an increasing concentration of Li$^+$ ions, the lifetimes of $^4S_{3/2}$ and $^4F_{9/2}$ states increase firstly and then decrease, and such trend is similar to the UC emission intensity change. The decay time of 10 mol% Li$^+$-doped sample is longer than other samples, indicating that the UC emission efficiency would be improved with proper concentration of Li$^+$ ions. The large increase in decay time contributes to a significant increase of UC photoluminescence intensity, which has been studied and reported.$^{32}$

Fig. 6a demonstrates the UC photoluminescence spectra of KLu$_2$F$_7$:16%Yb$^{3+}$, 2%Er$^{3+}$, 10%Li$^+$ with great enlargement of GRR under different excitation power density by normalizing the red emission. The GRR can be tuned by varying the excitation power density. The emission ratios are calculated by the integrated emission intensities of 525 and 543 nm to 668 nm. The change of GRR can be attributed to a fast and efficient energy transfer process due to the participation of more intensive photons in UC emission process. Since the electrons could be excited frequently before they decay under higher power density of 980 nm LD excitation, UC emission favors the transition from higher energy levels, which would promote the electrons
Figure 5. Photoluminescence decay curves of KLu$_2$F$_7$:16%Yb$^{3+}$, 2%Er$^{3+}$, x%Li$^+$ (x = 0, 5, 10, 15 and 20) samples monitored by 543 nm (a) and 668 nm (b). Stimulated from $^4S_{3/2}$ level. Thus, the emission intensity of the 525 nm peak increases drastically in comparison with 543 nm and the energy transition $^4G_{11/2} \rightarrow ^4I_{11/2}$ (380 nm) and $^2H_{9/2} \rightarrow ^4I_{11/2}$ (408 nm) occur as shown in Fig. 6a1. Therefore, an increasing excitation power density of 980 nm LD would not only adjust the UC emission color efficiently but promote the UC photoluminescence intensity in short wavelength. In addition, with the introduction of Li$^+$ ions, the GRR is enlarged more greatly as the increasing excitation power density compared with that of Li$^+$-free sample (Fig. 6a2) with the assistance of the elimination of the traps and the tailor of the crystal field around of Er$^{3+}$ ions. To visualize the improvement and the tunable color of the UC emission, a tunable color from yellow to green is clearly observed with the naked-eye. Fig. 6c shows the photograph model that the cuvette containing 2%wt sample is keeping away from convex lens gradually, which indicates a decrease of excitation power density. Evidently, as further apart from the focus, the GRR decreases, verifying the dependence of GRR on the power density, which are corresponding to the results of Fig. 6b. Furthermore, based on the spectral data of the UC photoluminescence, variation of color points of the 10 mol% Li$^+$ ions doped KLu$_2$F$_7$: Yb$^{3+}$, Er$^{3+}$ NPs as a function of power density are obtained, which is illustrated in the Commission International de l’Eclairage France (CIE) 1931 chromaticity diagram in Fig. 6d. Obviously, the color coordinates of UC emission falls in yellow regions under the excitation of 980 nm LD with a low power density. It ranges from yellow to green as the pump power density increase gradually. Fig. 7 is the schematic partial energy level diagram and energy transfer processes involved in the UC process. The energy transfer from Yb$^{3+}$ ions to Er$^{3+}$ ions can promote the electrons from the ground state to the $^4F_{7/2}$ level of Er$^{3+}$ ions under the excitation of 980 nm LD. The inset of (a) shows the amplification of UC spectra in short wavelength (a1) and the power density dependence of GRR of x = 0 and 10 samples (a2).
the increase of Li\(^{3+}\) ions will greatly enhance the scope of the applications of KLu\(_2\)F\(_7\): Yb\(^{3+}\), Er\(^{3+}\) NPs.

Acknowledgments

This work was financially supported by the National Science Foundation of China (61308091, 61506009), the Young Talents Support Program of Faculty of Materials and Engineering, Kunming University of Science and Technology (14078342), and the Postdoctoral Science Foundation of China (2013M540720).

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