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Lanthanide ions generally have abundant meta-stable excited states enabling lanthanide-doped nanocrystals (NCs) to display multiplex emission profiles. We address this issue by presenting a series of novel fluorides based nanophosphors exhibiting spectrally pure upconversion (UC) red fluorescence upon near-infrared (980 nm) excitation. Single-band, deep-red UC luminescence was achieved when Yb$^{3+}$-Er$^{3+}$ ion-pair was incorporated into K$_3$MF$_7$ (M = Zr, Hf). This UC luminescence feature of K$_3$MF$_7$Yb$^{3+}$,Er$^{3+}$ (M = Zr, Hf) NCs is independent of the doping levels of Yb$^{3+}$-Er$^{3+}$ and pump power of incident light. High-energy vibrational oscillators on the NCs surfaces are likely to result in the striking increase in the population of $^{9}F_{7/2}$ level of Er$^{3+}$, accounting for spectrally pure luminescence. The composition-optimized nanophosphor presents relatively perfect red monochromaticity.

Recently, lanthanide-doped upconversion (UC) nanoparticles have evoked considerable interest due to their unique properties including multicolor emission, large anti-Stokes shift, narrow emission bandwidth, high resistance to optical blinking and photobleaching, as well as low toxicity and deep tissue penetration depths (up to 10 mm) under exposure of NIR light (980 nm), which make them to be expected to have potential applications. To make up for this deficiency, wise choice of hosts is considered to be the most effective way to achieve single-band UC emission. Unfortunately, suitable host materials meeting that above requirement are only restricted to some specific cases like KMnF$_3$, MnF$_2$, ZrO$_2$, CaSc$_2$O$_6$, ScOF and Na$_2$ZrF$_6$. It is commonly believed that high-energy organic groups like OH usually act as primary centers of nonradiative transition. To the best of our knowledge, spectrally pure upconversion luminescence induced by high-energy organic groups has been much less well explored. Herein, we aimed to investigate single-band UC emission properties of potassium heptafluoro-zirconate/hafnate based nanocrystals (NCs). Pure and Yb$^{3+}$-Er$^{3+}$ co-doped K$_3$MF$_7$ (M = Zr, Hf) NCs were successfully prepared via a room-temperature complex procedure using oleic acid as chelating agent. Impressively, the presence of high-energy vibrational oscillators on the surfaces of NCs leads to the striking increase of population for $^{9}F_{7/2}$ level of Er$^{3+}$, giving rise to spectrally pure luminescence.

**Experimental Section**

**Materials.** All chemicals were of analytical grade and were used as received without further purification. Analytical grade rare earths oxides (Yb$_2$O$_3$, Er$_2$O$_3$, 99.99%), ZrOCl$_2$, 8H$_2$O (≥ 99.0%), HfOCl$_2$, 8H$_2$O (≥ 98.0%), KF, 2H$_2$O (≥ 99.0%), NH$_4$F (≥ 96.0%), concentrated nitric acid (HNO$_3$ ≥ 68.0%), ethanol (≥ 99.7%), and cyclohexane (≥ 99.5%) were purchased from Sinopharm Chemical Reagent Co., China. Rare earth oxides were separately dissolved in dilute HNO$_3$ solution and the residual HNO$_3$ was removed by heating and evaporation, resulting in the formation of aqueous solution of corresponding RE(NO$_3$)$_3$. Oleic acid (OA), potassium oleate (KOA), and oleylamine (OM) were supplied by Alfa Aesar Co., China.

**Synthesis.** Pure and lanthanide-doped K$_3$MF$_7$ (M = Zr, Hf) NCs were prepared via a solution-phase complex chemical method at room-temperature (25 °C). Herein we took the synthesis of K$_3$ZrF$_7$ NCs as

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an example. In a typical preparation, KOA (0.5 mmol, 2.62 g), 5.0 mL OM, and 20.0 g oleic acid were mixed together in a plastic beaker under stirring at room-temperature, followed by the addition of 40.00 mL alcohol solution of ZrOCl₂ (12.5 mM). The mixture was stirred vigorously for 6 hours. Subsequently, the aqueous solution of KF (0.19 g) and NaH₂F₄ (4.00 mL, 1.00 M) was slowly added into the mixture. After continually stirring for 30 min, the mixture was left to stand for 12 hours at 25 °C. The products were collected by centrifugation, washed sequentially with cyclohexane and ethanol for several times. After dried in a vacuum at room-temperature for 24 hours, K₃ZrF₇ powder was obtained. The synthetic procedure of lanthanide-doped K₃ZrF₇/(K,Hf)F₇,NCs was the same as that used to prepare K₃ZrF₇ host, except that the stoichiometric amounts of ZrOCl₂/HFCl₂ and Ln(NO₃)₃ (Ln = Yb³⁺/Er³⁺) mixed solutions were added into the initial mixture.

Physical characterization. The crystallographic structure and phase purity were determined by powder X-ray diffraction (XRD) using a Bruker D8 Advanced X-ray diffractometer with Ni filtered Cu Kα radiation (λ = 1.5406 Å) at a voltage of 40 kV and a current of 40 mA. The morphology and chemical composition of the samples were characterized on a Hitachi S4800 field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectroscopy (EDS). The photoluminescence properties were investigated in the solid state. Up-conversion fluorescence spectra were collected on an Edinburgh Instruments FLS920 spectrofluorimeter using a 980 nm laser diode (Module K98D08M-30mW, China) as excitation source. Fourier transform infrared (FT-IR) spectrum in transmission mode was measured on a Nicolet 5SXC infrared spectrophotometer using the KBr pellet technique. Raman IR) spectrum in transmission mode was measured on a Nicolet 5SXC 30mW, China) as excitation source. Fourier transform infrared (FT-

Results and Discussion

As shown in Figure 1, XRD patterns of K₃ZrF₇ and K₃HfF₇ samples exhibit sharp and intense peaks indicative of highly crystalline and can be well indexed as cubic K₃ZrF₇ (JCPDS no. 73-1530, space group Fm-3m), and cubic K₃HfF₇ (JCPDS no. 78-1827, space group Fm-3m), respectively. No trace of other characteristic peaks was observed for impurity phases. The calculated lattice constants are as follows: a = 8.951(1) Å for K₃ZrF₇, and a = 8.973(4) Å for K₃HfF₇, which is in good agreement with the corresponding standard values for the bulk cubic K₃MF₇ (M = Zr, Hf). In the lattice of both isostructural compounds K₃ZrF₇ and K₃HfF₇, [MF₇]³⁻ pentagonal bipyramidal (D₅h) species exist as isolated complex anions surrounded by K⁺ ions. The three-fold axis of [MF₇]³⁻ can be oriented parallel to any of the eight [111] directions. The nearest-neighbour F–F distances are 2.64 Å, which is slightly less than twice the ionic radius of fluorine (2.72 Å), and the average Zr–F distance is ~2.10 Å. M⁺ cations are coordinated to seven fluorine ions. According to the Debye-Scherrer formula, the average crystal sizes of K₃ZrF₇ and K₃HfF₇, NCs were estimated as ~69, and 87 nm, respectively, which matched well with the corresponding SEM observations. SEM images show that K₃ZrF₇ and K₃HfF₇ samples are quasi-spherical with a diameter ranging from 45 to 72 nm for K₃ZrF₇, 50 ~ 93 nm for K₃HfF₇ (Figure S1 in supporting information).

Since Yb³⁺–Er³⁺ ion-pair can be easily incorporated into the K₃ZrF₇ or K₃HfF₇ lattices (phase and compositional analyses of Yb³⁺–Er³⁺ co-doped K₃(Zr,Hf)F₇ nanophosphors were given in Figures S2–S6 in supporting information), the as-obtained K₃MF₇ (M=Zr, Hf) NCs is strongly expected to be suitable UC hosts for Yb³⁺–Er³⁺ in the view of structure characteristics. On the other hand, Raman spectra of K₃ZrF₇ and K₃HfF₇ samples are shown in Figure 2. The well-resolved sharp peaks indicated that all the samples were highly crystallized, which is in agreement with above XRD results. The strongest phonon mode is about 546 cm⁻¹, which is away from the frequency ranges of visible spectral region (1250–2500 cm⁻¹). More importantly, this photon frequency value is similar to those of calcium scandate (540 cm⁻¹) and sodium heptafluorozirconate (556 cm⁻¹), which are found to present perfect green and red UC monochromaticity upon doping of Yb³⁺Ho³⁺ and Yb³⁺–Er³⁺ ion-pairs, respectively. Obviously, we believe that the as-prepared K₃MF₇ (M=Zr, Hf) can act as promising host lattices for efficient single-band emission. To validate this point, we investigated the UC properties of Yb³⁺–Er³⁺ co-doped K₃MF₇ (M=Zr, Hf) in detail.

Figure 1. XRD patterns of as-obtained K₃ZrF₇ (bottom curve), and K₃HfF₇ (top curve) NCs (background uncorrected).

Figure 2. Raman spectra of K₃ZrF₇ and K₃HfF₇ hosts (the assignments of bands are also included).
the visible spectral region, based fluorides NCs which typically exhibit multiple-band emissions in samples.

was determined to be 2.0 mol% (Figure 3d). As exhibited in Figure 3e, as a function of Yb

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3 b). For KZrF 3:Yb 3+,Er 3+ (20/2 mol%) NCs, the optimal Er 3+ doping level was determined to be 2.0 mol% (Figure 3d). As exhibited in Figure 3e, the single-band emission characteristics of KZrF 3:Yb 3+,Er 3+ (20/2 mol%, 0.28 ≤ t ≤ 0.78) NCs is well maintained in all Hf 6+-modified samples.

All together, the above results suggest that single-band UC emission feature is independent of the doping levels of Yb 3+ -Er 3+ and the content of Hf 6+ in host lattice. Similar phenomena were also observed in tetragonal Na 2 ZrF 5:Yb 3+,Er 3+ [16b], and in Yb 3+ -Er 3+ co-doped Mn 2+ -containing NCs such as KMnF 3 and MnF 2 [10b,10c].

Firstly, we investigated UC emission intensity for 4F 9/2 → 4I 15/2 transition of Er 3+ as a function of incident power. It is well known that the UC emission intensity (I) is proportional to the pump power of the pump power (P) for the UC process. A plot of lg(I) against lg(P) yields a straight line with slope n. As shown in Figure 4, based on the best fit with a power function, the slope is calculated to be 1.44. According to Pollnau et al.,[36] slope of the pump power dependence of UC emission intensity is determined by the competition between the UC and decay process in the intermediate level. Specifically, while UC is the dominant process which depopulates the intermediate levels, slope tends to a limit of 1, while decay is the dominant process, slope tends to 2. In our case, the observed slope is near to 1, indicating that the UC for KZrF 3:Yb 3+,Er 3+ is mainly depopulation the intermediate levels.

Likewise, at the low-temperature (77 K) Yb 3+ -Er 3+ -codoped KZrF 3 NCs remained a single-band UC emission (Figure 5), indicating that the phonon participation in the transfer process has only a slight effect on the depopulation of the excited states.

Figure 3  (a) UC emission spectra and (b) red-emitting intensity as a function of Yb 3+ doping concentrations (x value) for KZrF 3:Yb 3+,Er 3+ (x/2 mol%). (c) UC emission spectra and (d) red-emitting intensity as a function of Er 3+ doping levels (y value) for KZrF 3:Yb 3+,Er 3+ (20/y mol%). (The intensities of the samples with y values of 1 mol%, 4 mol%, and 10 mol% are magnified 10 times for the sake of comparison). (e) UC emission spectra of KZrF 3:HfF 3:Yb 3+,Er 3+ (20/2 mol%) samples with various contents of Hf 6+ (t value).

Figures 3a and 3c depict UC emission spectra of Yb 3+ -Er 3+ co-activated KZrF 3 NCs. In comparison with Yb 3+ -Er 3+ co-doped routine rare-earth-based fluorides NCs which typically exhibit multiple-band emissions in the visible spectral region,[15,16] a deep-red emission band ranging from 640 nm to 680 nm (4F 9/2 → 4I 15/2 transition of Er 3+) for KZrF 3:Yb 3+,Er 3+ was observed, while the green emission was almost restrained. The red emission band is composed of two main peaks, which results from the split of Er 3+ 4F 9/2 generated by the crystal field.[16] UC emission behavior as a function of Yb 3+ or Er 3+ doping concentrations was investigated (Figure 3b and 3d). Significantly, the single-band emission feature of KZrF 3:Yb 3+,Er 3+ NCs remains the same on changing doping contents of Yb 3+ (5–40 mol%) and Er 3+ (1–10.0 mol%). As for KZrF 3:Yb 3+,Er 3+ (x/2 mol%) samples with fixed level of Er 3+, the UC emission intensity enhances with increasing Yb 3+ content from 5 to 20 mol% and then gradually weakens with further increasing Yb 3+ level to 40 mol% (Figure 3 b). For KZrF 3:Yb 3+,Er 3+ (20/y mol%) NCs, the optimal Er 3+ doping level was determined to be 2.0 mol% (Figure 3d). As exhibited in Figure 3e, the single-band emission characteristics of KZrF 3:HfF 3:Yb 3+,Er 3+ (20/2 mol%, 0.28 ≤ t ≤ 0.78) NCs is well maintained in all Hf 6+-modified samples.

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In order to investigate the high-energy groups adsorbed on the surface of NCs, the as-obtained K$_2$ZrF$_7$:Yb$^{3+}$/Er$^{3+}$ (20/2 mol%) NCs were annealed at 350 °C for 2 hrs. After then, the FT-IR (Figure S7) and UC (Figure 8) emission spectra of sample were measured. As exhibited in Figure S7, the stretching vibrations bands involving OH, CH$_2$ and COO groups disappeared, indicating the lack of high-energy organic groups. However, the green luminescence from $^4$I$_{15/2}$→$^4$I$_{11/2}$ and $^4$S$_{5/2}$→$^4$I$_{15/2}$ transitions of Er$^{3+}$ in the sample calculated at 350 °C was enhanced compared to that of as-obtained nanophosphor, which resulted in yellow emission rather than red fluorescence upon 980 nm excitation. (Figure 6) In this case, the corresponding CIE chromaticity coordinates were shifted to $(x = 0.3648, y = 0.5615)$, located in the yellow light region. The variation of emission color suggested that the high-energy groups can greatly influence the decay of $^4$I$_{15/2}$ and $^4$I$_{11/2}$ intermediate states of Er$^{3+}$. $^4$I$_{11/2}$ and $^4$I$_{13/2}$ levels are the intermediate states responsible for green and red emissions, respectively.

Depopulation of an excited state may occur either via a direct transition to a lower lying state, which is radiative, or via a phonon-assisted transition, which is non-radiative (also referred to as non-radiative decay). In the excited state of Er$^{3+}$, excited photon loss due to transfer of energy to the near-by surrounding phonons of high energy group is usually achieved via a multiphonon relaxation (MR). The gap energies between $^4$I$_{15/2}$ and $^4$I$_{11/2}$ states and between $^4$F$_{5/2}$ and $^4$F$_{7/2}$ states of Er$^{3+}$ are around 3600 and 3000 cm$^{-1}$, respectively. According to the following equations 1 and 2 ($k$ is inversely proportional to the phonon numbers),

$$K = A \exp(-\beta g) \quad (1)$$

$$g = \Delta E / \hbar \omega_m \quad (2)$$

where $K$ is MR rate constant, $A$ (in hertz) and $\beta$ are constants, $g$ is phonon numbers needed in the MR, $\Delta E$ stands for the energy gap to the next lower level, and $\hbar \omega_m$ is the phonon cutoff frequency. Bridging the gap, using phonon energies of 546 cm$^{-1}$, is not very favorable due to the requirement for the availability of a large number of phonons (at least seven phonons). As exhibited in Figure S8, the organic groups OH and CH$_2$ possess high-energy vibrational modes (2800-3600 cm$^{-1}$), in comparison with the dominant phonon modes in K$_2$ZrF$_7$ (546 cm$^{-1}$). $^4$I$_{11/2}$ level can easily decay to the lower level (energy gap ~3600 cm$^{-1}$) with the aim of high-energy organic groups such as OH and CH$_2$. In such case, $^4$I$_{11/2}$ level non-radiative decay to the lower-lying, intermediate level ($^4$I$_{13/2}$) occurs, leading to red emission. Hence, we believed that the single-band UC emission can be ascribed to the striking increase in the population of $^4$I$_{13/2}$ level reduced by high-energy organic groups on the surfaces of K$_2$ZrF$_7$:Yb$^{3+}$/Er$^{3+}$ NCs.

As shown in Figures 3b and 3d, the strongest UC emission is realized for a 20/2 mol% Yb$^{3+}$/Er$^{3+}$-doping concentration. The Commission Internationale de L’Eclairage (CIE) chromaticity coordinates for the emission spectrum are calculated to be $(x = 0.5846, y = 0.3227)$, located in the red light region (point a Figure 7). To evaluate the spectral purity quantificationally, Chan et al. recently introduced a parameter ($S_p$), $S_p = (A_y - A_h)(A_h + A_y)$, where $A_y$ and $A_h$ are the integrated areas from 500 to 600 nm and from 600 to 700 nm, respectively. $S_p$ varies from −1 to +1 with −1 (+1) corresponding to purely red (green) emission. According to this definition, $S_p$ value of K$_2$ZrF$_7$:Yb$^{3+}$/Er$^{3+}$ (20/2 mol%) nanophosphor is calculated as −0.90, which is close to the highest value for NaYF$_5$:Er$^{3+}$,Tm$^{3+}$ (2/2 mol%) NCs with almost completely pure red emission ($S_p = −0.95$).

Conclusions

In summary, we have demonstrated for the first time the preparation and UC luminescent feature of single-phase potassium heptfluoro-zirconate/hafnate NCs obtained by a simple complex chemical route under ambient conditions. Cubic K$_2$MF$_7$ (M = Zr, Hf) were found to be perfect host materials for efficient UC generation of lanthanides ions. Single-band UC luminescence under 980 nm excitation is achieved in Yb$^{3+}$-Er$^{3+}$ co-doped K$_2$MF$_7$ (M = Zr, Hf) samples. The presence of high-energy vibrational oscillators on the surfaces of K$_2$ZrF$_7$:Yb$^{3+}$/Er$^{3+}$ NCs is likely to result in the striking increase in the population of $^4$I$_{13/2}$ level of Er$^{3+}$, giving rise to spectrally pure luminescence. The spectral purity was evaluated and the value found for composition-optimized K$_2$ZrF$_7$:Yb$^{3+}$/Er$^{3+}$ was $S_p = −0.90$, which is close to the highest value for NaYF$_5$:Er$^{3+}$,Tm$^{3+}$ (2/2 mol%) NCs achieved so far.

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Notes and references


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A series of novel fluorides based nanophosphors (NPs) exhibiting spectrally pure upconversion (UC) red fluorescence upon near-infrared (980 nm) excitation. Single-band deep-red UC luminescence feature of $K_xM_F_7:Yb^{3+},Er^{3+}$ (M = Zr, Hf) NPs is independent of the doping levels of Yb$^{3+}$-Er$^{3+}$ and pump power of incident light. High-energy vibrational oscillators on the NPs surfaces are likely to result in the striking increase in the population of $^4F_9/2$ level of Er$^{3+}$, accounting for spectrally pure luminescence.