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The novel upconversion properties of $LiYbF_4$:Er microcrystals compared to the Na counterpart†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Experimental section

Materials

All the Rare-earth oxides in this work including Yb_2O_3 (99.99 %) and Er_2O_3 (99.9 %) were purchased from Sinopharm Chemical Reagent Company of China. Lithium fluoride (LiF), sodium fluoride (NaF), ammonium fluoride (NH_4F), nitric acid (HNO_3) and ethylenediamine tetraacetic acid (EDTA) were of analytical grade and used directly without further purification. Deionized water was used throughout the experiments.

Microcrystals synthesis

Erbium-doped $NaYbF_4$ (or $LiYbF_4$) microcrystals have been fabricated via a facile hydrothermal route assisted with EDTA. Briefly, 0.75 mmol of EDTA (0.5 mol/L) was added to a mixture containing 0.3 mmol of rare-earth nitrate (1.5 mL of 0.2 mol/L $RE(NO_3)_3$, RE =Yb and Er) and 15 mL deionized water. The solution was then thoroughly stirred for 30 min to form a chelated RE-EDTA complex. Then, a solution 8 mL (1.0 mol/L) of NH_4F and 4 mL (1.0 mol/L) of NaF (or LiF) aqueous solutions were dropped into chelated RE-EDTA complex under thoroughly stirring. The pH value of the mixture was tuned around 4.0 with nitric acid. Subsequently, the milky colloidal solution was transferred to a 40.0 mL Teflon-lined autoclave, and heated at 200 ^{0}C for 24 h. The final product was collected by centrifuging and washed with water and ethanol. The collected microcrystals were dried under 80 ^{o}C for 12 h.

Characterizations

The phase compositions of the as-prepared products were examined by XRD with a D/Max2400 X-ray diffraction meter with Cu *Ka* (40 kV, 100 mA) irradiation (λ =0.15406 nm). SEM micrographs were obtained using a Hitachi S-4800 FE-SEM. The photoluminescence were recorded with a Ti sapphire continuum laser (MBR-110) and a YAG:Nd^{3+} (Quanta Ray Lab-170) laser as the excitation source. All the measurements were performed at room temperature.

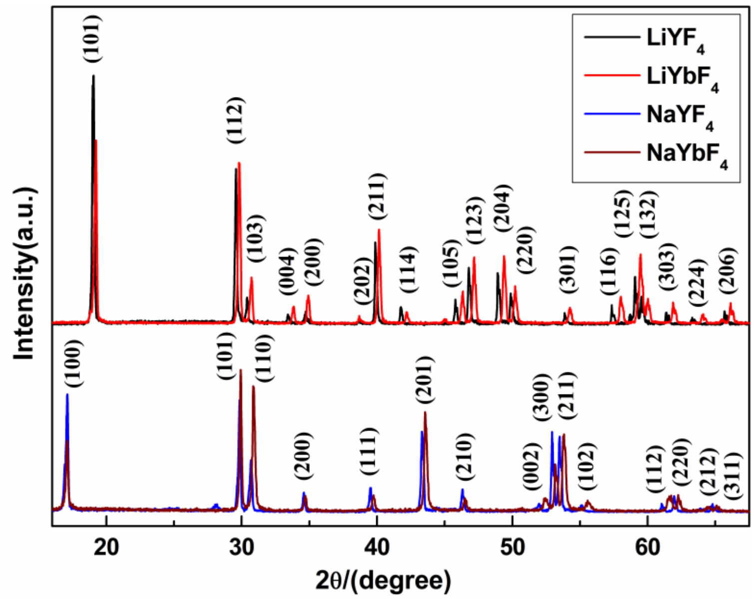

Fig. S1 XRD patterns of different fluoride microcrystals.

XRD patterns in Fig. S1 show that the crystal phases of the $NaYbF_4$ (or $LiYbF_4$) microparticles closely resemble to those of the $NaYF_4$ (or $LiYF_4$) microparticle counterparts except for the shift of the diffraction peaks of $NaYbF_4$ (or $LiYbF_4$) toward higher 2θ angle.

The blue shift of the spectra

The similar phenomenon of the blue shift appear in $LiYF_4$:Er relative to $NaYF_4$:Er, which indicate that the shift may be ascribed to dissimilar crystal phase construction.

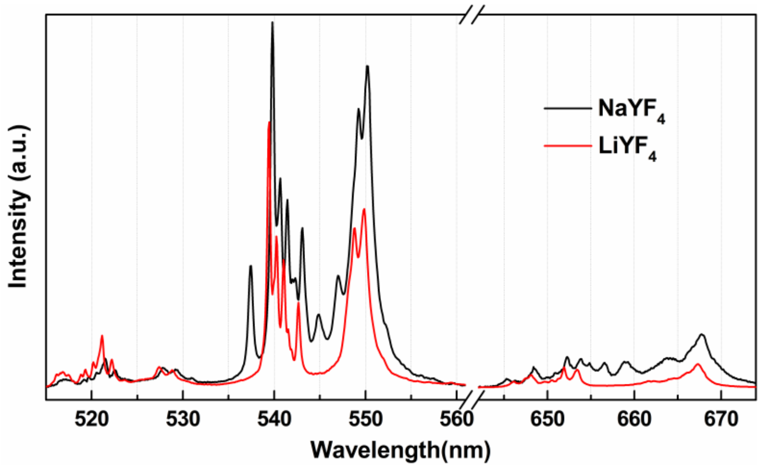

Fig. S2 UC emission spectra of 2 mol% Er doped fluoride microcrystals. The samples were excited with 980 nm photons.

Thermal population

The thermal effect caused by the exposure of the 980 nm laser has to be considered. For Er^{3+} ions, the energy separation between the two nearest excited states $^2H_{11/2}$ and $^4S_{3/2}$ is only several hundred wave numbers. This will lead the intensity ratio of $^2H_{11/2}$-$^4I_{15/2}$ to $^4S_{3/2}$-$^4I_{15/2}$ to be sensitive to the Yb^{3+} concentration and excitation power owing to Boltzmann's thermal population. Figure S3 shows the ratio of $^2H_{11/2}$-$^4I_{15/2}$ to $^4S_{3/2}$-$^4I_{15/2}$ as a function of temperature in different samples. The larger value of ratio was found in $LiYbF_4$, which indicates the higher Yb^{3+} concentration and stronger thermal effect in $LiYbF_4$.

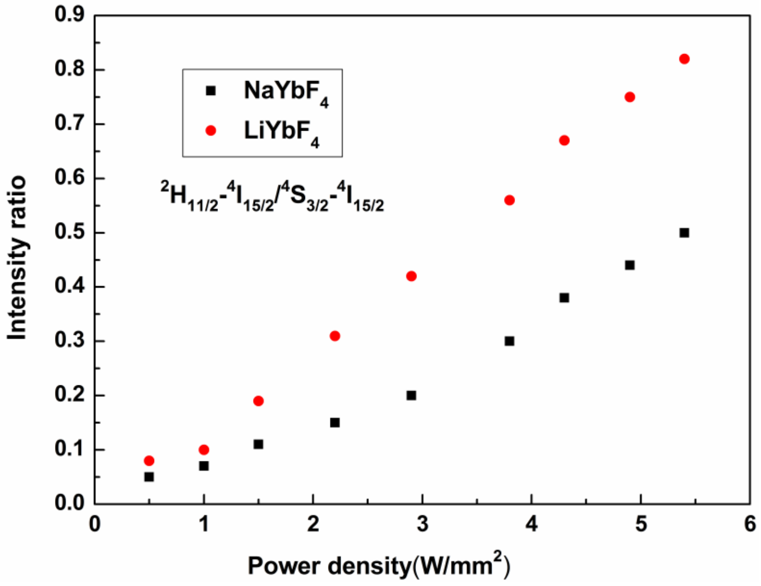

Fig. S3 Intensity ratios of $^2H_{11/2}$-$^4I_{15/2}$ to $^4S_{3/2}$-$^4I_{15/2}$ as a function of excitation power in different samples.