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Synergistic effect of crystal structure and concentration quenching on photoluminescence of Er^{3+} doped upconversion nanocrystals

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Abstract: $YbF_{2.357}$, YbF_3, Ba_2YbF_7, and BaF_2 upconversion nanocrystals doped with emitter Er^{3+} ion were synthesized in the same solvent system just with changing the molar ratio of Ba^{2+} to Yb^{3+} in the precursor, which corresponed to the crystal phases of rhombohedral, orthorhombic, tetragonal, and cubic, respectively. All the samples emitted both 660 nm red light and 543/523 nm green light which originated from Er^{3+}-$4f^n$ electronic transitions $^4F_{9/2}$-$^4I_{15/2}$ and $^4S_{3/2}/^2H_{11/2}$-$^4I_{15/2}$, respectively. It was worth mentioning that YbF_3:Er^{3+}, Ba_2YbF_7:Er^{3+}, and BaF_2:Er^{3+} could emit dazzlingly bright light even under the excitation of a 980 nm CW laser with output power of 0.1 W. Upconversion emission mechanism analysis indicated that the intensity ratio of red to green light highly depended on the synergistic effect of crystal structure, concentration quenching, and particle size, but were not sensitive to crystallinity as previously reported for $NaLnF_4$ (Ln=lanthanide).

Keywords: upconversion; luminescence; nanocrystal; crystal structure; concentration quenching; rare earths

Lanthanide (Ln) doped upconversion nanocrystals (UCNCs) are widely used in various specific fields, such as lasers[1], color display[2,3], biological molecules detection[4,5], cell imaging[6–8], solar cells[9,10], nuclear magnetic resonance (NMR) developer[11,12] and scintillator[13], due to their unique properties including converting low energy infrared photons to high energy visible photons, narrow emission band, high emission color purity, sharp optical absorptivity, low phonon energy, and high conversion efficiency[14]. Especially, potential application in biomedical imaging has made these UCNCs attract much attention in recent years[15,16], owing to their deep penetration to tissues, low radiation damage, and weak auto-fluorescence[17–19].

It is well known that the property of material can be tuned and controlled by impurities doping. Up to now, much effort has been made to investigate the photoluminescence of lanthanide doped fluorides and oxides[20]. Recently, the influence of Ln-dopants on crystalline phase, size and shape and luminescence property of nanocrystals was deeply investigated. For instance, Prasad and co-workers[21] reported the synthesis and magnetic resonance properties of bi-functional $NaYbF_4$:Tm^{3+}/$NaGdF_4$ core/shell nanocrystals while Liu and co-workers[2] demonstrated rational tunability of the size and phase of $NaYF_4$ nanocrystals by lanthanide doping. However, we note that the alkaline-earth fluoride doped with lanthanides has rarely been investigated for their upconversion luminescence and the dependences on crystal structures and coordination charges as in $NaLnF_4$ (Ln=lanthanide).

Actually, it has been reported that upconversion efficiency of alkaline-earth fluoride doped with lanthanide ions can be even higher than most efficient hexagonal $NaYF_4$[22]. The particle size and crystal structure of alkaline-earth fluoride (MF_2, M^{2+}=Ca^{2+}, Sr^{2+}, Ba^{2+}) nanocrystals are highly dependent on alkaline doping. Here, we showed that upconversion luminescence of lanthanide Er^{3+} doped $YbF_{2.357}$, YbF_3, Ba_2YbF_7, and BaF_2 nanocrystals is dependent on the synergistic effect of crystal structure, concentration quenching, and particle size, but not sensitive to crystallinity as previously reported for $NaLnF_4$ (Ln=lanthanide)[23].

1 Experimental

Rare earth oxides with the purity of 99.99% were purchased from Beijing Chemical and used as starting materials without further purification. Rare earth nitrate $RE(NO_3)_3$ (RE=Yb and Er) solutions were prepared by dissolving the corresponding rare earth oxide in nitric acid at a high temperature, excess nitric acid was evaporated by heating. All other chemicals were of analytical grade and used without further purification.

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1.1 Synthesis of Er^{3+} doped $YbF_{2.357}$, YbF_3, Ba_2YbF_7, and BaF_2 nanocrystals in the same solvent system

Upconversion nanocrystals doped with 1 mol.% Er^{3+} NCs with different proportions of Ba^{2+} and Yb^{3+} in the precursor were synthesized by a solvothermal method using oleic acid as both a stabilizing and a chelating agent. The typical synthesis involved the addition of 8 mL of ethanol to 2 mL of aqueous solution containing 0.6 g of NaOH under stirring to form a homogeneous solution. Then, 15 mL of oleic acid was added to form a sodium-oleic acid complex. Subsequently, $Ba(NO_3)$ solution (0.25 mol/L), $Yb(NO_3)_3$ solution (0.5 mol/L) and $Er(NO_3)_3$ solution (0.05 mol/L) with designed molar ratios were introduced into the former transparent homogeneous solution. At last, a 1 mL aqueous solution containing 3 mmol NH_4F was added under constant vigorous stirring for 10–20 min. The resulting solution was transferred into a 50 mL stainless Teflon-lined autoclave, which is operated at 220 ºC for 24 h. After reaction completion, the system was naturally cooled down to room temperature. The resulting samples were washed several times with ethanol and deionized water to remove oleic acid and other residual solvents, and then dried at 70 ºC for 10 h.

1.2 Characterization

The X-ray diffraction (XRD) patterns of the synthesized samples were recorded by a D/max-γ System X-ray diffractometer with Cu Kα (λ=0.15406 nm) radiation. The morphology and microstructure were characterized by a transmission electron microscope (TEM, JEOL 2100) equipped with an Oxford instrument energy dispersive X-ray spectroscopy (EDS) system. The upconversion emission spectra were measured by a spectrophotometer (R 500) under the excitation of an unfocused 980 nm laser diode with a power density of 1 W/cm^2 at room temperature.

2 Results and discussion

2.1 Crystal structure, particle size and shape evolution of the products with decreasing the content of Yb^{3+} ion in the precursor

In order to investigate the influence of crystal structure and Yb^{3+} content on the upconversion emission, the samples were synthesized with various mole ratios of Ba^{2+} to Yb^{3+} in the precursor by hydrothermal method. X-ray diffraction (XRD) spectra of the synthesized samples were measured and are shown in Fig. 1. It is clear that the crystal structures of these samples depend highly on the molar ratio of cation Ba^{2+} to Yb^{3+}. For the molar ratio of 0% Ba^{2+}, XRD pattern of sample reveals a rhombohedral phase of $YbF_{2.357}$ (JCPDS#36-0826). Differentially, with increasing the molar ratio of Ba^{2+} from 10% to 40%, the crystal structure transferred to orthorhombic

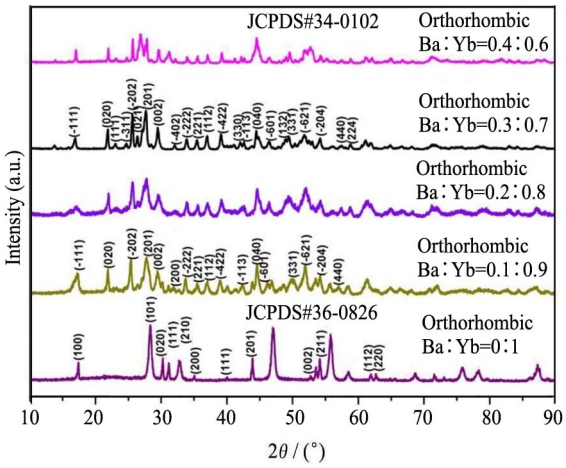

Fig. 1 XRD patterns of the synthesized nanocrystals with the molar ratios of Ba^{2+} to Yb^{3+} from 0:1 to 0.4:0.6, which corresponds to two types of crystal phases, i.e., rhombohedral $YbF_{2.357}$ and orthorhombic YbF_3, respectively

YbF_3 (JCPDS#34-0102). Very interesting, with further increasing the content of Ba^{2+} ion to the molar ratio of 50% (see Fig. 2), tetragonal Ba_2YbF_7 phase (JCPDS#41-0823) occurs instead of orthorhombic YbF_3 (JCPDS#34-0102). This indicates that the concentration of 50 mol.% Ba^{2+} ion is of a critical value for the crystal structure transformation from orthorhombic to tetragonal phase in the solution system containing two kinds of cations Ba^{2+} and Yb^{3+}. When the molar ratio of Ba^{2+} ion increases up to 90%, a new phase, i.e., cubic BaF_2 (JCPDS#85-1341), occurs besides of the original tetragonal Ba_2YbF_7 phase (JCPDS#41-0823). This indicates that the concentration of 90 mol.% Ba^{2+} ion is a critical value for the crystal structure transformation from tetragonal Ba_2YbF_7 to cubic BaF_2. Unexpectedly, pure cubic BaF_2 crystal phase was obtained with the molar ratio of Ba^{2+} ion reaching to 100%.

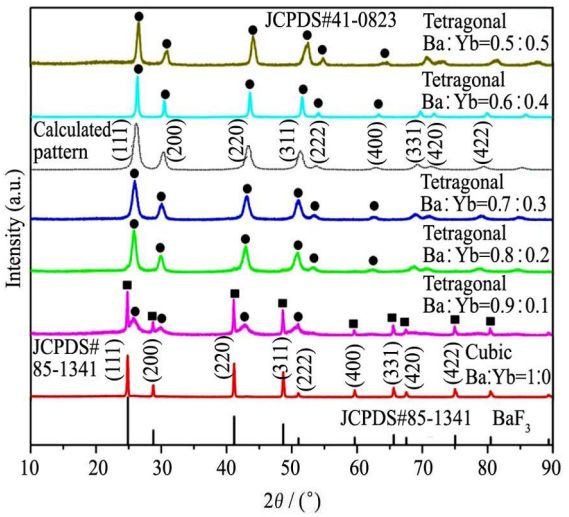

Fig. 2 XRD patterns of the synthesized nanocrystals with the molar ratios of Ba^{2+} to Yb^{3+} from 0.5:0.5 to 1:0, which corresponds to two types of crystal phases, i.e., tetragonal Ba_2YbF_7 and cubic BaF_2, respectively