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Chelation-controlled compound transition of luminescent fluoride crystals

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ABSTRACT

It is interesting that the natural phenomenon of chelator citrate stabilizing nanocrystals in bone could be learned and utilized in manipulating man-made nano-materials. During the synthesis of upconversion luminescent fluorides, it appeared that, the more citrate participated, the more difficult the resultant material transformed from cubic phase KY_3F_{10} nanocrystals, through hexagonal KYF_4 , to orthorhombic YF_3 crystals or mesocrystals, which clearly indicates the critical role of citrate in stabilizing KY_3F_{10} nanocrystals. Particles with different size, morphology, composition, and phase were controlled through the only variation of citric acid content. Meanwhile, the self-assembled mesocrystals showed emergent luminescent property with 63 times higher intensity, compared with the nanocrystals. The same sized YF_3 single crystals and YF_3 mesocrystals also exhibited dramatic difference in luminescent intensity.

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1. Introduction

Organic reagents have been tremendously important in the crystallization of the nature's biominerals, such as coccoliths [1,2], sea urchins [3] or aragonite tablets in nacre [4,5], which was recognized to involve a non classical mesoscale particle mediated formation process [1,4–6]. Macromolecules like proteins and small organic compounds such as citrate are frequently found in the biological organic mineral composites [7–10]. Citrate was discovered to regulate bone demineralization 40 years ago [11], and has been widely utilized as a biological additive to promote the repair of bone and enhance bone remodeling. Very recently, through direct NMR analysis, scientists demonstrated that citrate was strongly bound to the apatite nanocrystals in fish, avian and mammalian bone and indicated its critical role in interfering with crystal thickening and stabilizing the apatite nanocrystals in bone, but still leading to intriguing questions, such as the source of citrate in bone [12].

Practically, organic additive mediated precise manipulation of man-made nanocrystals has always been a challenging research focus [13–20]. For example, through controllable release of metal ions from metal–chelator complex, LaMer model [13] was widely applied to synthesize monodisperse nanocrystals. For morphology,

Murphy et al. demonstrated that the preferential adsorption of organic molecules onto different crystal facets directs the growth of particles into various shapes [14]. Also, aggregative growth was proposed in the control of nanoparticle size [15]. And molecule was utilized to intercalate nanoparticles into layered 2D galleries [16]. Recently, through molecule mediated self-assembly, fabrications of superstructures from individual inorganic nanocrystals for the needs of many practical applications were investigated [17–20]. Similarly, this superstructure could be a regular shaped particle, which is composed of iso-oriented and organic additive capped primary nanoparticles, formed by mesoscale self-assembly, identical with single crystal in electron scattering behavior, and widely termed as mesocrystal [1,4,6,21–23].

Here we report an unprecedented compound transformation determined by citric acid content in the hydrothermal synthesis of Yb^{3+} , Tm^{3+} codoped KY_3F_{10} nanocrystals, YF_3 crystals and mesocrystals. Lanthanide doped fluorides as the best upconversion luminescence material are currently attracting broad attention owing to their prospective applications in bio-labeling with nanosized crystals [24], three-dimensional displays with uniformly arrayed pixel crystals [25], and solar cell with high quantum efficiency crystals [26]. In this work, synthesis of Yb^{3+} , Tm^{3+} codoped YF_3 and KY_3F_{10} , with the assistance of a decisive organic additive–citric acid, not only meet different type applications with different size, morphology and luminescent intensity particles, but more importantly, it provides a new and simple technique of controlling compound transformation and might lead to new directions for nanocrystal manipulation.

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2. Experimental

7.6 ml 0.6 M $\text{RE}(\text{NO}_3)_3$ ($\text{RE}=\text{Y}^{3+}$ 81%, Yb^{3+} 18.5%, Tm^{3+} 0.5%) solution was mixed with citric acid monohydrate, 2.8 g KF dihydrate and 72 ml H_2O (18.25 M Ω cm) using 30 drops of 10 M KOH solution to slowly adjust pH value to 2 in a glass beaker. Content of citric acid for all experiments were in the range of 0.12 g (Chelator to Rare earth molar ratio, C/R 0.5/4) to 0.47 g (C/R 1.96/4) which all resulted in the same pH value around 2.5 while they were dissolved in water. After 20 min stirring, the mixture was transferred into a 100 ml Teflon liner autoclave for hydrothermal reaction at 190 °C. After washing by water and ethanol, the nanocrystals were separated by centrifugation and dried into powder for further characterization.

TEM and HRTEM were performed with a JEM-2100F field emission transmission electron microscope (JEOL). SEM was carried out with a JSM-6700F field emission scanning electron microscope (JEOL). FTIR spectra were collected on a Nicolet 7199-CFT-IR and samples were dried overnight at 353 K prior to KBr-pellet fabrication. Upconversion photoluminescence spectra of the dried powders were recorded by a spectrofluorometer (Fluorolog-3, Jobin Yvon, France) with 980 nm diode laser excitation. XRD patterns were obtained on a Rigaku D/Max-2550V X-ray diffraction meter using $\text{CuK}\alpha$ ($\lambda=1.54$ Å) radiation.

3. Results and discussion

Rare earth doped different fluorides were characterized with X-ray Diffraction and typical results are shown in Fig. 1a. Schematically, Fig. 1b further exhibits the compound transformation with the variation of citric acid content. With low citric acid content, the XRD peaks could all be identified as orthorhombic phase YF_3 (space group Pnma, JCPDS 74-0911). With high citric acid content, the XRD peaks could be located as cubic phase KY_3F_{10} (space group Fm-3m, ICSD 155135) with all peaks consistent with the previous reports

[27–29]. Adjusting the content of citric acid resulted in compound mixtures of YF_3 and KY_3F_{10} with every XRD peak pinpointed.

SEM, TEM and HRTEM images in Fig. 2 gave further insight into the size, morphology and crystal structure evolution with the alteration of citric acid content. As the citric acid content decreased, the size of the resulting particles increased dramatically from 25 nm to 4 μm , the morphology changed from sphere to finally a two-side truncated octahedron shape, and the rare earth doped compounds transformed from KY_3F_{10} nanocrystals to YF_3 mesocrystals or YF_3 single crystals. TEM image in Fig. 2a revealed the monodispersed KY_3F_{10} nanocrystals, a Chelator/RE molar ratio (C/R for short) 1.96/4 sample, as apparently that high content chelator capping on different facets of KY_3F_{10} nuclei balanced the growth rate in different directions resulting in sphere shape nanocrystals. Fig. 2b–e shows the TEM, EDS, SAD and HRTEM images of C/R 1.21/4 sample, a KY_3F_{10} nanocrystals and YF_3 mesocrystal mixture. Red color EDS patterns (Fig. 2c, d) semi-quantitatively recorded the element composition of small and big particles in the mixture, and the small particles were further confirmed to be KY_3F_{10} with the SAD pattern (inset of Fig. 2c). Although SAD image of the big particle in Fig. 2d exhibited a single crystal electron diffraction behavior, we confirmed it to be YF_3 mesocrystal with HRTEM image in Fig. 2e showing the oriented ordering of small YF_3 nanocrystals along [001] zone axis on the edge of big particle. The stepped plane, convex concave and porous surface pattern in the SEM image of Fig. 2f indicated the mesocrystal characteristics of sample C/R 0.96/4. Furthermore, smooth particle surface in SEM image of Fig. 2g and single crystal electron diffraction in Fig. 2h demonstrated a single crystal YF_3 particle of sample C/R 0.5/4.

To understand the compound transformation mechanism, control experiments for sample C/R 0.5/4 were conducted under different reaction time. As described above, after 72 h hydrothermal reaction, precursor C/R 0.5/4 resulted in pure single crystal YF_3 particles. XRD pattern in Fig. S1 in Supporting Information showed that this precursor resulted in cubic phase KY_3F_{10} in 1 h, cubic KY_3F_{10} in 1.5 h, cubic KY_3F_{10} and orthorhombic phase YF_3 mixture in 3 h, orthorhombic YF_3 in 9 h and 18 h. TEM image and HRTEM analysis in Fig. 3a confirmed cubic phase of 15 nm KY_3F_{10} nanocrystals in 1 h reaction.

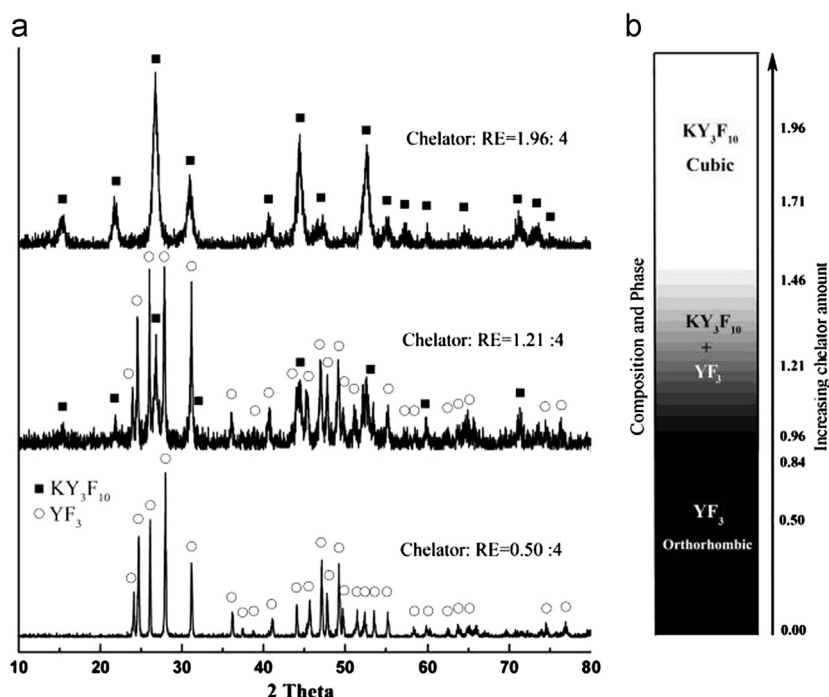


Fig. 1. (a) XRD patterns of fluorides synthesized with different chelator contents and (b) schematic illustration of compound transformation with the variation of chelator content.

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