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Hydrothermal synthesis, characterization and up/down-conversion luminescence of barium rare earth fluoride nanocrystals

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ABSTRACT

Mixed hydrothermal system H_2O–OA (EDA)–O-A(LO-A) is developed to synthesize barium rare earth fluorides nanocrystals (OA = oleylamine, EDA = ethylenediamine, O-A = oleic acid and LO-A = linoleic acid). They are presented as $BaREF_5$ (RE = Ce, Pr, Nd, Eu, Gd, Tb, Dy, Y, Tm, Lu) and Ba_2REF_7 (RE = La, Sm, Ho, Er, Yb). The influence of reaction parameters (rare earth species, hydrothermal system and temperature) is checked on the phase and shape evolution of the fluoride nanocrystals. It is found that reaction time and temperature of these nanocrystals using EDA (180 °C, 6 h) is lower than those of them using OA (220 °C, 10 h). The photoluminescence properties of these fluorides activated by some rare earth ions (Nd^{3+}, Eu^{3+}, Tb^{3+}) are studied, and especially up-conversion luminescence of the four fluoride nanocrystal systems (Ba_2LaF_7:Yb, Tm(Er), Ba_2REF_7:Yb, Tm(Er) (RE = Gd, Y, Lu)) is observed.

1. Introduction

Rare earth fluoride and complex fluoride possess low phonon vibration energy, which is a suitable host for the near infrared luminescent RE^{3+} ions since they are easily quenched [1,2]. This virtue makes it a potential candidate in many practical fields such as up/down-conversion luminescence, laser devices or optical fiber and special magnets [3–6]. In the recent years, many researches are focused on the application of rare earth fluorides up-conversion nanocrystals in biological imaging [7–16]. Especially β-$NaYF_4$ is generally regarded as the most efficient up-conversion host for Yb–Er and Yb–Tm ion pairs and serving as the workhouse for photon up-conversion from near infrared to ultraviolet and visible light, whose near infrared excitation at 980 nm and visible emission at 550, 650 nm make them low background noise and lower price of continuous laser device than pulse one [17–20]. Besides, $LiREF_4$ belongs to a class of crystal materials with special property such as Ising dipolar ferromagnet and a wide variety of collective quantum effects, ranging from quantum tunneling of single moments and domain walls to quantum annealing, macroscopic quantum entanglement, coherent spin oscillations (Rabi oscillations), quantum phase transition and disordered system of random field [21–24].

To presence, there are some methods to synthesize rare earth fluoride nanocrystals based on liquid phase reaction. Li and Lin have given an extensive review on the synthesis, surface modification and applications of rare earth fluoride nano/micro-crystals [25]. One is hydrothermal synthesis, which has been successful for the preparation of functional solids, unique condensed materials. The main reaction system involves fluoride sources of NaF/NH_4F, rare earth precursors $RE(O\text{-}A)_3$/$Y(LO\text{-}A)_3$ sodium salts of NaO-A/NaLO-A in mixed solvents of H_2O and ethanol (oleic acid = O-A, linoleic acid = LO-A) [26–32]. Wang and Li et al. puts forward a general strategy (L(liquid)–S(solid)–S (solution)) to typical inorganic nanocrystals including rare earth fluorides through hydrothermal technology, whose typical hydrothermal system is H_2O–ethanol–linoleic acid system [33]. Further, a hydrothermal in-situ chemical conversion path is utilized to prepare rare earth fluorides, in which precursors usually not only act as reactants but also as a template to control the shape of the products [34–37]. The other method to prepare rare earth fluorides is so-called high temperature solution synthesis, whose typical reaction systems are NH_4F, $RE(O\text{-}A)_3$, NaO-A, O-A(ODE) and CF_3COOLi/Na, $RE(CF_3COO)_3$, O-A(ODE) (ODE = 1-octadecene) [38–46]. Besides, the ionic liquids (non-volatile, non-flammable and thermally stable organic salts) behave as 'green' alternative to the conventional organic solvents and are used to synthesize of rare earth fluoride, whose low melting point, relatively low

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viscosity and wide electrochemical window are benefit for the further practical application [47–49]. Our group also has achieved the ultralow temperature to synthesize high-quality β-$NaYF_4$:Yb, Er/Tm up-conversion nanocrystals, as low as 80 °C, and 40 °C for β-$NaGdF_4$:Yb, Er/Tm by manipulating surfactants and chemical potential of monomers in hydrothermal system [49]. Besides, we have also achieved the synthesis of some rare earth fluorides with new phase structure such as γ-REF_3 (RE = Eu–Tm, Y), hexagonal $LiREF_4$ (RE = Nd–Lu, Y) and porous zeolitic phases $(C_2H_{10}N_2)_{0.5}RE_3F_{10} \times xH_2O$ (RE = Ho–Lu) in diffusion-controlled nucleation and growth model, and also assembled the $LiYF_4$–$LiLuF_4$ core-shell nanostructure [49,50].

Among alkaline-earth rare-earth complex fluorides have obtained relatively little attention despite that their barium yttrium fluoride crystals such as BaY_2F_8 and $BaYF_5$ are excellent host matrices to activate rare earth ions, exhibiting the strong broadband emission in the near UV spectra region (360–440 nm) and highly efficient infrared-to-visible up-conversion light [51–58]. Solution-based routes are limited in the syntheses of barium lanthanide fluorides and only a few literatures on the syntheses of alkaline-earth lanthanide ternary fluorides via solution-based methods until now. Huang et al. have reported a facile synthesis of cubic-phase $Ba_{0.92}Y_{2.15}F_{8.29}$ submicro spheres via a solution-based method in a hydrothermal environment using ethylenediaminetetraacetic acid (EDTA) and $NaBF_4$ as chelator and fluoride source in the reaction [59,60]. Compared with other fluorides, tetragonal $BaYF_5$ bulk crystal is considered to be an excellent host matrix for up/down-conversion luminescence. But the detailed study on the chemical synthesis of barium rare earth fluorides covering all the rare earth ions has not been compared deeply.

In this paper, our aim is to select a modified hydrothermal system to prepare barium rare earth fluorides for all the typical rare earth ions and clarify the phase structure of barium rare earth fluorides for different rare earth ions. At the basis of the synthesis and structure, the luminescence, especially the up-conversion luminescence of them is discussed in details.

2. Experimental

2.1. Starting materials

Rare earth oxides (99.9% purity, RE_2O_3 (RE = La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Tm, Yb, Lu), Pr_6O_{11} and Tb_4O_7) were firstly to be dissolved in nitric acid solution and dried up by evaporation of water, resulting in the corresponding $RE(NO_3)_3 \times xH_2O$. $Ce(NO_3)_3 \times xH_2O$ (99.9%) was from Aladdin. $Ba(NO_3)_2$ (99+%), ethanol (98%), NH_4F (98+%), ethylenediamine (98%), linoleic acid (LA) (80%) were all from Xuchang Yuanhua Biotechnology Co., Ltd., China. Oleylamine (OM, C18, 80–90%) was from Aladdin and oleic

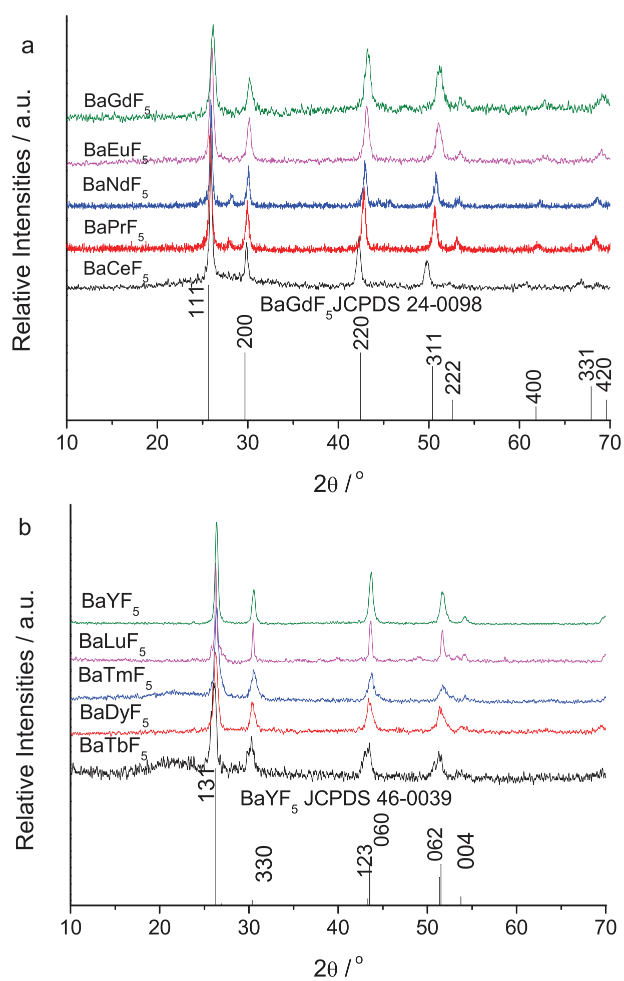

Fig. 1. XRD patterns of the $BaREF_5$ nanocrystals (RE = Ce, Pr, Nd, Eu, Gd) (a) and (RE = Tb, Dy, Y, Tm, Lu) (b).

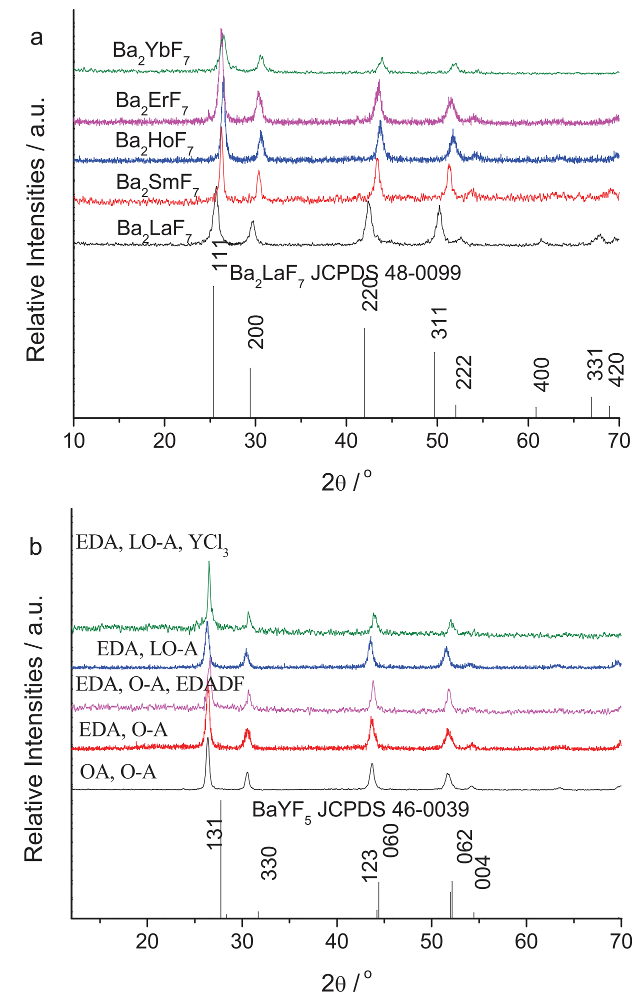

Fig. 2. XRD patterns of the Ba_2REF_7 nanocrystals (RE = La, Sm, Ho, Er, Yb) (a) and $BaYF_5$ nanocrystals from different reaction systems (b).