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Mild molten-salt synthesis and photoluminescence property of LaF_3 and its white-light emission with Eu doping

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ABSTRACT

Mild molten salt synthesis (MSS) method was utilized to synthesize rare earth fluorides nanocrystals with favorable fluorescence efficiency. LaF_3 nanocrystals were achieved through this modified MSS method by only using $La(NO_3)_3 \cdot 6H_2O$ and NH_4HF_2 as starting materials. NH_4HF_2 is difunctionality as both fluorine source and the flux. The effects of reaction time and temperature to the synthesis of LaF_3 nanocrystals were discussed in detail. The fluorescence of LaF_3 nanocrystals was detected with excitation wavelength of 360 nm, the results showed a broad band emission centered at 475 nm. The photoluminescence properties of pure LaF_3 nanocrystals and Eu^{3+} doped samples were also investigated. In our work, white light emission was achieved in single element (Eu^{3+}) doped LaF_3 nanocrystals by adjusting the concentration of Eu^{3+} ions. This would be the combination of broad emission of LaF_3 nanocrystals and sharp line emission of Eu^{3+} in the LaF_3:Eu^{3+} nanocrystals.

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1. Introduction

Over the past few decades, rare earth doped nanocrystals (NCs) have attracted lots of attentions due to their potential applications in many fields such as phosphors, lasers, optoelectronic devices, optical telecommunication, and biological labels [1–3]. Most fluorescence of rare earth compounds derives from the electron transitions within the 4f shell. For instance, the lanthanum compounds doped with activated ions have been widely used in the luminescent materials. However, the luminescence of pure rare earth fluorides, especially for lanthanum fluorides, has rarely been investigated. Because the absence electrons on the 4f shell of La^{3+}, the f-f transitions luminescence in the La^{3+} compounds cannot exist [4]. To the best of our knowledge, there is no paper reported on the synthesis of the pure LaF_3 NCs with the photoluminescence (PL) property. It is known that LaF_3 is an excellent fluorescent host matrix because of its low phonon energy, adequate thermal and environmental stability [5–7]. In addition, LaF_3 is an ideal substrate because it can be easily doped with other rare earth ions, which has attracted special interests for the synthesis of various materials [8–13]. Generally, in order to obtain the white light emission, two or more lanthanide were employed to form the co-doping lanthanide compounds [14,15]. If the host possesses the fluorescence emission, white light emission could also be obtained through the doping of the host with a single lanthanide element. Therefore, it is important and meaningful to synthesis the host with the PL property.

To date, LaF_3 NCs have been synthesized via effective methods, such as the hydrothermal method, wet chemical technique, organic ionic liquid route and the single-source precursor route [2,16–20]. Templates or structure directors are usually used in these methods, which are organics and often import impurity or byproducts [21–23]. Recently, the development of the nanotechnology has been focused on not only obtaining large quantities with reproducible size and structures, but also developing environmentally friendly synthesis methods [24,25]. The molten salt synthesis (MSS) method has been commonly used in the preparation of one-dimensional nanostructures for its environmentally sound and cost-effective [26–29]. In the traditional MSS method, typically either NaCl or an eutectic mixture of salts (such as NaCl/KCl, $NaNO_3/KNO_3$) were chosen as the desired salt [30,31]. Compared to conventional solid-state reactions [32], the MSS method was promoted for its simple operation, versatility, and cost-effectiveness.

Herein, we report a facile process for the preparation of LaF_3 NCs with exceptive fluorescence property through the modified MSS method. Notably, NH_4HF_2 was used as both reactant and flux instead of the desired salts mentioned above, it will not only prepare the pure products without introducing other impurity ions, but also reduce the reaction temperature to as low as 100 °C. Namely, the milder reaction conditions lower energy consumption was the case. Size-controlled LaF_3 NCs can also be prepared by controlling the reaction time in our work. In addition, the white light emission was achieved through only one element (Eu^{3+}) doping in LaF_3 NCs. We explored this strategy to generate white light by taking advantage of the fluorescence of the host and the typical transitions of the dopant ions. This approach provides not only a general route for the development of tunable fluorescence

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by lanthanide doped compounds, but also an effective way to obtain other fluorides.

2. Experimental section

2.1. Materials

$La(NO_3)_3 \cdot 6H_2O$ (99.99%) was purchased from Tianjin Chemical Reagent Company. $Eu(NO_3)_3 \cdot 6H_2O$ (AR) and $Nd(NO_3)_3 \cdot 6H_2O$ (AR) were purchased from Shandong Yutai Qingda Chemical Reagent Company. $Pr(NO_3)_3 \cdot 6H_2O$ (99.99%) was obtained from Aladdin Chemical Reagent Company and NH_4HF_2 (AR) was purchased from Beijing Chemical Company. Ethanol (AR) was purchased from Beijing Fine Chemical Company. All chemicals were used as received without further purification.

2.2. Molten-salt synthesis of LaF_3 NCs

$La(NO_3)_3 \cdot 6H_2O$ and NH_4HF_2 were mixed in a crucible maintained at 180 °C for 1 h. The final quantity of 1.0 mmol referred to La^{3+}, and the feed molar ratio of La^{3+}/F^- was controlled to be 1/10. The autoclave was cooled down to room temperature (25 °C) naturally. The products were then washed several times with deionized water and ethanol respectively, and dried at 60 °C.

LnF_3, where Ln was replaced with either Pr or Nd, were prepared using a similar procedure of LaF_3, in which $La(NO_3)_3 \cdot 6H_2O$ was exchanged for $Pr(NO_3)_3 \cdot 6H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$.

2.3. Fabrication of Eu^{3+} doped LaF_3 NCs

Eu^{3+} doped LaF_3 NCs were prepared using a similar procedure of pure LaF_3. The only modification was in replacing the usual amount of $La(NO_3)_3 \cdot 6H_2O$ with $Eu(NO_3)_3 \cdot 6H_2O$. To control the level of Eu^{3+} doping, a different amount of $Eu(NO_3)_3 \cdot 6H_2O$ was used to achieve an unchanged molar ratio of Ln^{3+}/F^-.

2.4. Characterizations

The phase purity of the LaF_3 NCs were examined by X-ray powder diffraction (XRD) measurements performed on a Rigaku D/max 2550VB diffractometer with a scanning rate of 10°/min in the 2θ range from 10° to 80°. Elemental analysis was performed by energy-dispersive spectroscopy (EDS) using an Oxford INCA energy-dispersive analysis system. The morphology and size of the as-synthesized products were observed by both scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) and transmission electron microscopy (TEM, Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD cinema). The chemical composition of the as-prepared NCs was analyzed using inductively coupled plasma mass spectrometry (ICP, PerkinElmer Optima 3300DV). The PL excitation and emission spectra were measured with an Edinburgh Instruments FLS920 spectrophotometer. Quantum yield was measured with an integrating sphere (C-701, Labsphere Inc.), with 365/405 nm Ocean Optics LLS-LED as the excitation source, and the laser was introduced into the sphere through the optical fiber. All optical measurements were performed under ambient conditions.

3. Results and discussion

3.1. Molten-salt synthesis of pure LaF_3 NCs

3.1.1. Characterization of LaF_3 NCs

Fig. 1a shows the XRD pattern of LaF_3 NCs which were synthesized at 180 °C for 1 h. In the pattern, all the diffraction peaks have a quite high intensity and fit very well to the hexagonal phase of LaF_3 (JCPDS: 32-0483), indicating the single-phase and high-purity LaF_3 NCs were successfully obtained. The SEM image of the sample (Fig. 2a) shows that the LaF_3 nanosheets, prepared at 180 °C for 1 h, are all hexagonal shape with similar thickness. The spectrum of EDS of the LaF_3 NCs is shown in Fig. 2b. Besides the two element peaks of La and F, no other peaks were detected in the spectrum, indicating that no impurities were embedded in the sample. The result accords quite well with the XRD detection.

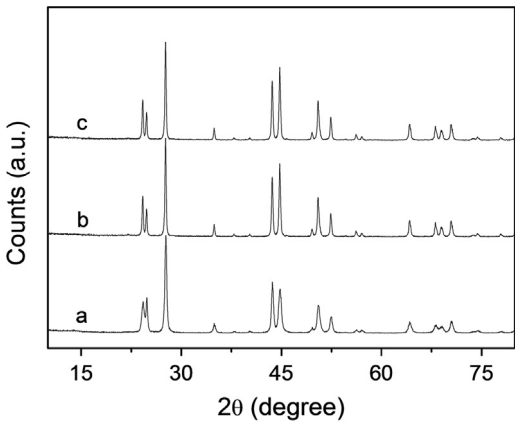

Fig. 1. XRD patterns of the LaF_3 prepared at 180 °C for different time. (a) 1 h, (b) 12 h, and (c) 24 h.

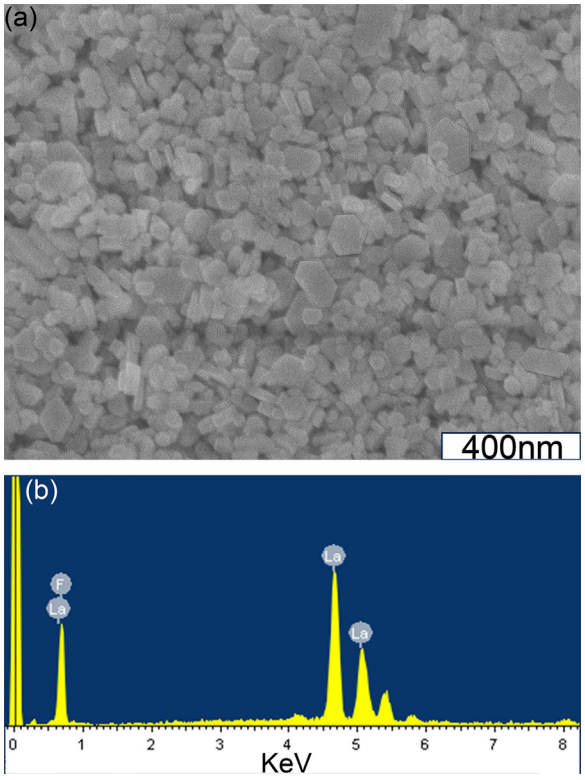

Fig. 2. SEM image and EDX spectrum of LaF_3 NCs synthesized at 180 °C for 1 h.

With the same MSS method utilizing NH_4HF_2 as the bifunctional reagent, we also synthesized other two rare-earth fluorides, PrF_3 and NdF_3. The XRD patterns of these products are given in Fig. S1. Both are highly crystallized and in pure-phase, indicating that our modified MSS method is universally applicable for the synthesis of other rare earth fluorides NCs.

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