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Systematic studies for the novel synthesis of nano-structured lanthanide fluorides

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HIGHLIGHTS

- The concept of "slow release anions for the assembly of crystals" was tried by a new method.
- Both the crystalline phases and the microstructures could be controlled.
- Red and green emissions could be excited by multiple wavelengths.

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ABSTRACT

The concept of "slow release anions for the assembly of crystals" was successfully carried out through a facile, effective and environmental friendly supersonic and microwave co-assistance (SMC) approach at very low temperature in less than 40 min. It has been found that the rational design of multiple irradiations, lanthanide contraction and fluoride sources would make it possible to control both the crystalline phases (hexagonal or orthorhombic) and the microstructures (including nanoparticles, nanoplates or micro-meter scale particles). The photo-luminescent properties of EuF_3 and TbF_3 revealed that characteristic red and green emissions can be excited by multiple wavelengths. Moreover, the results demonstrated that there are efficient energy transfers from Gd^{3+} to Eu^{3+} and Tb^{3+} in GdF_3: Eu^{3+} and GdF_3: Tb^{3+} phosphors based on this new method.

1. Introduction

Based on their unique electronic structures and numerous transition modes involving the 4f shell, rare earth compounds usually own outstanding optical, electrical, and magnetic properties, which have aroused considerable research interests in recent years [1–4]. As an important family, lanthanide fluorides have been widely used in many fields, such as optical telecommunication, lasers, new optoelectronic devices, diagnostics, and biological labels [5–9].

Researchers have contributed to the design and preparation of lanthanide fluorides LnF_3 with different shapes and sizes [9–17]. Their corresponding novel properties and potential applications have been investigated. So far as synthetic approaches are concerned, the ways of thermal decomposition [10,11], liquid–solid solution [12], reverse micelle method [13], hydrothermal [14,15] and ionic liquid [16,17] have been reported. Nevertheless, relatively high temperature (more than 150 °C) and long time (overnight) will be required. Therefore, the search for more efficient and environmental friendly synthetic ways is being continued.

Recently, ultrasonic and microwave irradiations were emerged as efficient techniques to fabricate diverse kinds of semi-conductor materials [18,19]. The electromagnetic heating of microwave as well as the microjets and shockwaves of ultrasound can greatly improve the reaction and increase the crystal growth rate as compared with conventional heating method. Up to now, no reports have concentrated on the design and synthesis of functional lanthanide fluorides. In this paper, by means of the slow hydrolyzation of $NaBF_4$, we successfully synthesized a series of lanthanide fluorides with multiform crystal structures (hexagonal and orthorhombic). Three types of morphologies (nanoparticles, nanoplates and micro-particles) were readily achieved via a novel supersonic

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microwave co-assistance (SMC) approach at very low temperature (80 °C) within only 40 min (Fig. 1). It was considered that during the synthetic procedure, F^- has been slowly released to form precipitate with Ln^{3+}, so as to make the growth of crystals gradual and controllable. The results indicate that the lanthanide ionic radii have a remarkable effect on the final stable crystal phase and morphology. Additionally, the photo-luminescent properties of EuF_3, TbF_3, GdF_3: Eu^{3+} and GdF_3: Tb^{3+} phosphors were also investigated. It is worth noting that this SMC method gains the advantages of saving-energy, efficiency and convenience in comparison with other conventional methods. It may provide an alternative and promising way for constructing other kinds of inorganic materials with novel morphologies and nanostructures.

2. Experimental

All the starting materials were obtained from commercial suppliers and used as received. Y_2O_3, La_2O_3, $Ce(NO_3)\cdot 6H_2O$, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3 and $NaBF_4$ were provided by Aldrich company. Lanthanide nitrates were obtained by dissolving their oxide in nitric acid except for $Ce(NO_3)_3\cdot 6H_2O$. The supersonic assisted microwave reactor (Fig. S1) was commercially available and produced by Nanjing Xianou technology company, China (XO-SM50).

For the formation of lanthanide fluoride, $NaBF_4$ was chosen as a fluorine source which will release fluoride slowly under the irradiation of microwave and ultrasound. In a typical synthesis, 20 ml of 0.1 mol/L $Ln(NO_3)_3$ and 20 ml of 0.2 mol/L $NaBF_4$ aqueous solution were mixed. Subsequently, the mixture was transferred to a three neck flask which adapted for the reactor. Microwave power was set as 400 W and reaction temperature was remained to be 80 °C. Supersonic power was 300 W with the reverse duty cycle 2 s. All the operation time was fixed as 40 min (Fig. 1). The as-prepared product was retrieved by centrifugation, washed by deionized water and alcohol three times and then dried at 60 °C in vacuum.

The X-ray powder diffraction was investigated on Bruker D8 diffractometer with Cu Kα radiation (λ = 0.1541 nm) in the range of 2θ = 10–90°. Scanning electron microscope (SEM) was measured with JSM-6360LV. Luminescence spectra were measured on an Edinburgh FLS920 spectrometer. The crystal phase identification of the obtained samples was examined using a MDI Jade 5.0 system.

3. Results and discussion

3.1. Structural analysis

The crystal structures of lanthanide fluorides prepared by SMC method were extensively investigated by X-ray diffraction (XRD). It is well established that lanthanide contraction phenomenon led to gradual changes of physical and chemical properties.

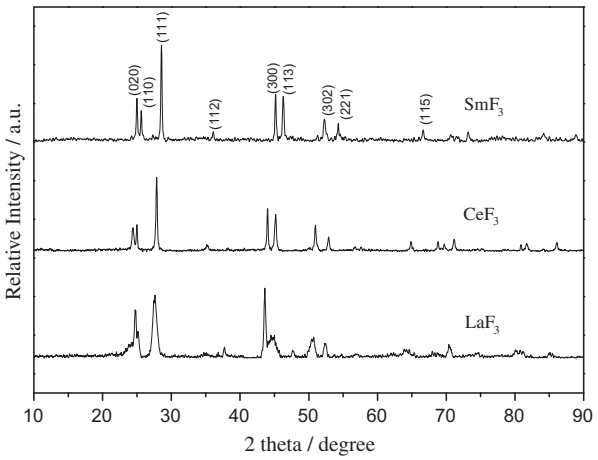

Fig. 2. XRD patterns of hexagonal phase LnF_3 (Ln = La, Ce, Sm).

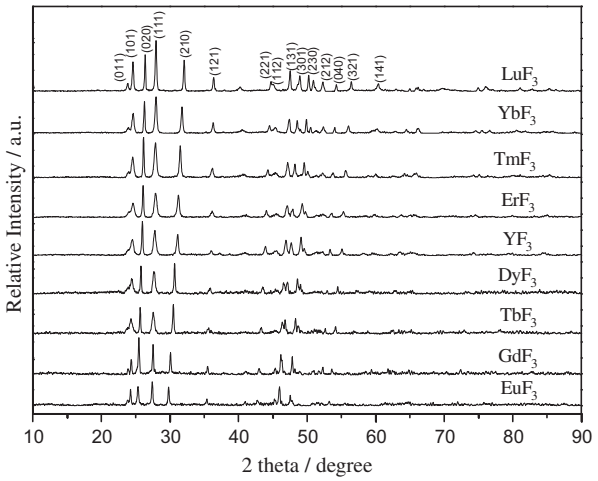

Fig. 3. XRD patterns of orthorhombic phase LnF_3 (Ln = Eu, Gd, Tb, Dy, Y, Er, Tm, Yb, Lu).

Previous studies [14,15,20–22] concerning lanthanide hydroxides, fluorides, phosphates and orthovanadates have demonstrated that the crystal structures changed with the decrease of ionic radii. As shown in Figs. 2 and 3, the XRD patterns of lanthanide fluorides can be clearly classified into two types. For the first group (La, Ce, Sm), all the diffraction peaks located at 2θ values of 10–90° can be perfectly attributed to the characteristic diffractions of hexagonal phase LaF_3, CeF_3 and SmF_3 respectively. In the case of the second group (Eu–Lu, Y), samples assembled under the same conditions are no longer hexagonal phase but orthorhombic. The

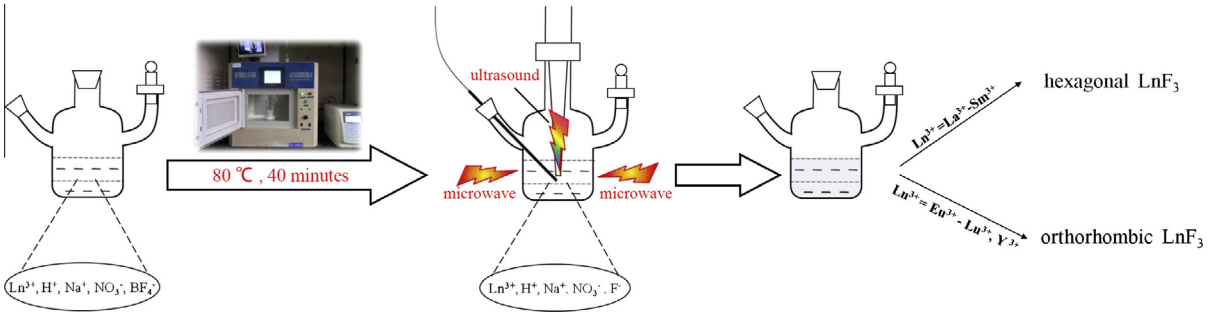

Fig. 1. Synthesis processes of LnF_3 prepared by SMC method.