



Novel ionic liquid-assisted hydrothermal method for the assembly of luminescent lanthanide fluorides with controllable morphologies



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ABSTRACT

An amphiphilic ionic liquid (diallyldimethylammonium tetrafluoroborate) assisted hydrothermal method has been applied for the synthesis of lanthanide fluoride nanoparticles. It has been carried out under mild conditions and large scale amounts of samples can be facily achieved by this efficient way. Luminescence features of the phosphors were studied by steady state fluorescence and the samples could present striking $^3D_0 \rightarrow ^7F_1$ transition with orange-red color, suggesting that Eu^{3+} ions are located in the crystal lattice with inversion symmetry. The particle size distribution was investigated by scanning electron microscope and the results showed that different microstructures such as nano-rods and nanoplates were obtained.

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1. Introduction

Ionic liquids (ILs) have been paid much attention for the synthesis of inorganic nano-materials owing to the outstanding properties like good thermal stability, negligible vapor pressure and extremely high ionic conductivity. They can not only play as solvents, but also use as template and ligand reagent [1]. Excellent capability for the dissolution and stabilization of metal cations were shown by these amphiphilic compounds, which will benefit the homogeneous synthesis of nano-sized inorganic materials [2].

Due to intrinsic structure and excellent luminescent performances, rare earth materials have been extensively studied [3–6]. As a well-known luminescent host, lanthanide fluorides (LnF_3) have great advantageous features in comparison with the conventional oxygen-based system such as low vibration energies, good optical transparency over a wide wavelength range and minimal quenching of the excited state of doped ions [7]. Up to now, most researchers have tried NaF , NH_4F , NH_4BF_4 , NaBF_4 or KBF_4 as fluoride sources [8]. Though these inorganic reagents are easily accessible, ILs still demonstrated the promising property of multi-functional positions in the reaction [9–13]. Recently, a few teams have reported the fabrication of lanthanide solid state materials in

the presence of polymerizable ionic liquid under irradiations [9,14]. This important organic salt (here is diallyldimethylammonium tetrafluoroborate ($[\text{DADMA}]\text{BF}_4$)) with environmentally benign features could be utilized as the structure directing reagent. It displays great potentials in optical application and phosphor industry. BF_4^- acted as a good replacing source of F^- upon decomposition. In addition, DADMA^+ moiety is commercially available and easily polymerizable cation [14]. In brief, this specific ionic liquid molecule is a preferable fluoride donor and efficient synthesis of lanthanide fluorides could be possibly realized by this way. The main advantage of choosing this ammonium cation type ionic liquid in the inorganic synthesis is its effectiveness for the dissolution and combination of metal salts, which permits it with the behavior of acting as surfactants. In addition, its melting point and viscosity were not very high. Therefore, in our work, $[\text{DADMA}]\text{BF}_4$ was incorporated to assemble $\text{LnF}_3:\text{Eu}^{3+}$ ($\text{Ln} = \text{Y}, \text{Gd}, \text{La}$) nanoparticles. Different controllable morphologies were achieved and the photoluminescence properties of the nanocrystals were also discussed in detail.

2. Experimental

2.1. Preparation

Y_2O_3 , La_2O_3 , Eu_2O_3 , Gd_2O_3 , NaF and NaBF_4 were purchased from Sigma-Aldrich Company. Diallyldimethylammonium chloride (60% aqueous) was provided by Aladdin. All the other reagents were purchased from Guangzhou Chemical Reagent Factory and used without

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further purification. Lanthanide nitrates were obtained by dissolving their oxides in concentrated nitric acid.

Ionic liquid and phosphor synthesis: diallyldimethylammonium chloride (5 g, 0.031 mol) in dichloromethane (10 ml) was added together with NaBF_4 (3.4 g, 0.031 mol) and stirred under room temperature for 72 h. The white precipitate was removed by filtration. The clear solution was washed with small quantities of water to remove remaining chloride. The solvent was removed in vacuo and the clear ionic liquid ($[\text{DADMA}]\text{BF}_4$) was dried at 80°C under dynamic vacuum for 24 h. Following procedures were the assembly of phosphors, 5 ml of 0.1 mol/l $\text{Ln}(\text{NO}_3)_3$ and 2.5 ml of 0.01 mol/l $\text{Eu}(\text{NO}_3)_3$ were mixed. Subsequently, the $[\text{DADMA}]\text{BF}_4$ (0.1 M) solution was added dropwise to the previous solution under magnetic stirring. Until a homogeneous solution was formed, the above mixed solution was transferred to Teflon-toclave and maintained at 160°C for 10 h. After naturally cooling down to room temperature, the product was collected by centrifugation and dried in vacuum at 70°C . Similar synthesis procedures were carried out to prepare YF_3 nanocrystals through employing other fluoride sources (NaF and NaBF_4).

The determination of $\text{Eu}(\text{III})$ was briefly described as follows: 0.5 g sample, 3 ml HF, 7 ml HNO_3 , 3 ml HCl and 2 ml H_2O_2 were transferred into the tetrafluorometoxil reaction vessels and microwave assisted digestion was performed. After cooling, the resultant sample was diluted with ultrapure water to final volume of 50 ml. ^{115}In (for Eu) was used as internal standard elements. Corresponding ICP-MS analysis results were added in Table 1.

2.2. Characterization

The X-ray powder diffraction was investigated on Bruker D8 diffractometer with $\text{Cu K}\alpha$ radiation ($k = 0.1541 \text{ nm}$) in the range of $2\theta = 10\text{--}90$. 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. Inductively coupled plasma mass spectrometry (abbreviated as ICP-MS) was carried out on an Agilent7500a (Agilent, USA). The samples were digested in a Mars 5 microwave reaction system (CEM Corporation, USA). Overall quantum yields were detected at room temperature based on an integrating sphere (Edinburgh FLS920 spectrometer) method and the sample was placed inside the integrating sphere. The excitation light was entered into the sphere by the optical fiber. When specific excitation wavelength (394 nm) was selected, the quantum yield values were calculated automatically.

3. Results and discussion

X-ray diffraction analysis is an effective way for the identification of the composition of the phosphors. It has been considered as the reliable method to determine the crystalline structures of different compounds. In order to study the feasibility of the ionic liquid as the precursor, we assembled a group of $\text{YF}_3:\text{Eu}^{3+}$ phosphors by using various fluoride sources such as NaF , NaBF_4 and $[\text{DADMA}]\text{BF}_4$. The collected results supported that the materials crystallized well (Fig. 1). Peak positions

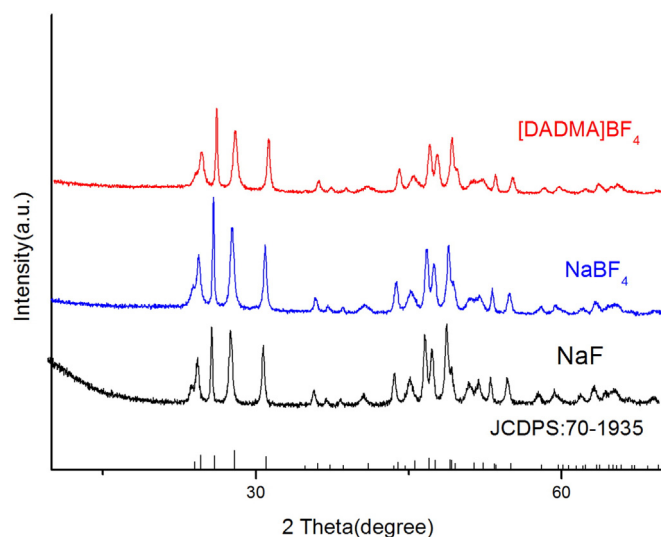


Fig. 1. XRD patterns of orthorhombic phase $\text{YF}_3:\text{Eu}^{3+}$ ($\text{F} = \text{NaF}, \text{NaBF}_4, [\text{DADMA}]\text{BF}_4$). The reference pattern for orthorhombic YF_3 from JCPDS file is also included.

and intensities of the three samples were analogous and consistent with the pure orthorhombic phases as indicated in the JCPDS card (No. 70-1935). It demonstrated that $[\text{DADMA}]\text{BF}_4$ could replace conventional fluoride source like NaF in the fabrication of europium doped phosphors.

For the sake of confirming the reliability of ionic liquid, we carried out photoluminescence measurements concerning the three optical materials (Fig. 2). The typical intense transitions observed in the emission spectra were derived from the $^5\text{D}_0$ level to the sublevels of $^7\text{F}_1$, $^7\text{F}_2$, $^7\text{F}_3$ and $^7\text{F}_4$. There were no apparent changes among the three samples, showing that the ionic liquid would act as an alternative precursor to prepare the desired solid state materials. The variation of lanthanide emission curves and shapes was also studied in a series of inorganic hosts including LaF_3 , GdF_3 and YF_3 . Fig. 3 gave the excitation (monitored at 593 nm) and emission spectra (excited at 394 nm) of LaF_3 assembled under hydrothermal conditions. The excitation band consists of a group of sharp peaks covering from 300 nm to 500 nm due to the direct transitions from ground state into higher excited states from the europium f-electrons. The characteristic peaks in terms of f-f transitions in Eu^{3+} were attributed to $^7\text{F}_0 \rightarrow ^5\text{H}_6$ (317 nm), $^7\text{F}_0 \rightarrow ^5\text{D}_4$ (361 nm), $^7\text{F}_0 \rightarrow ^5\text{G}_2$ (383 nm), $^7\text{F}_0 \rightarrow ^5\text{L}_6$ (394 nm), $^7\text{F}_0 \rightarrow ^5\text{D}_3$ (414 nm), $^7\text{F}_0 \rightarrow ^5\text{D}_2$ (464 nm) and $^7\text{F}_0 \rightarrow ^5\text{D}_1$ (525 nm). Under excitation at 394 nm, it can be observed that the derived narrow peaks were corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (593 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (615 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (650 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (702 nm) transitions. It has been accepted that $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (615 nm) is a forced electric dipole transition which would be prevalent due to small deviation from inversion symmetry. $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (593 nm) is the magnetic dipole transition which is insensitive to environmental differences. In this research, it is clear that europium ion occupies in the crystal lattice a site with inversion symmetry [15]. The results indicated that $^5\text{D}_0 \rightarrow ^7\text{F}_j$ emissions were very favorable to investigate the transition probabilities of sharp spectral features of lanthanide elements. In these lanthanide fluorides, $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission peak was dominating and transition to level with even J values ($J = 2$) was forbidden. When Gd or Y takes place of La in the matrices, the majority bands were also identified (Figs. 4 and 5). It demonstrated that the 4f orbitals of Eu^{3+} are hardly affected by the crystal field and host lattices because of the shielding effect of the $5s^2 5p^6$ electrons.

It is known that the size, shape and positioning of the microstructures were very attractive for potential applications in optical fields. We have carried out SEM measurements to have a better understanding of the morphological results (Figs. 6–8). The images showed a very high yield of the regular shaped nanostructures. YF_3 and GdF_3 exhibited one

Table 1
Elemental measurements of $\text{LaF}_3:\text{Eu}^{3+}$ (sample 1), $\text{GdF}_3:\text{Eu}^{3+}$ (sample 2) and $\text{YF}_3:\text{Eu}^{3+}$ (sample 3) by ICP-MS after microwave digestion ($n = 6$).

Sample	Certified concentration (mg/g)	Added concentration (mg/g)	Experimentally measured concentration by ICP-MS (mg/g)	Relative standard deviation (%)
1	37.30	10	47.44	2.2
2	34.22	10	44.38	1.9
3	49.45	10	59.26	2.0

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