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# Synthesis and spectral properties of lutetium-doped CeF<sub>3</sub> nanoparticles

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### Abstract

 $CeF_3$  and lutetium-doped  $CeF_3$  nanoparticles with the dopant concentration of 17, 25, 30, 42 and 50 mol% (molar ratio, Lu/Ce) were synthesized. XRD patterns were indexed to a pure  $CeF_3$  hexagonal phase even under the dopant concentration of 50 mol%. Environmental scanning electron microscopy-field emission gun (ESEM-FEG) was used to characterize the morphology of the final products. From the luminescence spectra of the products, we can get a broad emission ranging from 290 to 400 nm with peak at 325 nm. Lutetium-doping increases the luminescence intensity. We got the most intense luminescence at the dopant concentration of 30 mol%.

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## 1. Introduction

Lanthanide ions, due to their characteristic sharp absorption and emission bands in the ultraviolet, visible and infrared wavelength region, originated by f–d and f–f transitions, have been widely investigated as dopants for compounds used in luminescence devices, such as fluorescent lamps, scintillators and lasers [1]. Among these lanthanide ions,  $Ce^{3+}$ -doping has been extensively studied, since the broad UV emission from 5d to 4f transition makes  $Ce^{3+}$  possible to develop a tunable short-wave solid-state laser [2–4], amplifier [5,6], efficient scintillator [7,8], and sensitizer [9]. In scintillating material research,  $Ce^{3+}$ -doped or based materials as fast scintillators are of great interest due to the fast and generally intense parity allowed 5d–4f transition leading to blue-UV fluorescence. Therefore,  $CeF_3$  single crystals, as excellent scint-

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illators for high energy physics experiments [8,10,11], have been extensively studied. Recently, due to different properties of nanoscale materials from bulk materials [12], the study about CeF<sub>3</sub> nanoparticles has attracted great interest [13,14]. On the other hand, described by Shimamura et al. [1], the light yield of CeF<sub>3</sub> single crystals would be improved when doped with Lu<sup>3+</sup>. However, the study and of Lutetium-doped CeF<sub>3</sub> nanoparticles have not been reported in the literature by now, to the best of our knowledge.

The present work explores the synthesis and luminescence characterization of Lu:CeF<sub>3</sub> with different dopant concentration. Nanoparticles of Lu:CeF<sub>3</sub> were prepared from the reverse microemulsion technique which was first developed by Boutonnet et al. [15], to make colloidal, zerovalent nanoparticles. A microemulsion system was made by cetyltrimethylammonium bromide as the surfactant, *n*-butanol as cosurfactant, *n*-octane as continuous phase and salt solution as the dispersed aqueous phase.

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Cetyltrimethylammonium bromide (CTAB, 99.5%), and  $NH_4F$  (99.5%) were purchased from Beijing chemical plant; n-butanol (99.0%), n-octane (99.0%) were produced by the Shanghai reagent plant. The spectrographically pure Ce2O3 and Lu2O3 were purchased from Jiujiang nonfemet factory of China. Ce(NO<sub>3</sub>)<sub>3</sub> and Lu (NO<sub>3</sub>)<sub>3</sub> were prepared in our laboratory by dissolving Ce<sub>2</sub>O<sub>3</sub> or Lu<sub>2</sub>O<sub>3</sub> in nitric acid and then re-crystallizing. Water was distilled. All the chemicals used in this study were not further purification. Following Pillai and Shah [16], and Porti and coworkers [17,18], lutetium-doped CeF<sub>3</sub> nanoparticles were prepared from the quaternary reverse micelles (I and II) of cetyltrimethylammonium bromide (CTAB), *n*-butanol, *n*-octane, and water with identical compositions (% w/w values of components, 18.5, CTAB; 15.1, *n*-butanol; 51.8 *n*-octane; 14.6 · H<sub>2</sub>O solution) but different aqueous phase. The aqueous phases in reverse micelle I was the mixture of 0.12 mol/L  $Ce(NO_3)_3$  and Lu  $(NO_3)_3$  solutions with concentration of 0, 0.02, 0.03, 0.36, 0.05 and 0.06 mol/L corresponding to samples 1-6, respectively, and aqueous phases in reverse micelle II was solution of 0.7 mol/L NH<sub>4</sub>F. Stirred these two reverse micelles solely at 25 °C until a well-distributed system was obtained, and then mixed them rapidly under vigorous stirring. After 15-min reaction, the final products were collected by centrifuging. The precipitate was then washed five times with a 1:1 mixture of methanol and dichloromethane to remove oil and surfactant, followed by centrifugal recovery and vacuum drying before final products of lutetium-doped CeF<sub>3</sub> were obtained.

The phase purity of the lutetium-doped CeF<sub>3</sub> particles was examined by X-ray diffraction (XRD) measurement performed on Rigaku D/max-II B X-ray Diffractometer with monochromatic Cu Ka radiation (wavelength  $\lambda = 1.5418$  Å). The step-scan covered the angular range from 20° to 100° in step of 0.02° and the scanning rate of  $4.0^{\circ}$  min<sup>-1</sup> using silicon as internal standard. The morphology of the final products was characterized by Philips XL-30 environment scanning electronic microscopy-field emission gun (ESEM-FEG). Powdered samples (5 mg) were dispersed in 15 mL absolute ethanol by ultrasonication for 5 min in a KQ-250B ultrasonic bath, and allowed to dry on a silicon slice. The results of FTIR spectroscopy was obtained via a FTS-40 Fourier transform infrared spectrometer in the range 400–4000  $\text{cm}^{-1}$ . The samples were pressed KBr pellets for the spectral measurements. The luminescence properties of the particles were characterized by a Hitachi F-4500 FL Spectrophotometer. The ICP (TJA, POEMS) data were used to quantitatively analyze the elements in the final products.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared CeF<sub>3</sub> nanoparticles (sample 1) and lutetium-doped CeF<sub>3</sub> particles at the dopant of 30 and 50 mol% (samples 4 and 6), respectively.

All the peaks in Fig. 1a-c, can be indexed to a pure hexagonal phase [space group: P63/mcm (193)] of CeF3 with lattice constant a = 7.112 Å, c = 7.279 Å (PDF#08-0045). No other peaks or impurities are detected. Therefore, X-ray diffraction confirmed the phase purity of both the undoped and lutetium-doped CeF<sub>3</sub> particles obtained from the reverse micelles. This result shows that the obtained products were pure phase of  $CeF_3$  even at higher  $Lu^{3+}$ -dopant concentration (50) mol%) and there was no other phase detected. However, as shown in Fig. 1, at lower dopant concentration, the full width at half maximum (FWHM) is slightly wider than that at higher dopant concentration, and the FWHM of undoped CeF<sub>3</sub> particles is slightly wider than that of the other two. This indicates that doping of Lutetium into CeF<sub>3</sub> nanoparticles increased the particle size slightly according to Scherrer equation (the average diameter of particles corresponding to a-c in Fig. 1 calculated from Scherrer equation is 14.5, 17.3 and 19.6 nm, respectively).

The infrared spectroscopy was used to determine whether there was remnant organic species in the products after washing by noting characteristic absorption bands for the alkyl and C–O groups in the C–H and C–O stretching region. The results showed that there was no IR band corresponding to organic species (e.g., C–H, C–O, C=O) detected, which implied that after washing procedure, little or no CTAB, *n*-octane, or *n*butanol was present on or in the particles. The ICP data show that the content of Lu in the final products is slightly lower than initial usage when examined sample



Fig. 1. XRD patterns of  $CeF_3$  nanoparticles with the lutetium-dopant concentration of: (a) undoped; (b) 30 mol% and (c) 50 mol%.

4 (30 mol%) and 6 (50 mol%). The molar concentration of Lu to Ce in samples 4 and 6 shown by ICP data is 28.7 and 48.2 mol%.

ESEM observation shows that dopant concentration did not affect the size and shape of the asprepared CeF<sub>3</sub> particles significantly but the monodispersity as shown in Fig. 2. Fig. 2a is image of undoped CeF<sub>3</sub> particles, from which we can get majority of monodispersed particles with diameters of about 15–20 nm, although there are still some polydispersed particles. Fig. 2b is the images of particles at the dopant concentration of 30 mol%. We can see that the size and shape of them are not significantly different from those in Fig. 2a but the monodispersity. Similarly, the particles in Fig. 2c are more polydispersed. Therefore, increase of dopant concentration did not change the shape and size of CeF<sub>3</sub> nanoparticles significantly but the monodispersity, which is similar to the phenomenon observed previously when examined erbium-doped BaF<sub>2</sub> particles [19].

The emission spectra of CeF<sub>3</sub> nanoparticles exited at 254 nm are shown in Fig. 3. Curve a–f, is corresponding to CeF<sub>3</sub> nanoparticles with the lutetium-doping concentration of 30, 25, 17, 42, 50 mol%, and undoped, respectively. From these spectra, we can get a broad emission ranging from 290 to 400 nm peaked at 325 nm, which can be attributed to 5d–4f



Fig. 3. Emission spectra of as-prepared lutetium-doped CeF<sub>3</sub> nanoparticles under the dopant concentration of: (a) 30 mol%; (b) 25 mol%; (c) 17 mol%; (d) 42 mol%; (e) 50 mol% and (f) undoped. The inset is the Lorentzian fitting curve of emission intensity and lutetium-doping concentration.

transition of  $Ce^{3+}$ . The emission peak of nanosized  $CeF_3$  red-shifted about 30 nm contrasted to that of  $CeF_3$  single crystals [1]. We can also see the increase of luminescence intensity of  $CeF_3$  nanoparticles when doped with lutetium. We got the most intense luminescence at the dopant concentration of 30 mol%.



Fig. 2. ESEM images of as prepared lutetium-doped CeF<sub>3</sub> nanoparticles under the dopant concentration of: (a) undoped; (b) 30 mol% and (c) 50 mol%.

When the doping concentration is lower than 30 mol%, the luminescence intensity increase with it and when dopant concentration is greater than that value, luminescence intensity decrease with it, but the intensity is also greater than that of undoped particles. The inset in Fig. 3 is the Lorentzian fitting curve showing the relationship between the emission intensity of CeF<sub>3</sub> nanoparticles and lutetium-doping concentration.

## 4. Conclusion

In conclusion, we have synthesized lutetium-doped CeF<sub>3</sub> nanoparticles for the first time from the quaternary reverse micelles of cetyltrimethylammonium bromide (CTAB), *n*-butanol, *n*-octane, and water. The asprepared products were single CeF<sub>3</sub> hexagonal phase even under the dopant concentration of 50 mol%. The luminescence spectra of the products were a broad emission ranging from 290 to 400 nm with the peak at 325 nm which red-shifted about 30 nm contrasted to that of CeF<sub>3</sub> single crystals. The doping of lutetium to CeF<sub>3</sub> can increase the luminescence intensity, and we got the most intensity emission of Ce<sup>3+</sup> at the dopant concentration of 30 mol%.

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