Synthesis and Optical Characterization of Samarium Doped Cerium Fluoride Nanoparticles

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Abstract: CeF₃ nanoparticles doped with 0; 1.0; 1.5; 2.0; 2.5; 3.0 and 4.0 mol% Sm³⁺ were prepared by co-precipitation technique. These nanoparticles were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence (PL), photoluminescence excitation (PLE) spectra, energy-dispersive X-ray (EDS) and absorption spectra. The PL spectra exhibit a group of four emission lines, which are assigned to the transitions from the excited state ⁴G₅/₂ to the ground states ⁶H₉/₂; ⁷/₂; ⁹/₂ and ¹₁/₂ of Sm³⁺ ion. The intensity of PL related to Sm³⁺ ion reached to a maximum when the Sm dopant content was 2 mol%. The PLE spectra show 8 lines, which are attributed to the absorption transitions from the ⁶H₉/₂ ground state to the ⁴H(1)₉/₂, ⁴D(2)₃/₂, ⁶P₇/₂, ⁴F(3)₃/₂, ⁴P₃/₂, ⁴M₄/₂, ⁴I(3)₁₃/₂ and ⁴M₁₅/₂ excited states. Six lines among eight excitation lines were observed in the diffuse reflection spectra.

Keywords: Co-precipitation, samarium doped cerium fluoride, nanoparticles, absorption, photoluminescence.

1. Introduction

Lanthanide fluorides have been applied in luminescence devices, such as sensor, displays, fluorescent lamps, scintillators, up-converters, optical amplifiers and lasers. Lanthanide fluorides provide some special advantages, such as high resistivity, excellent thermal and environmental stability, and in particular, these materials possess very low vibrational energies, e.g., phonon energy in lanthanum fluoride (LaF₃) is about 350 cm⁻¹, which will decrease the non-radiative rate and thus increase the luminescence intensity [1]. Among these lanthanide fluorides, cerium fluoride (CeF₃) nanostructures have promising applications as inorganic scintillators, luminescent host materials as well as solid lubricants [2]. In addition, CeF₃ nanoparticles shows Faraday effect, which is applicable to optoelectronics such as an optical isolator, optical switches or optical memory [3].
With the development of nanotechnology, many techniques have been developed to synthesize CeF$_3$ nanostructures such as thermal decomposition [1], hydrothermal [2,4], polyol [3,5], reverse micelles [6], precipitation [7,8], sonication assisted [9], sol-gel [10] and microemulsion [11]. CeF$_3$ nanostructures with varying morphology, such as nanoparticles [1,3,5-10], core/shell nanoparticles [1,4,5,8], nanocages, nanorings [2], nanoplates [4], nanodiskettes [11], etc, have been fabricated using a variety of growth methods.

It is well-known that the rare-earth (RE) ions have sharp absorption and emission bands from the UV to infrared range. For that reason, the RE doped materials possess potential applications in many different fields such as optoelectronics, photonics and biomedicine applications. However, to the best of our knowledge, for CeF$_3$ most of previous studies have been focused only on doping CeF$_3$ with terbium ion (Tb$^{3+}$) [1,4,5,11]. Samarium (Sm$^{3+}$) ion is an important luminescent center, which is doped in many glasses [see, for example, 12]. However, the optical properties of Sm$^{3+}$-doped CeF$_3$ (CeF$_3$:Sm$^{3+}$) nanoparticles have not been reported before.

In this report, we fabricated CeF$_3$:Sm$^{3+}$ nanoparticles by co-precipitation method. The structure, absorption, PL and PLE properties of the samples are investigated in detail.

2. Experimental

Undoped and Sm$^{3+}$-doped CeF$_3$ nanoparticles were prepared by co-precipitation method from cerium nitrate Ce(NO$_3$)$_3$, samarium nitrate Sm(NO$_3$)$_3$ solution and NH$_4$F powder. An appropriate amount of NH$_4$F was dissolved in ethanol under constant stirring for 15 min to prepare NH$_4$F solution. In a typical synthesis, stoichiometric amounts of Ce(NO$_3$)$_3$ and Sm(NO$_3$)$_3$ aqueous solutions were mixed. The molar ratio of Sm:Ce was equal to 0; 1.0; 1.5; 2.0; 2.5; 3.0 and 4.0 mol% Sm$^{3+}$. Then, appropriate amounts of NH$_4$F solution were added into the mixed nitrate solution under stirring for 3 h at room temperature. After that, the resulting precipitate was filtered off and washed many times in water and ethanol to remove chemicals remaining in the final products. The last products were dried in air at 70 °C for 4 h.

Crystal structure of the obtained powders was analysed by X-ray diffraction (XRD) using an X-ray diffractometer SIEMENS D5005, Bruker with Cu K$_\alpha_1$ ($\lambda = 1.54056$ Å) irradiation. The surface morphology of the samples was observed by using a JEOL JEM 1010 transmission electron microscope (TEM). The composition of the samples was determined by an energy-dispersive X-ray spectrometer (EDS) OXFORD ISIS 300. The room temperature PL and the PLE spectra were carried out on a spectrofluorometer Fluorolog FL 3-22 Jobin-Yvon-Spex with a 450 W xenon lamp as an excitation source. Diffuse reflection measurements were carried out on a UV-VIS-NIR Cary-5000 spectrophotometer. The spectra were recorded at room temperature in the wavelength region of 300-600 nm. Absorption spectra of the samples were obtained from the diffuse reflectance data by using the Kubelka-Munk function [13]:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$
where \( R, K \) and \( S \) are the reflection, the absorption and the scattering coefficients, respectively.

3. Results and Discussions

3.1. Structure characterization and morphology

Typical XRD patterns of \( \text{CeF}_3 \) nanoparticles doped with 0; 1.0; 1.5; 2.0; 2.5; 3.0 and 4.0 mol\% \( \text{Sm}^{3+} \) are presented in Fig.1. In all case, the powder XRD analysis evidenced that the obtained \( \text{CeF}_3 \) samples have a hexagonal crystal structure. No diffraction peaks of the other material phase are detected. The lattice constants of the \( \text{CeF}_3 \) nanocrystals determined from the XRD patterns are \( a = 7.12 \pm 0.02 \) Å and \( c = 7.28 \pm 0.01 \) Å, which are in good agreement with the standard values \( a = 7.112 \) Å and \( c = 7.292 \) Å (JCPDS 08-0085). The average size of the nanocrystals was estimated by Debye-Scherrer’s formula [14]:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \( \beta \) is the full width at half maximum (FWHM) in radians of the diffraction peaks, \( \theta \) is the Bragg’s diffraction angle and \( \lambda = 0.154056 \) nm. The calculated size of the \( \text{CeF}_3 \) nanocrystals was estimated to be 14 nm.

Figure 1. XRD patterns of the \( \text{CeF}_3 \) nanoparticles doped with different \( \text{Sm}^{3+} \) contents.

TEM image of the 2 mol\% \( \text{Sm}^{3+} \)-doped \( \text{CeF}_3 \) samples are illustrated in Figure 2.

As can be seen from the image, the samples \( \text{CeF}_3 \) are composed of nanoparticles. The size of the \( \text{CeF}_3:2 \) mol\% \( \text{Sm}^{3+} \) nanoparticles ranges from 15 to 25 nm, which are slightly bigger than that calculated by Debye-Scherrer’s formula.

The result of EDS analysis for the \( \text{CeF}_3 \) nanopowders doped with different \( \text{Sm}^{3+} \) contents is given in Table 1. The undoped \( \text{CeF}_3 \) nanoparticles mainly consist of cerium (Ce), fluor (F) elements,
whereas in the CeF$_3$:1%Sm$^{3+}$ and CeF$_3$:3%Sm$^{3+}$ samples Sm element appeared, indicating the incorporation of Sm$^{3+}$ ions into the host lattice. It is noted that the oxygen (O) observed in the EDS spectra is the residual not totally removed during washing.

![Figure 2. TEM image of the CeF$_3$ nanoparticles doped with 2 mol% Sm$^{3+}$.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>CeF$_3$:0%Sm</th>
<th>CeF$_3$:1%Sm</th>
<th>CeF$_3$:3%Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>O (at.%)</td>
<td>8.55</td>
<td>11.58</td>
<td>10.66</td>
</tr>
<tr>
<td>F (at.%)</td>
<td>66.09</td>
<td>62.36</td>
<td>63.07</td>
</tr>
<tr>
<td>Ce (at.%)</td>
<td>25.36</td>
<td>24.48</td>
<td>23.98</td>
</tr>
<tr>
<td>Sm (at.%)</td>
<td>0</td>
<td>1.58</td>
<td>2.29</td>
</tr>
</tbody>
</table>

It is known that effective radii of Ce$^{3+}$ and Sm$^{3+}$ ions in hexagonal crystal are 1.48 and 1.38 Å, respectively [15]. It is expected that the Sm$^{3+}$ ions can substitute for the Ce$^{3+}$ ions in CeF$_3$:Sm$^{3+}$ lattice because ionic radii for Ce$^{3+}$ and Sm$^{3+}$ are close. The second reason for this is that both Ce and Sm are RE metals, they possess similar chemical properties. Can be seen from table 1, the Ce atomic percentage decreases with increasing the Sm atomic percentage, which proves that the Sm$^{3+}$ ions have substituted for the Ce$^{3+}$ ions in CeF$_3$:Sm$^{3+}$ lattice.

3.2. Photoluminescence and absorption properties

Figure 3 illustrates the room temperature PLE spectrum monitored at 594 nm emission line and the PL spectrum under excitation wavelength of 400 nm of the CeF$_3$ nanoparticles doped with 2 mol% Sm$^{3+}$. As will be seen below, the lines in the spectra are interpreted as the absorptive and radiative intra-configurational f-f transitions within the Sm$^{3+}$ ions.
The room temperature PL spectra of CeF$_3$ nanoparticles undoped and doped with 1.0; 2.0; 3.0 and 4.0 mol% Sm$^{3+}$ excited by 400 nm wavelength are shown in figure 4.

The undoped CeF$_3$ nanoparticles do not exhibit the groups of emission lines in the wavelength range from 525 to 750 nm, whereas the Sm$^{3+}$-doped CeF$_3$ nanoparticles show a group of four emission lines at 560, 594, 640 and 703 nm. The inset of figure 4 indicates that the intensity of PL related to Sm$^{3+}$ ion reaches to a maximum when the Sm dopant content is 2 mol%.
Figure 5 shows typical PL spectrum excited by 400 nm wavelength of 2 mol% Sm$^{3+}$-doped CeF$_3$ nanoparticles. The group of emission lines at 560, 594, 640 and 703 nm are assigned to the transitions from the excited state $^4\mathrm{G}(4)_{5/2}$ to the ground states $^6\mathrm{H}_J$ with $J = 5/2; 7/2; 9/2$ and $11/2$ of Sm$^{3+}$ ion, respectively.

It is worth noting that all the mentioned above emission lines have the same excitation spectra, which demonstrates that all these lines possess the same origin. Typical PLE spectrum monitored at 594 nm emission line of 2 mol% Sm$^{3+}$-doped CeF$_3$ nanoparticles is illustrated in figure 6. The excitation lines located at 344, 362, 373, 400, 415, 443, 463 and 480 nm are attributed to the absorption transitions from the $^6\mathrm{H}_{5/2}$ ground state to the $^4\mathrm{H}(1)_{9/2}$, $^4\mathrm{D}(2)_{3/2}$, $^6\mathrm{P}_{7/2}$, $^4\mathrm{F}(3)_{7/2}$, $^6\mathrm{P}_{5/2}$, $^4\mathrm{M}_{17/2}$, $^4\mathrm{I}(3)_{13/2}$ and $^3\mathrm{M}_{15/2}$ excited states, respectively.

Figure 6. PLE spectrum monitored at 594 nm emission line of CeF$_3$ nanoparticles doped with 2 mol% Sm$^{3+}$. 
Figure 7 depicts diffuse reflection spectra measured at room temperature of the undoped CeF$_3$ and the 4.0 mol% Sm$^{3+}$-doped CeF$_3$ nanoparticles. Can be seen that none of the absorption lines appears in the diffuse reflection spectrum of the undoped CeF$_3$ nanoparticles, while six weak absorption lines located at 360, 372, 400, 415, 462 and 477 nm are clearly observed in the spectrum of 4.0 mol% Sm$^{3+}$-doped CeF$_3$ nanoparticles.

Figure 8. Plot of Kubelka-Munk function F(R) proportional to absorption coefficient for the undoped CeF$_3$ and the 4.0 mol% Sm$^{3+}$-doped CeF$_3$ nanoparticles.
Absorption spectra obtained from the diffuse reflectance data by using the Kubelka–Munk function \( F(R) \) for the undoped \( \text{CeF}_3 \) and the 4.0 mol\% \( \text{Sm}^{3+} \) doped \( \text{CeF}_3 \) nanoparticles are shown in figure 8. It is interesting to note that six mentioned above absorption lines observed in the plot of Kubelka-Munk function have appeared in the excitation spectra as shown in figure 6. The absorption lines located at 360, 372, 400, 415, 462 and 477 nm are assigned to the optical transitions from the \( ^6\text{H}_{5/2} \) ground state to the \( ^4\text{D}(2)_{3/2}, ^4\text{F}(3)_{7/2}, ^4\text{P}(5/2), ^4\text{I}(3)_{13/2}, \) and \( ^4\text{M}(15/2) \) excited states, respectively.

**Conclusion**

The \( \text{Sm}^{3+} \) - doped \( \text{CeF}_3 \) nanoparticles were prepared by co-precipitation method. The XRD analysis showed that the nanoparticles exhibit a pure hexagonal structure. TEM images show that \( \text{CeF}_3 \) nanoparticles have the size from 15 to 25 nm. The PL intensity is strongest in the \( \text{CeF}_3 \) samples doped with 2 mol\% \( \text{Sm}^{3+} \). The PL and PLE spectra of \( \text{Sm}^{3+} \) ions result from the optical intra-configurational f–f transitions. Some excitation lines were observed as well in diffuse reflection spectra measured at room temperature.

**References**

[1] Shili Gai, Piaoping Yang, Xingbo Li, Chunxia Li, Dong Wang, Yunlu Dai, Jun Lin, Monodisperse \( \text{CeF}_3 \), \( \text{CeF}_3: \text{Tb}^{3+} \), and \( \text{CeF}_3: \text{Tb}^{3+}@\text{LaF}_3 \) core/shell nanocrystals: synthesis and luminescent properties, J. Mater. Chem. 21 (2011) 14610-14615.


