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Photoluminescence properties of LaF_3: Eu^{3+} nanoparticles prepared by refluxing method

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Abstract: The europium-doped LaF_3 nanoparticles were prepared by refluxing method in glycerol/water mixture and characterized with X-ray diffraction(XRD), field emission scanning electron microscopy(FE-SEM), UV-vis diffuse reflectance spectrum, and photoluminescence spectra. The results of XRD indicated that the obtained LaF_3: Eu^{3+} nanoparticles were well crystallized with a hexagonal structure. The FE-SEM image illustrated that the LaF_3: Eu^{3+} nanoparticles were spherical with an average size around 30 nm. Under irradiation of UV light, the emission spectrum of LaF_3: Eu^{3+} nanoparticles exhibited the characteristic line emissions arising from the $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3, 4) transitions of the Eu^{3+} ions, with the dominating emission centered at 590 nm. In addition, the emissions from the $^5D_1$ level could be clearly observed due to the low phonon energies (–350 cm^{-1}) of LaF_3 matrix. The optimum doping concentration for LaF_3: Eu^{3+} nanoparticles was determined to be 20mol.%.

Keywords: LaF_3: Eu^{3+}; doped; luminescence; refluxing method; nanoparticles; rare earths

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Rare earth ions-doped nanostructure materials have been widely investigated because of their sharp and intense emission originating from the electronic transitions within the 4f shell of the doping ions and their applications in many fields. In comparison with the conventional oxide-based luminescent materials, fluorides are advantageous as fluorescent host materials owing to their low vibrational energies and the subsequent minimization of the quenching of the excited state of the rare-earth ions[1]. Hence, rare earth ions-doped nanostructural fluorides have attracted extensive interests due to their potential applications in lighting and displays[2,3], upconverters[3–8], magnetic resonance imaging (MRI)[9], biological fluorescent labels[10–14], optical amplifiers[15], transparent glass[16], scintillators[17], photonic crystals[18], etc. Among these fluorides, LaF_3 host matrix exhibits the photochemical stability, the biocompatibility, and the relative low crystalline temperature, and its phonon energy is as low as 350 cm^{-1}[19,20]. Rare earth ions (Eu^{3+}, Ce^{3+}, Tb^{3+}, Nd^{3+}, Er^{3+}, Pr^{3+}, Ho^{3+}, Yb^{3+}, Tm^{3+}) doped LaF_3 nanoparticles[21–24], LaF_3 triangular nanoplates[24,25], and silica-coated[19], or organic ligands[20,26] modified LaF_3 luminescent nanoparticles have been reported in literatures.

Rare earth ions-doped LaF_3 at nanoscale can be synthesized by using coprecipitation technique[11,15], single-source precursor (SSP) strategy[24], polyol method[22], and hydrothermal method[27]. Veggel and coworkers have systematically investigated the synthesis, surface modification, and luminescent properties of rare earth ions-doped LaF_3 nanoparticles[18–21]. Using lanthanide salts and sodium fluoride or ammonium fluoride as starting materials, they synthesized the doped LaF_3 nanoparticles in ethanol/water medium at 75 ºC by using coprecipitation technique[28]. The role of ethanol as solvent can adjust the solubility of sodium fluoride or ammonium fluoride in solution and control the growth of the doped LaF_3 particles[29]. However, the agglomeration of lanthanide-doped LaF_3 nanocrystals occurs without adding the stabilizer because the nanocrystals tend to decrease the exposed surface in order to lower the surface energy. Meanwhile, the reaction temperature is about 75 ºC because of the low boiling point (b.p.) of ethanol (~78.4 ºC), which is disadvantageous to increasing the crystallinity and luminescent intensity of lanthanide-doped LaF_3 nanoparticles.

In this article, the europium-doped LaF_3 nanoparticles were prepared by refluxing method in glycerol/water mixture and characterized with X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectrum (EDS), UV-vis diffuse reflectance spectrum (DRS), and photoluminescence (PL) spectra.

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The glycerol/water system can not only alter the solubility of fluorides but also increase the reaction temperature and consequently improve the crystallinity of luminescent nanoparticles. Furthermore, as a polyol, the glycerol (b.p., 290 ºC) acts as solvent, stabilizer, and chelating agent, which can bind to the surface of the growing nanocrystals to limit the growth of the nanoparticles[22]. Hence, no other capping agent is needed, and the as-prepared nanoparticles are water-soluble due to the polar functional groups of glycerol capped on the surface of the nanoparticles.

1 Experimental

1.1 Preparation of LaF_3: Eu^{3+} nanoparticles

LaF_3:Eu^{3+} nanoparticles were prepared by the refluxing method. Typically, stoichiometric weights of La_2O_3 (99.99%) and Eu_2O_3 (99.99%) were dissolved in diluted hydrochloric acid (HCl, analytical reagent, A.R.), and then the water in above solutions was distilled off by heating. The resulting lanthanide salts and a stoichiometric amount of NH_4F (96.0%, A.R.) were added to the 100 ml of glycerol/water mixture (volume ratio=1:1), and the metal ion concentration was kept at 0.02 mol/L. The mixture was heated to boil under vigorous stirring and refluxed at the boiling temperature for 2 h, and the temperature of the boiling mixture is about 110 ºC. Thereafter, the suspension was cooled down to room temperature and diluted with excessive ethanol followed by centrifugation. In order to remove residual glycerol, the solid was resuspended in ethanol for three times and centrifuged again. Finally, the solid was dried at 70 ºC for 12 h.

1.2 Characterization of LaF_3: Eu^{3+} nanoparticles

X-ray diffraction (XRD) was carried out on a Y-500 diffractometer with Cu Kα radiation (λ=0.15406 nm). Scanning electron microscopy micrographs were obtained by using a field emission scanning electron microscope (FE-SEM, XL30, Philips). UV-Vis diffuse reflectance spectrum was obtained by using a UV/Vis spectrophotometer (V-550, JASCO, Japan) equipped with an integrating sphere attachment (ISV-469). $BaSO_4$ was used as a reference sample. The excitation and emission spectra were taken on an F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source.

2 Results and discussion

2.1 XRD analysis

Fig.1 shows the XRD patterns of LaF_3 (1), $La_{0.85}Eu_{0.15}F_3$ (2) nanoparticles and the standard data for bulk LaF_3 (3, JCPDS card No. 32-0483). The results of XRD indicate that LaF_3 and $La_{0.85}Eu_{0.15}F_3$ nanoparticles are well crystallized, and the patterns are in good agreement with hexagonal structure (Space group: $P\bar{3}c1$ (165), Cell=0.7187×0.7187×0.735 nm^3, $\alpha=\beta=90°$, $\gamma=120°$) known from bulk LaF_3 (3, JCPDS card No.32-0483). The nine nearest-neighbor F^- ions present a sufficiently distorted environment, and the symmetry is D_{3d}^4 ($P\bar{3}c1$) with a C_2 point symmetry at the La site[30]. The calculated cell parameters are as follows: $a=b=$ 0.7168 nm and c=0.7297 nm for the $La_{0.85}Eu_{0.15}F_3$ nanoparticles, which are smaller than those of LaF_3 nanoparticles ($a=b=$ 0.7185 nm and c=0.7473 nm). The decrease in the lattice parameters of LaF_3:Eu^{3+} nanoparticles can be attributed to the smaller radius of Eu^{3+} ion (0.107 nm) compared with that of La^{3+} ion (0.116 nm)[28]. This indicates that Eu^{3+} ions were doped into the LaF_3 lattice and occupied the site of La^{3+} ions, with the formation of a $La_{0.85}Eu_{0.15}F_3$ solid solution even at relatively higher Eu^{3+} doping concentration (25mol.%)[24]. Such a large solubility in $La_{1-x}Eu_xF_3$ nanoparticles can be attributed to the smaller crystallographic mismatch between LaF_3 and EuF_3 crystal, as these two crystals belong to hexagonal system and the radius of Eu^{3+} ion is near that of La^{3+} ion[29]. As shown in Fig.1, broadening of diffraction peaks for both LaF_3 and $La_{0.85}Eu_{0.15}F_3$ nanoparticles were observed, which reveals the nanocrystalline nature of the samples. According to Scherrer equation, after subtraction of the equipment broadening, the full width half maximum (FWHM) of the strongest peak (111) at 2θ=27.6º was used to calculate the average crystallite size, and the average crystallite size of LaF_3 and $La_{0.85}Eu_{0.15}F_3$ nanoparticles are around 11.4 and 16.0 nm, respectively.

2.2 Morphology analysis

The morphology of the representative $La_{0.85}Eu_{0.15}F_3$ nanoparticles was observed by FE-SEM image, as shown in Fig.2(a). It shows that the as-prepared $La_{0.85}Eu_{0.15}F_3$ nanoparticles are composed of spherical particles with size

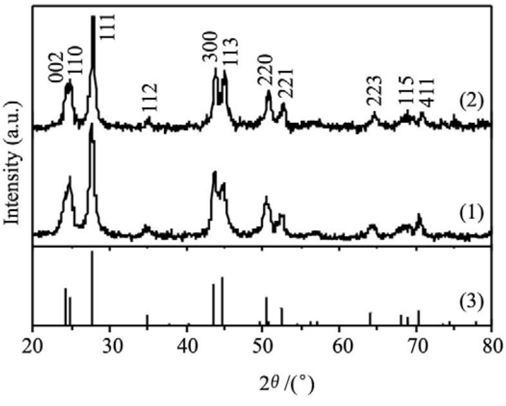

Fig.1 XRD patterns of LaF_3 (1), $La_{0.85}Eu_{0.15}F_3$ (2) nanoparticles and the standard data for bulk LaF_3 (3) (JCPDS card No. 32-0483)