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Co-precipitation synthesis and self-reduction of $CaF_2:Eu^{2+}$ nanoparticles using different surfactants

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ABSTRACT

Europium doped Calcium fluoride ($CaF_2:Eu^{2+}$) nanoparticles have been synthesized by co-precipitation method using different surfactants, in which anhydrous ethanol was used as solvent and the nanoparticles was sintered in air. The self-reduction was observed in the as-prepared $CaF_2:Eu^{2+}$ nanoparticles and can be explained by charge compensation model based on the substitution. Scanning electron microscope (SEM) and X-ray power diffraction (XRD) showed that the nanoparticles were about 50 nm–1 μm and in a single phase. A broad emission centered at 425 nm due to Eu^{2+} $4f^7$–$4f^65d^1$ transition has been observed with excitation bands between 337 and 385 nm by the fluorescence spectrometer. The corresponding excitation spectra showed a wide excitation range in the violet region due to $4f^7(^8S_{7/2}) \rightarrow 4f^65d^1(t_{2g})$ The luminescent properties of the phosphor was thoroughly examined. Furthermore, the effect of using different surfactants on the sizes of $CaF_2:Eu^{2+}$ nanoparticles, related mechanisms was also investigated.

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1. Introduction

Nanotechnology is about to revolutionize our world, involving the fabrication and use of nano-sized materials and devices. Various nano materials play an important role in modern science and have strong interest in anticipation that the unexplored range of material dimensions will yield size-dependent properties. In this field, the most interesting part is the precise control of the shape and size of grain driven by their interesting size- and shape-dependent properties [1,2].

Among the various nano materials, luminescent nanoparticles have become a vital materials. The optical properties of these materials is often affect by the grain size [3]. When the grain size reaches nano scale, the luminescence of the materials differ from those of the same material in bulk [4,5]. Luminescent nano materials have attracted more and more researchers in recent studies due to their applications in color displays [6], field-effect transistors (FET) [7], optoelectronics, medical and biological labels, solar cells [8], and laser light sources. Nanomaterials possess some particularity under the influence of surfactants. Among these nanomaterials, lanthanide-doped nanoparticles play a vital role in these fields [9].

Optical materials based on fluoride attract a great deal of interest as phosphors in many fields [10] and fluoride nanoparticles doped with lanthanide ions have been reported to display unique luminescence properties. It is well known that calcium fluoride (CaF_2) is a suitable host for rare earth ions, which has desirable properties such as high transmittance in the far UV to mid IR range, low refractive index, high chemical resistance, and high laser damage threshold. CaF_2 exhibits a cubic face-centered lattice, in which Ca^{2+} ions lie at the nodes in a face-centered lattice, while F^- ones lie at the centers of the octants [11]. This lattice is of special interest in the field of luminescence dosimetry. Because it is able to accept many impurities that give rise to defects, cluster formation and valence changes. Thus, CaF_2 has become an important optical material. Interests of using CaF_2 for various applications is still growing [12].

Luminescent nanomaterials should have a spherical shape and high luminescence efficiency for minimizing light scattering on their surfaces to improve light emission efficiency [13–15]. Different methods may affect the morphology of nanoparticles and their luminescence properties [16]. For irregular particles, the scattering are strongly strengthened on the particle surface and leads to intensity decrease. At the present stage, the main reason for such hard agglomeration is hydrogen bonds between

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chemically combined OH^- that generate oxygen bridge bonds [17,18]. However, surfactants can effectively control the size of particles in synthesis as well as inhibit the formation of hydrogen bonds. In addition, the surfactants coated on the surface of particles are able to reduce surface defects and improve the luminous efficiency [14]. There are many works reported on synthesis of luminescent nanomaterials with applying different surfactants. For instance, Abhijit Jadhav et al. used different surfactants to synthesize $Y_2O_3:Eu^{3+}$ and obtained different sizes [13]. Song also regulated the size of $YVO_4:Eu^{3+}$ by changing surfactants [19]. The lanthanide-doped CaF_2 bulk and powder materials have been studied for many years, and a lot of authors have reported the crystal structure and luminescent behavior. However, there are few works reported on the synthesis of $CaF_2:Eu^{2+}$ using different surfactants.

In this work, we have synthesized $CaF_2:Eu^{2+}$ nanoparticles with different surfactants using a co-precipitation method. The self-reduction was observed in the as-prepared $CaF_2:Eu^{2+}$ nanoparticles. Additionally, we also studied the influence of different types of surfactants and grain size on luminescence and self-reduce properties of nanoparticles.

2. Experimental

2.1. Chemicals

Sodium Dodecyl Sulfate (SDS), TWEEN-40, Octadecylamine and sodium oleate were received from Aladdin Industrial Corporation. Cetyltrimethylammonium bromide (CTAB) was purchased from Sanland-chem International Inc. $CaCl_2{\cdot}2H_2O$, NH_4F were obtained from TianJin Fuchen Chemical Reagent Factory. All chemicals were of analytical grade reagents and were used directly without further purification.

2.2. Synthesis

$CaF_2:Eu^{2+}$ nanoparticles were prepared by co-precipitation method. The Eu^{2+} ions occupy the Ca^{2+} sites in the CaF_2 host lattice with 2.5% of the doping concentration. The $EuCl_3{\cdot}6H_2O$ were obtained by adding hydrochloric acid to Eu_2O_3. In a typical synthesis, 7.02 mmol $CaCl_2{\cdot}2H_2O$ and 17.56×10^{-2} mmol $EuCl_3{\cdot}6H_2O$ were dissolved in 180 ml anhydrous ethanol. The concentration of metal ions was 0.04 M. Then, 0.6 mmol surfactants were added. After the solution was stirred for 15 min at 40 °C, 14.05 mmol NH_4F was slowly added. The mixture was stirred for 12 h. The precursor was separated by centrifugation and washed with ethanol for several times in order to remove Cl^- and NH_4^+. After that, the obtained product was calcined at 600 °C for 1 h in air.

For the synthesis of bulk $CaF_2:Eu^{2+}$, 0.05 mol $CaCl_2{\cdot}2H_2O$ and 1.5 mmol $EuCl_3{\cdot}6H_2O$ were added into 49 ml deionized water. Subsequently, 0.1 mol NH_4F dissolved in 1 ml deionized water was added to above solution. The precursor was separated by centrifugation and washed with deionized water. Finally, the product was dried at 60 °C and then calcined at 600 °C for 1 h in air.

2.3. Characterizations

The XRD measurements of synthesized samples were carried out using a XD-2X/M4600 X-ray diffractometer with Cu-Kα radiation (λ = 0.154056 nm) at 40 kV and 30 mA in a scan range 10–80°. The size and shape of the nanoparticles were examined by JSM-7001F. The photoluminescence (PL) of the powder samples was measured by a Shimadzu RF5301pc fluorescence spectrophotometer.

3. Results and discussion

3.1. Structure

The X-ray diffraction patterns of $CaF_2:Eu^{2+}$ with different surfactants and bulk sample are shown in Fig. 1. The diffraction peaks of different samples are indexed as pure cubic CaF_2 phase (fcc, space group: Fm-3m(225) [1]). There is no impurity peaks observed. The X-ray diffraction patterns of all the samples are in exact agreement with the corresponding standard cards, JCPDS:35-0816 and have no effect after doping Eu^{2+} ion or adding different kinds of surfactants. With addition of surfactants, the intensity of the diffraction peaks of the sample with CTAB increase as compared with the sample without any surfactant, which indicated the increase of crystallinity and the decrease of disorder extent. However, the diffraction peaks of the samples with Octadecylamine, Sodium oleate and TWEEN-40, respectively, significantly decreases. This may partly be ascribed to the long carbon chain affecting the grain growth.

3.2. SEM

Morphology is an important factor in luminescence performance. SEM can display morphology and size of $CaF_2:Eu^{2+}$ influenced by surfactants. The SEM micrographs of samples are shown in Fig. 2. Fig. 2a and b indicate that the particles are agglomerated in few microns. The reason for agglomeration is sulfonic groups or carboxylic groups of anionic surfactants have much negative charges result in Ca—O—S—O—Ca or Ca—O—C—O—Ca [13,17,18,20]. Fig. 2c is the TWEEN-40 modified $CaF_2:Eu^{2+}$ with stratiform texture. The mean size is about 76 nm. CTAB and Octadecylamine are cationic surfactants having similar effect. Comparatively speaking, cationic surfactants inhibit the formation of hydrogen bonds. This effect results in smaller particle size and uniform size distribution. Fig. 2d shows that distribution is better in the presence of Octadecylamine. The particle's mean size is about 54 nm. In addition, Fig. 2e indicates that the particle with CTAB is bigger than that with Octadecylamine. This suggests that the high molecular weight surfactants make particles smaller. For example without surfactant, serious aggregation is observed and the average grain size is 80 nm (Fig. 2f). Fig. 2 g is the bulk sample with good morphology in several microns. Thus, it can be seen that surfactants have better effect on dispersity.

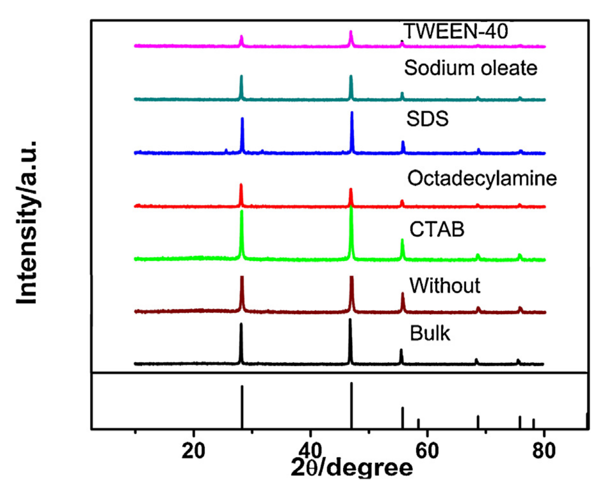

Fig. 1. The XRD pattern of $CaF_2:Eu^{2+}$ with different surfactants.

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