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Europium doped lanthanum zirconate nanoparticles with high concentration quenching

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ABSTRACT

A series of Eu^{3+} doped lanthanum zirconate ($La_2Zr_2O_7$) nanoparticles (NPs, 20 ± 5 nm in diameter) with cubic fluorite structure were facilely synthesized by a kinetically modified molten salt synthetic (MSS) process and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and photoluminescence spectra (PL). Under the excitation of 405 nm, intense red emission with high color purity can be observed in the Eu^{3+} doped $La_2Zr_2O_7$ NPs. Moreover, the as-prepared Eu:$La_2Zr_2O_7$ NPs possess high concentration quenching, which is as high as ~32.5 mol% of europium dopants in the $La_2Zr_2O_7$ host. The corresponding concentration quenching mechanism was discussed as well. Our results confirm that the kinetically modified MSS process is a promising approach for preparing rare earth (RE) ions doped $A_2B_2O_7$ nanoparticles with uniform RE doping and high concentration quenching.

1. Introduction

During the past several decades, trivalent rare-earth (RE^{3+}) ion doped luminescent materials have attracted considerable interest because of their unique optical properties originating from the *f*–*f* electronic transitions within the 4*f* shell of RE^{3+} ions, so that these materials have many potential applications in the fields of solid state lighting, displays, lasers, optical communication, biomedicine, etc. [1]. Among the RE ions, trivalent europium Eu^{3+} ion is an important activator which can emit red fluorescence because of the $^5D_0$ level transitions. Therefore, many materials doped with Eu^{3+} can be used as red phosphors and have a potential application in the white lighting diodes [2]. Also, Eu^{3+} ions can be used as a probe to reveal the symmetry of crystals [3]. This is mainly attributed to the fact that Eu^{3+} ion has the pure $^5D_0$–$^7F_1$ magnetic dipole and $^5D_0$–$^7F_2$ electric dipole transitions. The latter is called hypersensitive transition. Namely, when Eu^{3+} ions are located at the sites with noncentrosymmetric environment, the $^5D_0$–$^7F_2$ electric dipole transition is dominant in the emission spectra. Otherwise, the $^5D_0$–$^7F_1$ magnetic dipole transition is dominant. Therefore, the crystal symmetry of host materials can be deduced according to the emission spectra of Eu^{3+} ions.

In recent years, considerable research activity has been carried out to explore new luminescent materials on the nanometer scale, since nanostructures (e.g., nanoparticles, nanowires, and nanotubes) exhibit interesting luminescent properties, which is obviously different from the corresponding bulk. For example, the optical properties of materials including emission lifetime, luminescence efficiency, and quenching concentration can be changed greatly when the size of materials decreases below 100 nm [4]. Generally, the luminescent efficiency of nanosized phosphors is lower than that of the corresponding bulk materials. However, nanoparticles doped with rare earth ions may exhibit some superior performance characteristics over their micrometer counterparts, such as improved color purity [5]. So that they are also expected to have potential applications in areas of electronic and photonic devices and amplification in optical communications, luminescent thermometers, fluorescent and magnetic resonance imaging, and biolabeling. Therefore, there is a growing interest in the study of inorganic nanoparticles doped with rare earth ions. On the other hand, among various materials, hosts with $A_2B_2O_7$ composition, where A represents rare-earth elements or their mixtures with oxidation state of +3 and B denotes fourth group transition metallic elements or their mixtures with oxidation state of +4, doped with different RE ions or their combinations, have unique and attractive properties and gained growing attention [6]. These materials with $A_2B_2O_7$ composition can be widely used as viable nuclear waste host materials, effective high-temperature heating elements, thermal barrier layers, oxidation catalysts and

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scintillator materials in X-ray computed tomographic detectors [7–10]. Also, as a principle category of luminescent materials other than quantum dots, their rare-earth-doped derivatives are luminescent materials for light emitters, display devices, optical telecommunication components, active parts in lasers and bio-labels arising from the 4*f* electrons of rare-earth elements [8]. It is well known that the synthesis approach of luminescent materials can influence their luminescent properties greatly. By far, these materials with $A_2B_2O_7$ composition were prepared by a number of different routes, such as co-precipitation, combustion, sol–gel method, solid-state reaction and hydrothermal synthesis, or their combinations [8,11–16]. However, the size and morphology of materials prepared via above processes are not uniform and regular. Moreover, some of them need long reaction time and high reaction temperature. Therefore, it is still a big challenge to develop simple and reliable synthetic methods for preparation $A_2B_2O_7$ nanoparticles with uniform size and morphology. In recent years, molten-salt synthetic (MSS) process has appeared as an attractive route for the preparation of a wide range of nanomaterials, even though its capability to make RE-doped nanomaterials with high concentration quenching has not been demonstrated yet [6,17,18].

In this paper, we synthesized Eu^{3+} doped $La_2Zr_2O_7$ nanoparticles via a kinetically modified MSS process, in which a single-source complex precursor $(Eu_xLa_{1-x})_2(OH)_3{\cdot}ZrO(OH)_2{\cdot}nH_2O$ was utilized to synergistically reduce the transport distances of the reactive constituents to an atomic length scale and enhance diffusion of the reactants in the molten salt medium [6]. XRD, SEM and TEM results confirm that as-prepared samples have spherical shape with an average diameter of 20 ± 5 nm and cubic fluorite structure. Under the excitation of 405 nm, the as-prepared Eu^{3+} doped $La_2Zr_2O_7$ nanoparticles exhibit intense red light emissions with high color purity. Moreover, the optimal doping concentration of Eu^{3+} ions in the $La_2Zr_2O_7$ nanoparticles was confirmed to be high as of 32.5 mol%, the highest reported so far. The corresponding concentration quenching mechanism was discussed. Therefore, the kinetically modified MSS process is a promising route for the preparation of RE^{3+} doped nanoparticles with a wide variety of dopants and hosts, and more importantly, high concentration quenching.

2. Experimental procedures

2.1. Chemicals

Lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$, 99.0%), zirconium dinitrate oxide hydrate ($ZrO(NO_3)_2{\cdot}xH_2O$, 99.9%), europium (III) nitrate hexahydrate ($Eu(NO_3)_3{\cdot}6H_2O$, 99.9%), potassium nitrate (KNO_3, 99.9%), sodium nitrate ($NaNO_3$, 98%) and ammonia (NH_4OH, 28.0–30.0%) were purchased from Alfa Aesar, Ward Hill, MA. All the starting materials were used without further purification.

2.2. Synthesis

Undoped and Eu-doped $La_2Zr_2O_7$ samples with doping levels between 3 and 40% were prepared according to our previously reported molten salt synthesis [6]. To make the single-source complex precursor $(Eu_xLa_{1-x})_2(OH)_3{\cdot}ZrO(OH)_2{\cdot}nH_2O$, stoichiometric amounts of lanthanum hexahydrate, zirconium dinitrate oxide hydrate and europium (III) nitrate hexahydrate were dissolved in deionized water to form a clear solution, then followed by the dropwise adding dilute ammonia solution. The solution was stirred at room temperature for 2 h to form a complex precursor. After that, the precursor gel was filtered, washed with deionized water, and then air dried overnight at room temperature. To make the undoped and Eu-doped $La_2Zr_2O_7$ nanocrystal samples, 0.35 g of the precursor $(Eu_xLa_{1-x})_2(OH)_3{\cdot}ZrO(OH)_2{\cdot}nH_2O$ was first ground together with 60 mmol of nitrate mixture ($NaNO_3$:KNO_3 = 1:1, molar ratio). The mixture was transferred into a covered crucible and heated to 650 °C at a rate of 10 °C/min with a box furnace in air and then isothermally annealed at 650 °C for 6 h. After being cooled to room temperature at a ramp-down rate of 10 °C/min, the resulting product was washed with deionized distilled water several times and centrifuged for collection. After drying in an oven at 120 °C overnight, undoped or Eu-doped $La_2Zr_2O_7$ nanocrystals with Eu concentrations of 3–40 mol% with respect to La were obtained.

2.3. Characterization

The crystalline phase and purity of the synthesized $(Eu_xLa_{1-x})_2Zr_2O_7$ samples were examined on a Rigaku-Miniflex™ II X-ray diffractometer using Cu K_α radiation (λ = 0.15406 nm) with diffraction angle 2θ of 20–90° scanned at 1°/min and step width of 0.02°. The size and morphology of $(Eu_xLa_{1-x})_2Zr_2O_7$ nanocrystals were characterized using a field emission scanning electron microscope (Carl Zeiss Sigma VP FESEM) with an accelerating voltage of 10 kV. Specifically, the as-prepared $(Eu_xLa_{1-x})_2Zr_2O_7$ nanocrystals, after centrifugation, were sonicated for about 1 min and later air-dried upon deposition onto conductive carbon tape, which were attached onto the surfaces of SEM brass stubs for SEM measurements. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED) patterns were carried out on an FEI Tecnai G^2 F30 microscope with an accelerating voltage of 300 kV. Specimens for the TEM studies were prepared by sonicating aqueous suspension containing $(Eu_xLa_{1-x})_2Zr_2O_7$ nanocrystals, followed by depositing a drop of the suspension onto a 300 mesh Cu grid, coated with a lacey carbon film. Photoluminescence (PL) emission spectra were taken on a USB2000+ fiber optic spectrometer (Ocean Optics, Inc.) by using a 405 nm laser diode (ThorLabs, Inc.) as excitation source.

3. Results and discussion

3.1.1. XRD analysis

Fig. 1 shows the X-ray diffraction patterns of undoped and 10 mol% Eu^{3+}-doped $La_2Zr_2O_7$ nanoparticles synthesized by previously reported kinetically modified molten salt synthesis by our group [6]. It can be found that these samples have the similar XRD patterns and all of the diffraction peaks can be readily

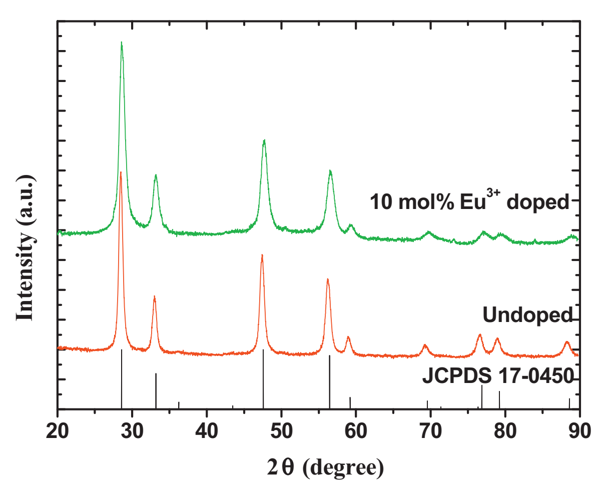

Fig. 1. XRD patterns of undoped and 10 mol% Eu^{3+}-doped $La_2Zr_2O_7$ nanocrystals synthesized via the facile molten salt synthetic route at 650 °C. The JCPDS No. 17-0450 is also shown as reference.