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Structure transition and enhanced photoluminescence of $Gd_{2-x}Y_xO_3$:Eu nanocrystals

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Abstract

The influence of Y doping on the crystallization behavior, structure transition and the photoluminescence enhancement of Gd_2O_3:Eu (Eu^{3+} doping concentration is kept as 10%) nanocrystals prepared by combustion method was investigated. The as-prepared Gd_2O_3:Eu was in monoclinic phase. As x increased to 0.14, cubic phase could be observed as well as monoclinic, and heavy Y doping ($x > 0.40$) changed the structure to cubic instead of monoclinic. Though it was prominent that cubic Y_2O_3:Eu, as the extreme case of Y substitution, had much stronger photoluminescence than monoclinic Gd_2O_3:Eu in a same Eu^{3+}-doping concentration, it is quite surprising that less Y doping increased the emission of monoclinic Gd_2O_3:Eu. This effect can be ascribed to the crystal field difference induced by lattice distortion, which is a much more significant behavior for the nanocrystals than the bulk.
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Keywords: Photoluminescence; Nanocrystals; Structure transition; Cubic and monoclinic phase; Gd_2O_3:Eu

1. Introduction

The development of new kinds of flat panel displays demands phosphors with improved or new properties. Nanostructured materials, with dimensions less than 100 nm, have been studied vigorously in recent years. Much of the research efforts is devoted on the exceptional optical properties induced by quantum confinement and thereby expected them to act as potential kinds of luminescent materials both for fundamental research and applications [1,2]. Yttrium and gadolinium oxide doped with Eu^{3+} ions are widely used as CRT and tricolor phosphors, and the research on composite Y_2O_3:Eu and Gd_2O_3:Eu is expected to improve the luminescent properties [3]. A number of methods, including colloidal and coprecipitation [4], sol–gel process [3,5,6], laser evaporation [7,8] and spray pyrolysis [9] were employed to prepare the nanosized spherical oxide particles with narrow size distribution. Recently, a simple large-scale synthesis of Eu^{3+}-ions-doped RE_2O_3 (RE = Y, Gd) was developed [10,11]. The main point of this method is the rapid decomposition of the rare earth nitrate in the presence of an assistant. The assistants adopted so far are nitrogen-containing complexes, such as urea [12], oxylydihydrazide [11] and glycine [10]. During the reaction, many gases, such as CO_2, N_2, NO_2 and H_2O, as well as a large amount of in situ generated heat, were released in a short period of time before the process terminated with white, foamy and crisp products. This method also offers a measure of preparation of composite oxide.

In this report, we focus on the structure transition and its consequences on the luminescent properties of Eu^{3+}-doped $Gd_{2-x}Y_xO_3$ nanocrystals fabricated by the combustion method. The morphology is characterized by transmission electron microscope (TEM) and field emission scanning electron microscope (FE-SEM). Structure transition is detected by X-ray diffraction (XRD) and photoluminescence spectra.

2. Experimental

The preparation is similar to that given in Ref. [10]. Stoichiometric rare earth nitrate and glycine were mixed in a porcelain crucible to form the precursor solution. For the composite $Gd_{2-x}Y_xO_3$, in which x varied from

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0 to 2, the corresponding precursor solutions were used. Excess water was evaporated during the condensation of the precursor solution. As the ignition occurred, the reaction went on vigorously for a few seconds, after which a foamy and crisp product was obtained. The appearance of the product depends on the molar ratio of glycine and rare earth ([G]/[RE]) of the precursor solution and thus it was kept as 2 for the complete decomposition of the glycine. No residual NO_3^- or rare earth nitrioxide was detected by IR and photoluminescence spectroscopy after the reaction [13].

The structures of the products were recorded with a Rigaku RINT D/MAX 2000 X-ray powder diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5408$ Å) generated at 40 kV/100 mA. The morphologies were studied with an Amary 1910 FE-SEM. The detailed formation of this as-prepared nanocrystalline was studied with a Hitachi H-9000 NAR TEM operating at 300 kV equipped with an EDAX detector. Photoluminescence was operated with a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150 W xenon lamp at room temperature. A 350 nm filter was used to get the real emission of the samples.

3. Results and discussion

According to the previous studies [13], several to tens of nanometers particles were obtained by the combustion method, and the networks of nanostructures were found as shown in the images of TEM (Fig. 1a) and SEM (Fig. 1b). "Particles" were connected by amorphous phase along the networks. EDAX studies confirmed the presumed composition of the product. The content ratio obtained from ICP is the same as that of the precursor. The particle size is about 10 nm from TEM. Lattice fringe images confirmed the microstructure of the product. The fragment and three-dimensional porous structure was the result of large amount of gas byproduct during the reaction. The fast crystallization and explosive gas is critical and responsible for the microstructure of the products.

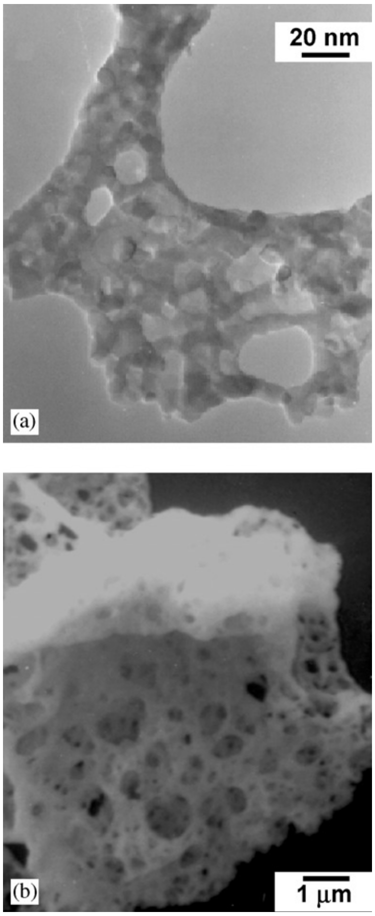

Fig. 1. Typical TEM and FE-SEM images of composite $Gd_{2-x}Y_xO_3$:Eu nanocrystals prepared by the combustion method.

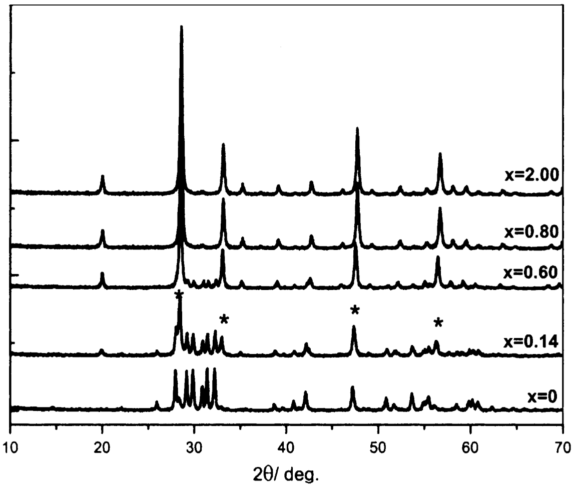

Fig. 2. X-ray diffraction patterns of $Gd_{2-x}Y_xO_3$:Eu nanocrystals. With increasing of x, the structure changed from monoclinic to cubic phase ($x = 0$ and $x = 2$ correspond to monoclinic Gd_2O_3:Eu and cubicY_2O_3:Eu nanocrystals, respectively).

Eu_2O_3 and Gd_2O_3 crystallize in cubic phase at low temperature and can be converted to the monoclinic phase when held at 1570 and 1670 K, respectively, for 1 h [13]. Eu_2O_3 and Gd_2O_3 synthesized by the combustion method ([G]/[RE] is 2) were of pure monoclinic phase, while Y_2O_3 was in cubic phase. The prepared monoclinic Gd_2O_3 with space group C_{2h} was studied as the host materials. The XRD patterns of $Gd_{2-x}Y_xO_3$:Eu are shown in Fig. 2. For the complex matrix, the substitution of Y^{3+} ions for Gd^{3+} ions in the lattice made the structure change from monoclinic to cubic with the increase of the Y^{3+}. XRD patterns of Y_2O_3:Eu and Gd_2O_3:Eu matched with the data given in JCPDS data files and they were cubic and monoclinic, respectively. As x increased to 0.14, in addition to monoclinic patterns of Gd_2O_3, new diffraction patterns appeared. These new peaks marked with asterisk could be identified as (222), (400), (440), (622) peaks corresponding to the cubic phase of Gd_2O_3. As x increased to 0.6, only a small trace of monoclinic phase was left, although Gd^{3+} remained in the majority. The diffraction intensity of cubic-phase Gd_2O_3 also increased with the content of Y^{3+} in the matrix. When x is larger than 0.8, no traces of monoclinic phase could be found. In this case, although 40% Gd^{3+} ions were replaced by Y^{3+} ions, the structure completely changed to cubic. Eu^{3+} and Gd^{3+} ions have nearly the same radius, 95 and 93.8 pm, respectively, but Y^{3+} is smaller (89.2 pm). In this case, Y^{3+} doping into Gd_2O_3:Eu will lead to the lattice distortion. The discrepancy caused a strong tendency for the matrix to form a more stable structure, the cubic phase.

The *f–f* transitions of Eu^{3+} ions are essentially free-ion-like in character and the relative intensity of the peaks is sensitive to the crystal environment [4,9]. Its emission can be used as the probe of the crystal structure [14]. Fig. 3 showed the photoluminescence spectra for a series of composite samples. The spectra consist of transitions from $^5D_0$ excited states to the ^7F_J ($J = 0$, 1, 2, 3, 4) of Eu^{3+} ions. $x = 0$ and $x = 2.0$ correspond to Eu^{3+} doped into monoclinic and cubic-structured nanocrystals, respectively, and the photoluminescence spectra are well characterized in the literatures [14]. From the photoluminescence spectroscopy of $x = 0.6$, except for the contribution from monoclinic structure, the transition that comes from the cubic phase can be identified as well. This is consistent with the structure revolution shown in Fig. 2. As x increased to 0.8, the spectroscopy behaved as an Eu^{3+}-occupied cubic structure.

It is noteworthy that besides the correlation of the photoluminescence and structure, the emission intensity changed as well. Compared with the Gd_2O_3:Eu nanocrystals, the composite $Gd_{2-x}Y_xO_3$:Eu ($x = 0.10$) has a higher emission intensity with the monoclinic structure. Furthermore, compared with the Y_2O_3:Eu nanocrystals, the composite $Gd_{2-x}Y_xO_3$:Eu ($x = 1.0$) has higher emission intensity although with the same cubic structure. The cubic-structured Gd_2O_3 or Y_2O_3 is the optimized luminescent host. Further studies confirmed the luminescent enhancement for the composite $Gd_{2-x}Y_xO_3$:Eu nanocrystals. Also, the highest luminescence can be obtained as $x = 1.0-1.4$. This suggested that the composite nanocrystal is a potential kind of advanced luminescent material.

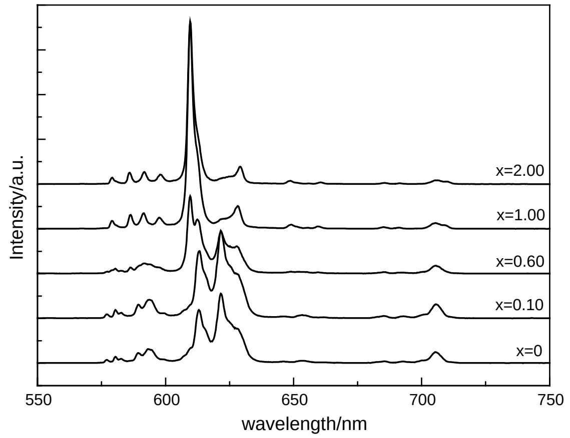

Fig. 3. Photoluminescence spectra of $Gd_{2-x}Y_xO_3$:Eu nanocrystals.

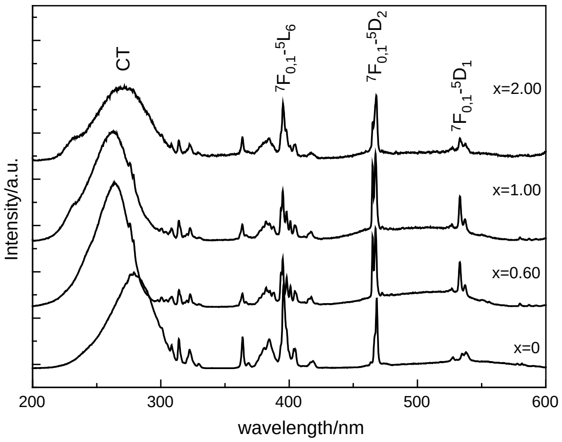

Fig. 4. Excitation spectra of $Gd_{2-x}Y_xO_3$:Eu nanocrystals.

The photoluminescent excitation spectra were studied as shown in Fig. 4. The spectra are composed of charge transfer (CT) in the host lattice and f transitions ($^7F_{0,1}-{}^5L_6$, $^7F_{0,1}-{}^5D_2$, $^7F_{0,1}-{}^5D_1$ at 395, 466 and 531 nm, respectively). It is also noticed that the f transition pattern correlated well with the structure. The CT bands of Eu^{3+}-doped Gd_2O_3 and Y_2O_3 are centered at 281 and 272 nm, respectively, and it blue shifted for the composite $Gd_{2-x}Y_xO_3$:Eu. It can be concluded that the Eu–O bond length [15,16] is shorter for composite nanocrystals, which is much beneficial for applications.

4. Conclusions

The combustion method was employed to prepare $Gd_{2-x}Y_xO_3$:Eu nanocrystals. With x varying from 0 to 2, the host matrix changed from Gd_2O_3:Eu to Y_2O_3:Eu, and the structure underwent transition from monoclinic to cubic. During the evolution, Y doping has an important impact on the structure of the composite. As x increased to 0.14, cubic phase can be observed as well as monoclinic, and heavy Y doping ($x > 0.4$) changed the structure to complete cubic phase. It is prominent that cubic Y_2O_3:Eu had much stronger photoluminescence than monoclinic Gd_2O_3:Eu although the Eu^{3+} doping concentration remains the same. But it is quite surprising that less Y doping increased the emission of monoclinic Gd_2O_3:Eu. In the meantime, compared with Y_2O_3:Eu nanocrystals, the composite

$Gd_{2-x}Y_xO_3$:Eu ($x = 1.0$) has a higher emission intensity although with the same cubic structure. These effects can be ascribed to the crystal field difference induced by the lattice distortion. The composite nanocrystals are supposed to be a new kind of advanced materials.

Acknowledgments

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