Optical Materials 32 (2010) 415–421

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Spherical porous $ZnAl_2O_4:Eu^{3+}$ phosphors: PEG-assisted hydrothermal growth and photoluminescence

Xiang Ying Chen *, Chao Ma

School of Chemical Engineering, Anhui Key Laboratory of Controllable Chemistry Reaction and Material Chemical Engineering, Hefei University of Technology, Hefei, Anhui 230009, PR China

ARTICLE INFO

Article history:
Received 27 February 2009
Received in revised form 15 August 2009
Accepted 4 October 2009
Available online 4 November 2009

Keywords:
$ZnAl_2O_4$
Phosphor
Mesoporous
Hydrothermal
Photoluminescence

ABSTRACT

Spherical porous Eu^{3+}-doped $ZnAl_2O_4$ phosphors have been prepared by post-annealing the sample at 800 °C for 3 h, which was firstly obtained *via* a simple PEG-assisted hydrothermal route. The as-prepared $ZnAl_2O_4:Eu^{3+}$ phosphors were well characterized by means of XRPD, FESEM, TEM, HRTEM, N_2 adsorption and desorption and PL techniques. The experimental results reveal that the amount of PEG 2000 in solution plays the crucial role in the formation of spherical porous $ZnAl_2O_4:Eu^{3+}$ phosphors. The N_2 adsorption and desorption data reveal the mesoporous property of $ZnAl_2O_4:Eu^{3+}$ phosphors, having the high surface area of 40.02 $m^2\,g^{-1}$. The photoluminescent excitation and emission spectra illustrate the red-emitting property of $ZnAl_2O_4:Eu^{3+}$ phosphors owing to the characteristic transitions of Eu^{3+} from $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, and 4).

1. Introduction

Semiconductor nanocrystals doped with rare earth ions have been investigated extensively in recent years. These materials show us the interesting enhanced optical properties, with potential applications in the design of optoelectronic materials and as efficient phosphor materials for flat-panel displays [1–2]. Among the rare earth ions, trivalent europium (Eu^{3+}) is regarded as an efficient red luminescent phosphors due to its $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, and 4) transitions [3]. So far, many kinds of Eu^{3+}-doped red-emitting phosphors using various inorganic materials as hosts were documented. For instance, Eu^{3+}-activated $MgAl_2O_4$ phosphors were prepared by the combustion method, resulting in a strong and intense red emission centered at 615 nm [4]. Red-emitting $LnOCl:Eu^{3+}$ phosphors were obtained by the solvothermal reaction followed by the calcination at 500 °C [5].

Aluminum-based spinels denote an interesting sort of oxide ceramics with significant technological applications. Of these, gahnite ($ZnAl_2O_4$) is a useful semiconductor (3.8 eV), and thus it can be used as transparent conductor, dielectric material, and optical material [6]. Recently, rare earth metal ions activated $ZnAl_2O_4$ phosphors have been studied thanks to the unique luminescent properties resulting from its stability and high emission quantum yields. This material can produce efficient visible emissions in a 4f shell, which is insensitive to the influence of its surroundings because of the shielding effect of the outer 5s and 5p orbitals [7]. For example, Ivakin et al. reported the synthesis of Eu^{3+}-doped $ZnAl_2O_4$ phosphors in water and water-ammoniac fluids [8]; $ZnAl_2O_4$ phosphors doped with Eu^{3+} were also prepared by the combustion method [7,9].

Besides, much attention has been focused on the preparation of porous materials by various synthetic methods, which can exhibit special properties such as low density, large surface area, delivering ability, and surface permeability [10–11]. As a kind of important technique for preparing nanomaterials, hydrothermal method has been also conducted to fabricate porous materials. Taking the following as examples, Zhang and co-workers reported the general hydrothermal approach to prepare porous crystalline TiO_2, $SrTiO_3$, and $BaTiO_3$ spheres [12]; hollow alloy spheres were rapidly synthesized using metal-compound-induced vesicles as efficient directors [13]. However, as far as we know, there is few report on the preparation of well-defined porous $ZnAl_2O_4$ spheres.

Very recently, we successfully prepared ultrafine $ZnAl_2O_4$ nanocrysparticles under hydrothermal conditions, using urea, hexamethylenetetramine, or hydrazine monohydrate as the basic sources [14]. It was found that the crystallinity of $ZnAl_2O_4$ nanocrystals obtained using urea as the basic source was much better than that in the case of hexamethylenetetramine or hydrazine monohydrate. Herein, we chose urea as the basic source to prepare Eu^{3+}-doped $ZnAl_2O_4$ phosphors and the surfactant of polyethylene glycol (PEG) was added into the reaction system to manipulate the characteristics of products. As a result, we obtained spherical porous $ZnAl_2O_4:Eu^{3+}$ phosphors, which were

* Corresponding author. Tel./fax: +86 551 2901450.
E-mail address: cxyhfut@gmail.com (X.Y. Chen).

0925-3467/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2009.10.001

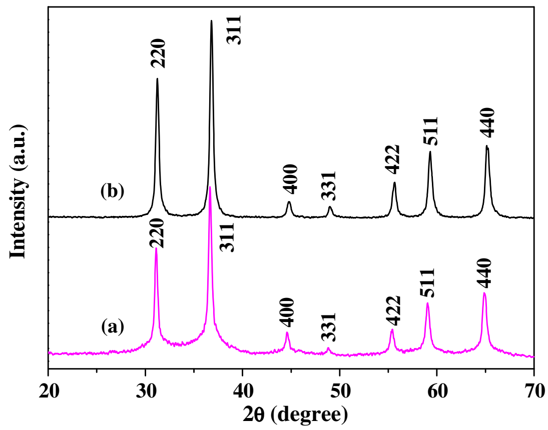

Fig. 1. XRPD patterns of the products: (a) hydrothermally synthesized at 200 °C for 24 h in the presence of PEG 2000 and (b) subsequently post-annealed at 800 °C for 3 h.

confirmed to be red-emitting phosphors from the excitation and emission spectra. The reaction mechanism for the spherical porous superstructures was also discussed in brief.

2. Experimental

All the chemicals are analytical grade and used as received without further purification. In present study, a series of contrast experiments were carried out by adjusting the species of PEG (*i.e.* PEG 2000, PEG 4000, PEG 6000, PEG 10000, and PEG 20000) and the amount of PEG 2000 (*i.e.* 5 g, 10 g, 15 g, 20 g). *Note:* Eu_2O_3 was dissolved in 10% nitric acid to prepare diluted solution containing $Eu(NO_3)_3$.

2.1. Typical procedure for preparing spherical porous $ZnAl_2O_4$:Eu^{3+} phosphors

$Zn(NO_3)_2{\cdot}6H_2O$ (2 mmol), $Al(NO_3)_3{\cdot}9H_2O$ (4 mmol), $CO(NH_2)_2$ (10 mmol), PEG 2000 (20 g) and $Eu(NO_3)_3$ (0.04 mmol) were in turn

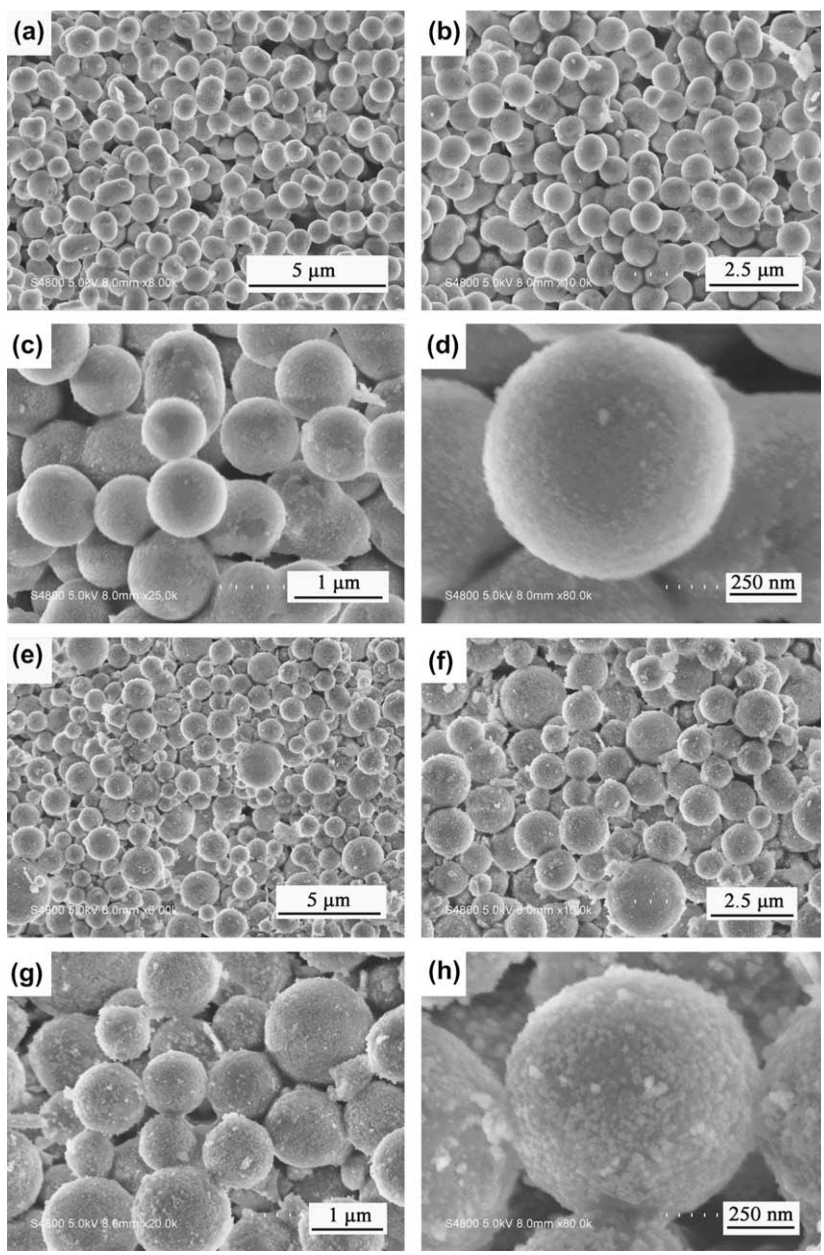

Fig. 2. FESEM images of the $ZnAl_2O_4$:Eu^{3+} samples hydrothermally synthesized at 200 °C for 24 h in the presence of (a–d) PEG 2000 (20 g) and (e–h) PEG 4000 (20 g).