Journal of Physics and Chemistry of Solids 74 (2013) 196–199

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

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

Photoluminescent properties of Eu^{3+} and Dy^{3+} ions doped $MgGa_2O_4$ phosphors

Hai Liu, Lixin Yu*, Fuhai Li

Nanchang University, Department of Materials Science and Engineering, 999 Xuefu Road, Nanchang 330031, China

ARTICLE INFO

Article history:
Received 5 April 2012
Received in revised form
13 September 2012
Accepted 16 September 2012
Available online 5 October 2012

Keywords:
D. Luminescence
D. Optical properties

ABSTRACT

Several concentrations Eu^{3+}-doped and Dy^{3+}-doped $MgGa_2O_4$ phosphors were prepared successfully by two-step firing synthesis. The sintered samples were characterized by means of X-ray diffraction (XRD) and fluorescence spectrophotometer. Little amount of rare earth doped will not change the host matrix structure and the maximum of the emission or excitation intensity of these phosphors will decrease as the concentration increasing for concentration quenching. The emissions of Eu^{3+} caused by the transitions of $^5D_0 \rightarrow {}^7F_j$ ($j=0, 1, 2, 3, 4$) were observed. And there are three groups of emission at 480 nm, 575 nm and 665 nm occurring at the spectrum of Dy^{3+} ions, which shows that $MgGa_2O_4$ phosphors doped with nanostructures ions have the potentiality to be applied for white LEDs applications.

1. Introduction

Just because white light-emitting-diodes (W-LEDs) have a longer lifetime, consume a lower energy, have a higher reliability and other advantages, they have been widely used into the class of lighting field and show a high possibility to replace conventional lamps, such as incandescent lamps and fluorescent lamps, perhaps becoming the fourth-generation lighting resource [1–3]. As for the W-LEDs composited by blue light and yellow light, there are several problems such as lower color-rendering index or lower luminous efficiency just because of lack of red light. Nowadays, thanks to the higher energy of near ultraviolet (UV) light to excite phosphor, we can obtain white light admixed with full-color-emission, which behaves more outstanding qualities than other phosphors [1,4].

Rare earth (RE) ions play a very important role in the improvement of phosphors' optical properties. The emission of phosphor almost originates from impurities, while the absorption of energy takes place due to the host lattice or impurities [5,6]. And the emission of RE caused by *f–f* transitions will be different from that of *d–f*, whose emission spectra consists of sharp lines, while the *d–f* transitions show broad bands. As is often thought that the RE doped into the phosphors could improve the CRI and the energy efficiency [5]. In addition, because Eu^{3+} ions ($^5D_0$) and Dy^{3+} ions are hypersensitive to the hosts and local microstructures, Eu^{3+} ions and doped hosts are universally applied to commercial phosphors and fluorescent probe.

Although as above described, the white light consisting of two kinds of colors has such those problems, thus the traditional sulfide phosphors are unstable under electron beam exposure [7,8]. So exploring the phosphors without sulfide is urgent for commercial application. In the present work, we chosen the $MgGa_2O_4$ doped with RE ions as the candidate to produce white light. It is hopeful that the RE ions could replace the Ga^{3+} ions sites, which occupy the eight tetrahedral sites and sixteen octahedral sites because both the RE and Ga^{3+} ions have same electronegativity and similar atomic size [7,9]. In our work, $MgGa_2O_4$ polycrystals doped with Eu^{3+} and Dy^{3+} were synthesized successfully via the solid state method. The research on $MgGa_2O_4$ doped other ions and relative results have been reported by many researchers [6–7,9–11] and $MgGa_2O_4$ doped with Eu^{3+} and Dy^{3+}, as the author known, has few reports on it. The result that the occurrence of two intense luminescent transitions from the $^6H_{15/2}$ and $^6H_{13/2}$ terminal levels in the blue region near 480 nm and in yellow region near 580 nm of Dy^{3+} indicates that the $MgGa_2O_4$ phosphors doped with RE ions have the potentiality to be used into the field of W-LEDs applications [1,12–13].

2. Experiment

The starting chemicals employed in this experiment are magnesium nitrate hexahydrate (AR), gallium oxide (3 N) and europium oxide (4 N) or dysprosium oxide (4 N). All chemicals are not further purified. The molar ratios of RE (Eu^{3+} or Dy^{3+}) to $MgGa_2O_4$ were 1%, 2% and 4%. Corresponding samples are labeled with Ga0.01Eu, Ga0.02Eu, Ga0.04Eu, Ga0.01Dy, Ga0.02Dy and Ga0.04Dy, respectively. First, all required chemicals was well

---

* Corresponding author. Tel.: +86 791 83969329.
E-mail address: yulixin72@yahoo.com.cn (L. Yu).

0022-3697/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jpcs.2012.09.006

mixed with a small amount of ethanol. Then the samples were polished for 1 h at room temperature. To evaporate the ethanol, the chemical obtained were dried at a certain temperature of 50 °C for several hours. Second, the dry powder was sent into the muffle furnace then heated to 900 °C for 1 h. Finally, the powder was heated to 1100 °C for 2 h. Then we obtained $MgGa_2O_4:Eu^{3+}$ and $MgGa_2O_4:Dy^{3+}$ phosphors.

The crystallization process and phase identification of the calcined powders were studied by powder X-ray diffraction (XRD), operating with a Cu-target tube ($\lambda = 0.15418$ nm, with 40 kV and 250 mA) as radiative source and a graphite monochrometer, and the photoluminescence properties of the samples were recorded by F-4600 fluorescence spectrophotometer at room temperature. A 150 W xenon lamp with light passed through a monochromator was used for excitation source. The resolution of F-4600 is ± 2 nm.

As comparison, $MgGa_2O_4$ being absent RE ions was also prepared and characterized in the same procedure.

3. Results and discussion

3.1. XRD results

The X-ray powder diffraction patterns of all samples are shown in Fig. 1. It can be seen that $MgGa_2O_4:Eu^{3+}$ and $MgGa_2O_4:Dy^{3+}$ could form stable solid state polycrystals at 1100 °C. It can be seen that the structures of RE doped gallate can be assigned to the spinel structure. No additional phases are observed. Almost diffraction peaks can be attributed to the cubic $MgGa_2O_4$ phase (JCPDS No.78-0551). Due to the difference in ions radius between Ga^{3+} and Eu^{3+} or Dy^{3+} ions, RE doped gallate hosts should replace the Ga^{3+} in the lattice sites to make the crystallinity decreased as the Eu^{3+} or Dy^{3+} content increased [8,14]. But from the XRD results, the exist of RE ions has little influence on the crystalline structure of the phosphor. These results indicate that the RE ions enter the $MgGa_2O_4$ lattice sites [15].

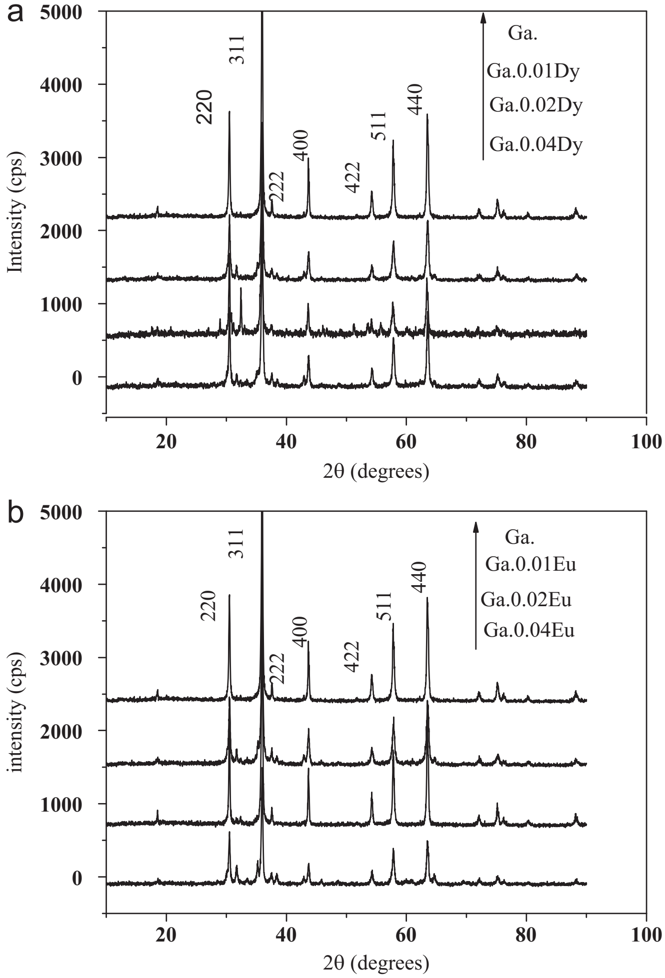

Fig. 1. XRD pattern of $MgGa_2O_4$ doped with Eu^{3+} and Dy^{3+} in different content.

3.2. Luminescent properties of $MgGa_2O_4:Eu^{3+}$

Fig. 2 shows the excitation spectra of the $MgGa_2O_4:Eu^{3+}$ phosphors monitored the emissions at 505 nm and 620 nm. It can be seen as monitoring the mission at 505 nm, there exists a broad band absorption peak at 240 nm in both $MgGa_2O_4$ and $MgGa_2O_4:Eu^{3+}$, which indicates that the broad band absorption is due to the $MgGa_2O_4$ hosts. As monitoring the emission at 620 nm, there is a broad band ranging from 250 nm to 350 nm peaking at 285 nm, which is assigned to the charge transfer band (CTB) absorption from $2p$ orbital of O^{2-} ions to the $4f$ vacant orbital of Eu^{3+} ions [4]. It can be seen clearly that the peak of CTB for different Eu^{3+} concentrations evidently changes, 280 nm in Ga.0.01 Eu, 258 nm in Ga.0.02 Eu and 291 nm in Ga.0.04 Eu, respectively. As known, the CTB depends on the local environments around Eu^{3+} ions. The above results indicate that the local structures surround Eu^{3+} ions evidently change because of the different Eu^{3+} contents. The sharp lines ranging from 350 nm to 450 nm are with the direct excitation of *f–f* shell transitions of Eu^{3+}. For different Eu^{3+} concentrations, the strongest absorption locates at about 395 nm, which contributes to the $^7F_0 \rightarrow {}^5L_6$ transitions in the near-UV region. The *f–f* transitions in the Eu^{3+}, $4f^6$ configuration in longer spectral region with $^7F_0 \rightarrow {}^5D_4$ (360 nm), $^7F_0 \rightarrow {}^5L_7$ (380 nm), and $^7F_0 \rightarrow {}^5D_3$ (410 nm) is also marked in Fig. 2. The activator concentration will affect the luminescent properties of the phosphor seriously, which could be seen clearly from Fig. 2, especially $MgGa_2O_4$ with the molar ratio 2% of Eu^{3+} ions. The origination of the blue shift of CTB is perhaps due to that electrons are very difficult to be transferred from O^{2-} orbital to the Ga^{3+} or Ga^{n+} ion at the strong degree of covalency of metal–O ligand bond [16].

Fig. 3 shows the emission spectra of $MgGa_2O_4:Eu^{3+}$ power phosphor at room temperature at 280 nm excitation. The $^5D_0$–^7F_J transitions ($J = 0, 1, 2, 3, 4$) ranging from 550 nm to 750 nm are observed. Among them, the $^5D_0$–$^7F_2$ transitions (about 620 nm) are the strongest. This replies that the red emission is much stronger than the orange emission of Eu^{3+} ions in $MgGa_2O_4$ phosphors. Also, we can see both $MgGa_2O_4$ and $MgGa_2O_4:Eu^{3+}$ having a broad band at the wavelength of about 505 nm, which is due to the emission of $MgGa_2O_4$ [17–19].

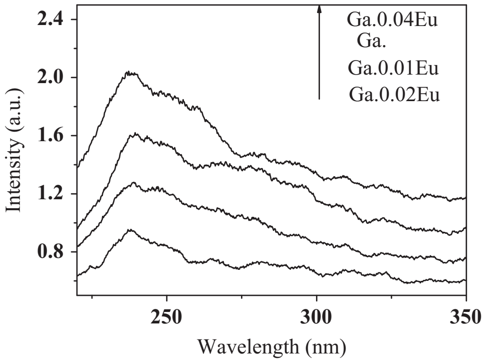

Fig. 2. Excitation spectrum of $MgGa_2O_4:Eu^{3+}$ power phosphor ($\lambda_{em} = 505$ nm and 620 nm).