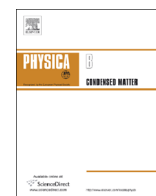




ELSEVIER

Contents lists available at ScienceDirect

Physica B

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

Luminescence of divalent europium activated spinels synthesized by combustion and the enhanced afterglow by dysprosium incorporation



Haoyi Wu*, Yahong Jin

School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Waihuanxi Road, No.100, Guangzhou 510006, PR China

ARTICLE INFO

Article history:

Received 3 November 2015

Received in revised form

27 January 2016

Accepted 5 February 2016

Available online 8 February 2016

Keywords:

Spinel

Luminescence

Afterglow

ABSTRACT

Herein we report a luminescent phenomenon of Eu^{2+} in the spinel MgAl_2O_4 and ZnAl_2O_4 samples which are successfully synthesized *via* a combustion method. The XRD shows cubic spinel structure is obtained from the prepared samples. The mean crystal sizes estimated from XRD data are 30 and 10 nm for MgAl_2O_4 and ZnAl_2O_4 respectively, and the large grain particles are the agglomeration of crystallites. The Eu^{2+} ions show a blue emission at around 480 nm and an afterglow phenomenon is observed after the removal of excitation. The afterglow spectrum of $\text{MgAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ shows two emissions at 480 and 520 nm while only one at 480 nm is observed in $\text{ZnAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$. The afterglow intensity and the persisting duration can be substantially enhanced by the Dy^{3+} incorporation because the trapping ability of the electron traps is reinforced. This is confirmed by the TL curves of the samples.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

As a gemstone mineral, the natural spinels have been discovered for more than 1000 years, and the color center appeared in the crystal renders the materials various kinds of colors. This feature makes spinels famous in artwork of jewels. Besides, spinels are also well-known semi-conducting materials which have been widely used in modern science. Due to the band gap around 3–4 eV, the materials can be easily excited by ultra-violet light and show transparent in visible range [1–3]. Therefore, they could be used as photocatalysts, optical ceramics and electronic materials [4–6]. Moreover, a spinel allows the appearance of energy level between the valence band (VB) and the conduction band (CB), by the introduction of some impurities. This energy level renders spinel additional optical features and extends its available applications, such as luminescence. By now, there has been numbers of literatures on lanthanides incorporated spinels, which show visible luminescence and potentially applied in light-emitting devices [7,8].

As the typical types of spinel, MgAl_2O_4 and ZnAl_2O_4 have been widely reported as the matrices for Cr^{3+} , Eu^{3+} , and Mn^{2+} with the synthesis methods of solid-state reaction, sol-gel, co-precipitation, micro-emulsion and so on [9–20]. They exhibit red or green emission under a ultra-violet (UV) excitation. Based on the transition of 5d to 4f states, the emission of Eu^{2+} shows different colors in different compounds because the energy levels of 5d states are

affected by the crystal fields. The coordinated environment of Eu^{2+} determines the gap between the lowest 5d and highest 4f levels, and then the emission color is tunable in hosts. Therefore, Eu^{2+} ions are widely employed as the luminescent center in many inorganic materials [21]. There were a few literatures reporting the luminescence of Eu^{2+} in spinels [22,23]. Yet reports on their afterglow phenomenon appeared infrequently. In present work, the Eu^{2+} incorporated spinels are synthesized through an urea-assisted combustion method. The X-ray diffraction (XRD) results demonstrate that this method is available for the synthesis of spinels at low temperature. Besides, the luminescence properties of Eu^{2+} , including photoluminescence (PL) and thermoluminescence (TL, afterglow) in MAl_2O_4 (M: Mg, Zn) typed spinel are investigated. The Eu^{2+} shows blue emission in the prepared samples as well as a visible afterglow. Moreover, the enhancement of afterglow has been found by simultaneously incorporating Dy^{3+} ions. The intensity and the persisting duration of the afterglow can be substantially enhanced by incorporating Dy^{3+} ions.

2. Experimental procedures

2.1. Synthesis

Four spinel-host luminescent samples, $\text{Mg}_{0.99}\text{Al}_2\text{O}_4: \text{Eu}_{0.01}^{2+}$ (denoted as MAE), $\text{Mg}_{0.97}\text{Al}_2\text{O}_4: \text{Eu}_{0.01}^{2+}, \text{Dy}_{0.02}^{3+}$ (denoted as MAED), $\text{Zn}_{0.99}\text{Al}_2\text{O}_4: \text{Eu}_{0.01}^{2+}$ (denoted as ZAE) and $\text{Zn}_{0.97}\text{Al}_2\text{O}_4: \text{Eu}_{0.01}^{2+}, \text{Dy}_{0.02}^{3+}$ (denoted as ZAED) were synthesized *via* a combustion method. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Damao Chemical Reagent Factory, Tianjin), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Damao Chemical Reagent Factory, Tianjin), Al

* Corresponding author.

E-mail address: manofchina@gmail.com (H. Wu).

(NO₃)₃·9H₂O (99%, Damao Chemical Reagent Factory, Tianjin), Eu₂O₃ (99.99%, Guangzhou Research Institute of Non-ferrous Metals) and Dy₂O₃ (99.99%, Guangzhou Research Institute of Non-ferrous Metals) were employed as the raw materials. Additional 10 mol% of H₃BO₃ (99%, Damao Chemical Reagent Factory, Tianjin) was added as a flux. Initially, the raw materials were weighed according to the stoichiometric compositions. The Eu(NO₃)₃ and Dy(NO₃)₃ were obtained by dissolving Eu₂O₃ and Dy₂O₃ in dilute nitric acid. The Mg(NO₃)₂·6H₂O/Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were dissolved in two cups of deionized water. After becoming transparent, two cups of solution were mixed with proper molar ratios and stirred for 1 h. After that, a proper amount of urea was added to form a precursor. The molar ratio for one sample to the urea was 1:20. After that, the precursor was stirred for 1 h, and then was put in a muffle furnace which was maintained at 620 °C. The precursor was boiled and then decomposed with the evolution of large amounts of gases. Then spontaneous ignition occurred and underwent smoldering combustion with enormous swelling, accompanied by the production of white foamy and voluminous ash. The entire process lasted for 5–10 min. Finally, the as-prepared MAE, MAED, ZAE and ZAED samples were obtained.

2.2. Characterization

The phase identification of all obtained samples was carried out by XRD using a XD-2 diffractometer (Beijing PGENERAL) with Cu K α irradiation ($\lambda=1.5406$ Å) at 36 kV tube voltage and 20 mA tube current. The scan range was 2θ from 10° to 70° with 6° min⁻¹ speed. The scanning electron microscope (SEM) images were recorded using a Philips XL-30 apparatus. The PL and the afterglow spectra were investigated by an F-7000 Fluorescence Spectrophotometer (Hitachi) with a Xe lamp excitation. Prior to the afterglow spectra measurement, the samples were excited by a mercury lamp (254 nm, 60 W) for 1 min and the measurement was carried out without external excitation (the Xe lamp was closed). The decay and thermoluminescence (TL) curves were measurement using a FJ427A1 thermoluminescent reader (CNNC Beijing Nuclear Instrument Factory). 0.001 g powder for each sample was employed. During detection of decay curves, the temperature was maintained at 30 °C. Before the detection, each sample was excited by a mercury lamp for 1 min. For the TL curves measurement, the heating rate was 1 °C s⁻¹. The range of the measurement was from room temperature to 300 °C. Prior to the measurement, each powder sample was also exposed to a mercury lamp for 1 min. The interval between the measurement and the removal of excitation was 10 min.

3. Results and discussions

3.1. Phase identification and morphology

The XRD patterns of the obtained samples are shown in Fig. 1. As can be seen, the MAE and MAED samples exhibit the similar patterns with approximate peaks location. According to the JCPDF standard card No. 86-2258, the structure of the samples can be regarded as cubic MgAl₂O₄. The samples are face-centered type with the space group of Fd-3 m (No. 227) and the cell parameters are about $a=b=c=8.07$ Å. No other structure is observed from the patterns. In addition, the ZAE and ZAED samples also exhibit cubic structure according to the JCPDF standard card No. 73-1961. The samples are also face-centered type and the space group is Fd-3 m (No. 227). The cell parameters are about $a=b=c=8.04$ Å. The incorporated Eu²⁺ and Dy³⁺ ions tend to substitute the Mg²⁺ and Zn²⁺ sites due to the similar ionic sizes (Mg²⁺, fourth coordination, 57 pm; Zn²⁺, fourth coordination, 60 pm; Al³⁺, sixth coordination,

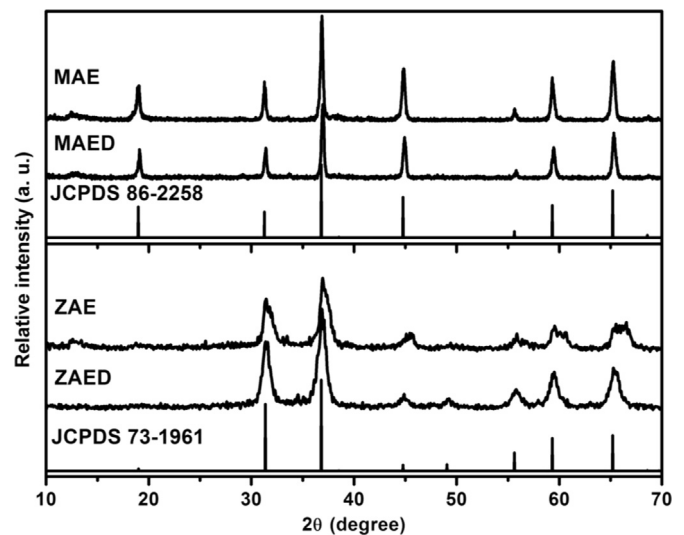


Fig. 1. XRD patterns of the samples.

53.5 pm; Eu²⁺, eighth coordination, 125 pm; Dy³⁺, eighth coordination, 102.7 pm) [24]. A small amount of Eu²⁺ and Dy³⁺ incorporation do not have a notable effect on the XRD patterns.

The mean crystal size of prepared samples can be calculated using Scherrer Formula [25]. The (220) and (311) crystal planes are selected to calculate the size and the formula is expressed as:

$$D = \frac{0.89\lambda}{\beta \cos(\theta)} \quad (1)$$

where D is the average crystal size for the samples. λ represents the wavelength of X-ray, which is 0.15406 nm in this work. β is the width at half intensity of the XRD peak and θ is the degree of the maximum intensity of the peak. The estimated results are listed in Table 1. The mean crystal size of the MgAl₂O₄ samples is around 30 nm and the one of ZnAl₂O₄ samples is around 10 nm. This result indicates that the obtained MgAl₂O₄ and ZnAl₂O₄ by combustion method have different crystal size although they have similar crystal structure. The MgAl₂O₄ seems crystalizing better than the ZnAl₂O₄.

Fig. 2 shows the SEM images of MAED and ZAEAD. The grain size of the particles is varying from a few microns to several tens of microns. The morphology of the particles seems to be formed from the agglomeration of crystallites. Pores can be observed on the surface of the bulk. This is caused by the vaporized gas in a rapid combustion process. The morphologies of MAE and ZAE are similar.

3.2. PL

The emission and excitation spectra of the samples are shown in Fig. 3. The shapes of the spectra of samples are similar. A broad emission band at 400–570 nm with a peak around 480 nm can be

Table 1
Estimated mean crystal size of the samples.

SAMPLES	CRYSTAL PLANE	2θ (degree)	β (degree)	D (nm)
MAE	(220)	31.384	0.23728	33.11
	(311)	36.956	0.24417	32.17
MAED	(220)	31.290	0.26356	29.81
	(311)	36.862	0.25845	30.40
ZAE	(220)	31.611	0.86085	9.13
	(311)	37.133	0.85401	9.20
ZAED	(220)	31.454	0.70263	11.18
	(311)	36.902	0.73407	10.70

Download English Version:

<https://daneshyari.com/en/article/1808432>

Download Persian Version:

<https://daneshyari.com/article/1808432>

[Daneshyari.com](https://daneshyari.com)