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Europium doped di-calcium magnesium di-silicate orange–red emitting phosphor by solid state reaction method

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ABSTRACT

A new orange–red europium doped di-calcium magnesium di-silicate ($Ca_2MgSi_2O_7:Eu^{3+}$) phosphor was prepared by the traditional high temperature solid state reaction method. The prepared $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor was characterized by X-ray diffractometer (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) with energy dispersive x-ray spectroscopy (EDX), fourier transform infrared spectra (FTIR), photoluminescence (PL) and decay characteristics. The phase structure of sintered phosphor was akermanite type structure which belongs to the tetragonal crystallography with space group $P\bar{4}2_1m$, this structure is a member of the melilite group and forms a layered compound. The chemical composition of the sintered $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor was confirmed by EDX spectra. The PL spectra indicate that $Ca_2MgSi_2O_7:Eu^{3+}$ can be excited effectively by near ultraviolet (NUV) light and exhibit bright orange–red emission with excellent color stability. The fluorescence lifetime of $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor was found to be 28.47 ms. CIE color coordinates of $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor is suitable as orange-red light emitting phosphor with a CIE value of (X = 0.5554, Y = 0.4397). Therefore, it is considered to be a new promising orange–red emitting phosphor for white light emitting diode (LED) application.

1. Introduction

Luminescent materials containing rare earth ions are able to absorb energy in the UV-regions and emit visible light. Recently, these materials have drawn increasing interest due to their promising applications in white light emitting diodes, display devices, storage bioluminescence and fluorescence labels (Sahu, Bisen, Brahme, Wanjari, Tamrakar, 2015b; Xu, Wang, Liu, Jia, & Sheng, 2014).

As a new solid state light source, the white light-emitting diodes (WLEDs) are considered to be the fourth generation general lighting devices that stands a real chance of replacing conventional lighting sources such as incandescent and fluorescent lamps due to its long lifetime, saving energy, reliability, safety and its environmental friendly characteristics (Jiao & Wang, 2012). Among the technological strategies of obtaining WLEDs, the phosphor converted (pc) emission method is the most common one, in which tricolor phosphors

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(red, green and blue) are pumped by UV InGaN chips or blue GaN chips and generate white light. At present, the commercially used green and red phosphors for NUV chips are ZnS:(Cu^{+}, Al^{3+}) and $Y_2O_2S:Eu^{3+}$, respectively. Unfortunately, both ZnS:(Cu^{+}, Al^{3+}) and $Y_2O_2S:Eu^{3+}$ show low chemical stability as they are sulfide based phosphors. Therefore, it is urgent to search for new green and red phosphors or an orange–red phosphor with high efficiency and excellent stability (Liu et al. 2014).

Generally, phosphors consist of activator and host, in order to obtain efficient red or orange–red emitting phosphor, host is another key factor (Wang, Lou, & Li, 2014). Eu^{3+} doped oxides were widely studied as efficient red emitting phosphors due to the abundant transitions from the excited $^5D_0$ level to the ^7F_J (J = 0, 1, 2, 3, 4) levels of the $4f^6$ configuration in the orange-red light area (Dong, Zhang, Zhang, Hao, & Luo, 2014; Gorller-Walrand, Fluyt, Ceulemans, & Carnall, 1995). Mellite are a large group of compounds characterized by the general formula $M_2T^1T^2{}_2O_7$, (M = Sr, Ca, Ba; T^1 = Mn, Co, Cu, Mg, Zn; T_2 = Si, Ge), have been investigated widely as optical materials. Due to their tetragonal and non-centrosymmetric crystal structure, lanthanides or transition metals can be accepted easily as constituents or dopants by the melilites, allowing the synthesis of high-quality doped single crystals. Recently, di-calcium magnesium di-silicate ($Ca_2MgSi_2O_7$) phosphor has attracted great interest due to its special structure features, excellent physical and chemical stability. They have been studied widely with Eu^{2+} doping, which shows that a green emission and long persistent luminescence by co-doping with some other rare earth ions. A calcium silicate phosphor would be ideal from the manufacturing point of view, because both calcium and silica are abundant and are relatively inexpensive (Talwar et al. 2009).

In the past, $Ca_2MgSi_2O_7$ phosphor doped with Eu^{3+} has been prepared by pulsed laser deposition method. High quality $Ca_2MgSi_2O_7:Eu^{3+}$ films phosphors were deposited on Al_2O_3 (0 0 0 1) substrates. The crystallinity, surface roughness and photoluminescence of the thin film phosphors were strongly dependent on the deposition conditions, which is the drawback of pulsed laser deposition method (Yang, Moona, Choi, Jeong, & Kim, 2012). Solid state reaction techniques is a traditional phosphors synthesis techniques is widely used to prepare silicate phosphors because samples prepared using this method have good luminescence and very good morphology, which has advantage over the pulsed laser deposition technique (Sahu, Bisen, & Brahme, 2015a, Shrivastava & Kaur, 2014).

In the present paper, we report the synthesis of europium doped di-calcium magnesium di-silicate ($Ca_2MgSi_2O_7:Eu^{3+}$) phosphor by high temperature solid state reaction method. The phase structure, crystallite size, particle size, surface morphology, elemental analysis, different stretching mode was analyzed by X-ray diffractometer (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDX), and fourier transform infrared (FTIR) spectra respectively. The luminescent behaviors of this phosphor were also investigated by photoluminescence (PL) and long afterglow (decay) characteristics.

2. Experimental

2.1. Material preparation

The $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor was prepared by the high temperature solid state reaction method. The raw materials are calcium carbonate [$CaCO_3$ (99.90%)], magnesium oxide [MgO (99.90%)], silicon di-oxide [SiO_2 (99.99%)] and europium oxide [Eu_2O_3 (99.99%)], all of analytical grade (A.R.), were employed in this experiment. Boric acid (H_3BO_3) was added as flux. Initially, the raw materials were weighed according to the nominal compositions of $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor. Then the powders were mixed and milled thoroughly for 2 h using mortar and pestle. The grinded sample was placed in an alumina crucible and subsequently fired at 1200 °C for 3 h in air. At last the nominal compounds were obtained after the cooling down of programmable furnace.

2.2. Characterization techniques

The phase structures of the prepared $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor was characterized by powder X-ray diffraction analysis (XRD). XRD pattern has been obtained from Bruker D8 advanced X-ray powder diffractometer using CuKα radiation and the data were collected over the 2θ range 10–80°. Particle size of prepared phosphor was determined by TEM using TECHNAI G2. The samples required for TEM analysis were prepared by dispersing the sintered $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor in methanol using an ultrasound bath technique. A drop of this dispersed suspension was put onto 200-mesh carbon coated copper grid and then dried into the air. An EDX spectra was used for the elemental analysis of the prepared phosphor (Sahu, Bisen, Brahme & Ganjir 2015c). FTIR spectra were recorded with the help of IR Prestige-21 by SHIMADZU for investigating the functional group (4000–1400 cm^{-1}) as well as the finger print region (1400–400 cm^{-1}) of sintered phosphor by mixing the sample with potassium bromide (KBr, AR grade). The PL measurements of excitation and emission spectra were recorded on a Shimadzu (RF 5301-PC) spectrofluorophotometer fitted with a sensitive photomultiplier tube. This spectrofluorophotometer provides corrected excitation and emission spectra in the 200–400 and 475–700 nm ranges, respectively. All measurements were carried out at the room temperature.

3. Results and discussion

3.1. XRD analysis

In order to determine the phase structure, powder XRD analysis has been carried out. The typical XRD patterns of $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor with the standard XRD pattern is shown in Fig. 1. The position and intensity of diffraction peaks of the prepared $Ca_2MgSi_2O_7:Eu^{3+}$ phosphor were matched and found to be consistent with the standard XRD pattern (COD card No. 96-900-6941) by MATCH 2 software. The figure of merit (FOM) while matching these was 0.9759 (97%) which