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Spectroscopic behavior, thermal stability and temperature sensitivity of Ca_2SiO_4: Eu^{3+} red emitting phosphor for solid state lighting application

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ABSTRACT

This paper reports the spectroscopic behavior, thermal stability and temperature sensitivity of Ca_2SiO_4: Eu^{3+} phosphors. A series of Ca_2SiO_4: Eu^{3+} phosphors were synthesized by using an efficient combustion method. The X-ray diffraction (XRD) results showed that the prepared phosphors consist of a single phase orthorhombic structure. The field emission scanning electron microscope (FESEM) results showed irregular and agglomeration of particles. Under the excitation wavelength 255 nm, the PL emission showed five peaks at the wavelengths 574, 594, 612, 656 and 707 nm corresponds to the transitions $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ respectively. The concentration quenching phenomenon was ascribed to dipole-dipole interaction. The intensity and spectral parameters for different J levels were estimated using the Judd-Ofelt theory. The prepared phosphor has retained the emission intensity about 70% at 475 K. The CIE chromaticity coordinates (x, y) were calculated from emission spectra and found to be in the red region.

1. Introduction

In the current scenario, the solid state lighting sources play a key role in our lives as well as industry worldwide owing to their fascinating characteristics such as excellent luminescence efficiency, better color rendering index, long lifetime, low power consumption and environmental friendliness. Recently, white lighting emitting diodes (WLEDs) based on phosphors has been considered as a next-generation solid-state lighting source which can be a better substitute for traditional lighting sources such as incandescent and fluorescent lamps because of their superior characteristics such as high efficiency, low power consumption, long operational lifetime and environmental friendliness [1–5]. Nowadays they have used in many fields such as a flashlight, indicator lights and display backlighting etc. Considering the demand for solid-state lighting, the researcher devoted to phosphors converted solid-state lighting sources due to their possible photonic applications, good luminescence characteristics, and stability in vacuum [6]. Traditionally, the white light obtained by pumping a blue InGaN LED chip with yellow emitting $Y_3Al_5O_{12}$: Ce^{3+} (YAG) phosphor. However, based on this phosphor, the white light emitting devices has certain disadvantages such as low color rendering index (Ra<80) at long wavelength and high correlated color temperature (CCT>5000 K) due to the lack of red light component [7,8]. An alternative approach involves the near-ultraviolet (NUV) or UV LED chip with tri-color (red, green and blue) phosphor or a combination of red and green phosphors with a blue LED chip [9]. Traditionally, the widely used red phosphors are Y_2O_3: Eu^{3+} and Y_2O_2S: Eu^{3+}. Y_2O_3: Eu^{3+} has a lower intensity than those of blue or green phosphors and Y_2O_2S: Eu^{3+} phosphor is not suitable for the long-term application because its stability is awful because it eventually releases the sulphide gas at high temperature. Therefore, it is urgent to explore efficient red phosphor which is suitable for obtaining white light emission. The lighting sources fabricated by this approach can provide high CRI appropriate CCT and high tolerance [10]. Realizing the need for high-efficient lighting sources, various researchers across the world are working to meet this challenge.

As well known that, the luminescent performances of rare earth ions activated materials depends strongly on the luminescent host material. Hence, choosing an appropriate host material is an important factor for getting better luminescence. Silicate-based host matrix has been more and more attractive host matrix due

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to some superior advantages such as facile synthesis, stable crystal structure, long lifetime and environment-friendly characteristics [11]. Silicate-based host activated by rare earth ions have been reported by many researchers due to its signification potential for optoelectronic applications. Among the silicate-based phosphors, Ca_2SiO_4 is an important host matrix because of their important characteristics such as wide band gap, low phonon energy, excellent physical, chemical and thermal stability [12,13].

Rare earth ions having the electronic configurations of $4f^n 5d^m 6s^2$ ($n = 1–14$, $m = 0–1$) which enrich them with a unique and fascinating optic, electric and magnetic properties, extensively used as activators in the variety of phosphors. Rare earth ions exhibit strong emission peaks due to intra 4f-4f transitions as well. Among the rare earth ions, Eu^{3+} is an important activator for efficient red phosphors and widely investigated due to its abundant transitions $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$). The dominant transition $^5D_0 \rightarrow {}^7F_2$ (610–615 nm) is an electric-dipole transition and it is the benefactor to improve the red color of the phosphors [14].

In order to understand the spectral properties of luminescence materials, the spectroscopic parameters are calculated using Judd-Ofelt theory. The Judd-Ofelt intensity parameters (Ω_2, Ω_4) of Eu^{3+} ion in the host matrix can reveal information about the covalency and the surrounding metal ion. The spectral properties of Eu^{3+} ion were described in several compounds [15–18]. A variety of research work successively done by the researchers in Ca_2SiO_4: Eu^{3+} phosphor [19–21]. However, there is no complete explanation of the radiative spectroscopic parameters based on the emission spectra of $CaSiO_4$: Eu^{3+} phosphor.

In this paper, we have synthesized a series of $Ca_{2-2x}Eu_{2x}SiO_4$ ($x = 0.01–0.06$) phosphors by combustion method. The structural properties are well investigated by XRD and FESEM studies. The optical properties of prepared phosphors were carried out by diffuse reflectance spectra (DRS) and photoluminescence (PL) spectra. The PL results showed that an intense red emission exists under the excitation wavelength 255 nm. In addition, temperature-dependent PL emission spectra of the prepared phosphor showed that the present phosphor has excellent thermal stability and sensitivity. The photometric results suggest that the prepared phosphor has high color purity 96.11% indicates that the prepared phosphor could be an eventual choice as the red component for white light emission. The Judd-Ofelt theory was applied to determine the intensity parameters and other radiative parameters such as radiative transition rates, radiative lifetime, asymmetry and branching ratios. All the obtained results suggest that the present prepared Ca_2SiO_4: Eu^{3+} phosphors used as a red component for the potential application of solid-state lighting application.

2. Experimental procedures

2.1. Samples preparation

A series of $Ca_{2(1-x)}Eu_{2x}Si_2O_4$ ($x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06$) phosphors were synthesized using the solution combustion method. The entire preparation procedures of samples are presented below. Firstly stoichiometric amounts of starting materials, calcium nitrate ($Ca(NO_3)_2$), silicon dioxide (SiO_2), europium oxide (Eu_2O_3) and urea ($CO(NH_2)_2$) are weighed. All the materials are analytic grade and the urea was used as a fuel. The stock solution of $Eu_2(NO_3)_3$ was prepared by dissolving Eu_2O_3 in HNO_3. Undoped Ca_2SiO_4 sample was prepared by mixing all the raw materials $Ca(NO_3)_2$, SiO_2 and $CO(NH_2)_2$ with adding the proper amount of deionized water. The complete solution was stirred using a stirrer and maintained the temperature of 80–85 °C until a highly viscous gel was formed. The resulting gel was taken in an alumina crucible and introduced into the preheated muffle furnace maintained at temperature 500 °C for 5 min. For doping purpose $Eu_2(NO_3)_2$ was mixed in different molar concentration with the mixtures of $Ca(NO_3)_2$, SiO_2 and $CO(NH_2)_2$ before stirring. The following relevant reaction formulas as follows:

$$6Ca(NO_3)_2 + 3SiO_2 + 10CO(NH_2)_2 \rightarrow 3Ca_2SiO_4 + 10CO_2\uparrow + 16N_2\uparrow + 20H_2O$$

The obtained powder was taken in the alumina crucible and introduce in the programmable furnace, which is heated at the rate 5 °C per minute and finally, the sample was fired at temperature 900 °C for 3 h in the air. The final products were obtained after cooling the sample to room temperature by natural cooling.

2.2. Characterization techniques

The phase purity and structural properties of Ca_2SiO_4: Eu^{3+} phosphors were checked by using XRD diffractometer recorded in the range of Bragg's angle 2θ (10°–80°) using a Bruker D8 Focus X-ray diffraction (XRD) with Cu-Kα radiation. The surface morphology of the prepared phosphors was examined by using field emission scanning electron microscopy (FESEM) with the help of 55- Supra (Germany) FESEM measuring instrument. The Ultra Violet Visible (UV–Vis) Diffuse reflectance studies of prepared samples were done using CARRY – 5000 spectrophotometers. The photoluminescence together with decay kinetics was studied using Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer. The temperature dependent photoluminescence studies were carried out using Optistate DN2 (Oxford Cryostat).

3. Structural properties

3.1. XRD studies

Fig. 1 (a) depicts the XRD patterns of undoped and 3 mol% Eu^{3+} doped Ca_2SiO_4 phosphors along with the standard pattern (JCPDS card no 86–0397) of Ca_2SiO_4 is shown as a reference which is an orthorhombic phase with space group Pbnm (62). It can be observed that all the diffraction peaks are well matched with the standard pattern of Ca_2SiO_4. There were three small impurity peaks at $2\theta = 27°$, 37° and 43° coming due to SiO_2 (JCPDS card no. 86–1628) which was used as raw material. It was also observed that no additional peak was found after Eu^{3+} doping, which means the Eu^{3+} ion did not cause any notable impurities or any structural variation due the similarities in the atomic radii (r), as the Eu^{3+} ions ($r = 0.095$ nm) are likely to be substituted by Ca^{2+} ($r = 0.099$ nm).

The average crystallite size of prepared phosphors was calculated using Debye-Scherrer formula and Williamson-Hall (W–H) equation [22,23].

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

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin\theta}{\lambda} \quad (2)$$

where D is the average crystallite size, β is the full-width half maxima (FWHM), λ is the wavelength of incident X-ray radiation, θ is the Bragg's angle of diffraction and ε is the microstrain. The Williamson-Hall plots are shown in Fig. 1 (b, c). The obtained crystallite size of the prepared phosphors for 0 and 3 mol% of Eu^{3+} ion were 25.54 and 27.72 nm from Debye-Scherrer formula and 29.07 and 31.15 nm from the W–H equation. The variation found in