



Synthesis Photoluminescence study of Ca2MgSi₂O7 : Ce, Dy, Eu micro Phosphor

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Abstract: This paper reports the photoluminescence properties of Ca2MgSi₂O₇ phosphor with different concentrations of trivalent cerium Ce, dyposium Dy and divalent Eu as dopant. The phosphor is synthesized using the solid state reaction. Photoluminescence studies is done on the prepared phosphor. For crystal structure and surface morphology SEM micrographs of Ca2MgSi₂O₇: Ce, Dy , Eu phosphor were also studied. From SEM confirms the formation of micro phosphor in the range around 100 μ m – 500 μ m

KEYWORDS: Photoluminescence (PL) , chromaticity diagram , Scanning Electron Microscopy (SEM),solid state reaction (SSR).

I.INTRODUCTION

 $M_2MgSi_2O_7$ doped with Eu^{2+} and Dy^{3+} , Ce^{3+} phosphor has shown quite good long lasting behaviour. Silicate

phosphors have few advantages over previously developed aluminate long lasting phosphors on chemical stability, heat stability, lower cost and varied luminescence colour from blue to yellow (Shi et al 2007). It is clear that the Eu2+ ion acts as the luminescent centre and it is known that some rare earth $(R^{3+)}$ co-dopants enhance the persistent luminescence obtained with Eu²⁺ doping alone. The exact role of the co-dopants and that of other lattice defects is uncertain, but the R^{3+} ions have been suggested to trap holes or electrons or just to create/modify defects due to charge compensation. The development and tailoring of new persistent luminescence (PLUM) materials would be greatly facilitated, if the mechanisms were known (Carlson et al 2009; Wu et al 2011a). Alkali earth silicates are useful luminescent hosts with high physical and chemical (Jiang *et al* 2004). $Ca_2MgSi_2O_7$: Eu^{2+} , Dy^{3+} , Ce^{3+} are known as an efficient phosphor with good stability, which also shows green emission with great stability and persistency (Yen and Weber 2004). Compared with previously developed aluminate materials, the silicate phosphors have more advantages on chemical stability, heat stability, lower cost, and excellent weather resistance [7, 8]. However, its afterglow intensity and duration are inferior to those of aluminate materials. So, it is necessary to further improve its long-persistence phosphorescence property, with aproper co-dopant. Delocalization of 5d electrons is much easier because the 5d energy state is often positioned near the conduction band. Eu^{2+} and Ce^{3+} are the two most important ions with 4f–5d transitions [9, 10]. Ce^{3+} activated long lasting phosphors have been reported by Jia et al. and Kodama et al. In addition, Ce^{3+} is well known as an efficient sensitizer, and Ce^{3+} to Eu^{2+} transfer is possible. It was reported that through energy transfer from Ce^{3+} to $Eu^{2+}CaS:Eu^{2+}$, Tm^{3+} , Ce^{3+} exhibited higher brightness and longer lasting afterglow than $CaS:Eu^{2+}$, Tm^{3+} [11]. In this paper, Ca2MgSi2O7 : Eu^{2+} , Dy^{3+} , Ce^{3+} phosphors with the different concentration ratios of dopant and co-dopant were prepared using high temperature solid-state reaction. The photoluminescence (PL) studies were done to identify the long lasting phosphor.

II. EXPERIMENTAL

The phosphor sample was prepared by solid state diffusion reaction method. The phosphor Ca2MgSi₂O₇ is prepared from the compounds calcium carbonate (CaCO3) and magnesium oxide (MgO), SiO₂ and CeO₂, Eu₂O₃, Dy₂O₃. The prepared phosphor Ca2MgSi₂O₇ is weighed and grounded into a fine powder using agate mortar and pestle about an hour. The grounded mixture was placed in an alumina crucible and heated from room temperature to 1200^{0} C in a muffle furnace with a heating rate of 5^{0} C/min. After reaching 1200^{0} C the phosphor heated for 3hours and the furnace was allowed to cool to room temperature along with the samples.

The basic reaction is as follows:

 $\label{eq:caCO3} \begin{array}{l} CaCO_3 + MgO + SiO_2 ^* H_2O = Ca2MgSi_2O_7 + 2CO_2 + \\ 2H_2O \end{array}$

III.CHARACTERIZATIONS

The characterizations of prepared phosphors are done using Photoluminescence (PL), SEM and particle size analysis. The photoluminescence spectra were recorded at room temperature using spectroflurophotometermeter (SHIMADZU, RF5301PC) xenon lamp as excitation source. The surface morphology and the particle sizes of the phosphors are observed from SEM.

(A) Scanning Electron Micro- Spectroscopy (SEM):

The morphology of material was determined by using high resolutions microscope. Here scanning electron microscopy (SEM) was used. Fig 1 shows the surface morphologies of the powder sample. The micro structure of the sample reflects the inherent nature of the solid state reaction process. The synthesized sample shows good morphology and connectivity with grains and formation of micro sized prepared sample.







Fig: SEM images of prepared samples (a) Ca2MgSi₂O₇:Dy³⁺ Phosphor (b) Ca2MgSi₂O₇: Ce³⁺ Phosphor (c) Ca2MgSi₂O₇:Eu²⁺ Phosphor

(A)Photoluminescence study:

When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually, these excitations relax and the electrons return to the ground state. If radiative relaxation occurs, the emitted light is called PL [28, 29]. Various important material properties (physical and chemical) of materials by using photons to induce excited electronic states in the material system and analyzing the optical emission as these states relax [30, 31].

Ca2MgSi₂O₇:Eu²⁺ Phosphor

Fig I(a) and fig I(b) shows the PL spectra of Ca2MgSi₂O₇:Eu²⁺ when excited 462nm. The excitation spectrum was observed in the range of 220-400 nm and emission spectra were recorded in the range of 400-650 nm. The excitation broad band due to transitions of 8S7/2 (4f7) ground state to the excited state $4f^{6}5d^{1}$ $[^{8}S7/2 (4f^{7}) 4f^{6}5d^{1}]$ configuration were observed under the ultra violet excitation. The excitation spectrum of the blue fluorescence (kem = 462 nm) shows two broad band's with their peaks at about 267 and 309 nm, respectively, which are due to the crystal field splitting of the Eu²⁺ d orbital. Under the ultra violet excitation of 309 nm, the emission spectrumshows a strong band with a peak at about 460 nm, which corresponds to $4f \rightarrow 5d$ transition of Eu2? ions. The 5d energy level of Eu^{2+} and the lower level of 4f state overlap, so the electron of 4f state can be excited to 5d state. The broad luminescence of Eu²⁺ is due to $4f^{6}5d^{1} \rightarrow 4f^{7}$ transitions. It is known that the blue emission peaked at 462 nm corresponds to the The PL emission spectra of samples were recorded for the excitation wavelength of 462 nm for different concentrations of Eu. The excitation of the Ca2MgSi₂O₇:Eu²⁺ phosphor with 462 nm wavelength generates photoluminescence emission at 237,252 and 267nm, 309 nm with intensities of around 550a.u. transitions of ${}^{4}F9/2 \rightarrow {}^{6}H15/2$ and this emission belongs to hypersensitive transition with J = 2. The prepared Ca2MgSi2O7:Eu²⁺ phosphor would emit blue light with peak at 462 nm [33, 34]. The special emission of Eu3? ions in the emission spectra [special Eu3? emission peak are found at the 590 nm (orange region) and 613 nm (red region)], were not found in Ca2MgSi2O7:Eu²⁺ phosphor, which implies that Eu³⁺ ions have been reduced as Eu²⁺ completly.



Fig 2(a) : Excitation spectra of the sample Ca2MgSi₂O₇:Eu²⁺ (b) Emission spectra of the sample Ca2MgSi₂O₇:Eu²⁺.

Ca2MgSi₂O₇:Dy³⁺ Phosphor

The excitation and emission spectra of Dy^{3+} doped samples are shown in Fig. 2. All the samples with different concentration of Dy^{3+} dopants have similar spectral shape , since both excitation and emission spectra comprise the characteristic lines of Dy^{3+} within 4f⁹ configuration. The emission spectra are composed of two groups of emissions peaking at 481nm and 575nm which can be assigned to the Dy^{3+} 4f transitions of ${}^{4}F_{9/2} - {}^{6}H_{13/2}$ respectively . The excitation spectra consist of a series of lines in the 320 nm – 470nm range with the strongest one at 350 nm and some other lines at 365nm , 387nm , 426nm and 453nm . Due to the dense and overlapped nature of the excitation states in the 4f configuration of Dy^{3+} in the blue spectral range. The whiteness mainly comes from the mixture of





Fig 3(a) : Excitation spectra of the sample $Ca2MgSi_2O_7:Dy^{3+}$ (b) Emission spectra of the sample $Ca2MgSi_2O_7:Dy^{3+}$.

Ca2MgSi₂O₇:Ce³⁺ Phosphor

The excitation and emission spectra are presented in fig. As depicted in fig , Ca2MgSi₂O₇:Ce³⁺ exhibits a broad emission band centered around 381nm. This band results from the 5d¹ to 4f¹ transition configuration of Ce³⁺ ions. The excitation spectra indicate that at least two absorption bands can be observed for Ca2MgSi₂O₇:Ce³⁺ . They are located at about 237nm , 254nm , 267nm and 310nm. The emission intensity of Ca2MgSi₂O₇:Ce³⁺ is much stronger than the other two phosphors Ca2MgSi₂O₇:Cy³⁺ and Ca2MgSi₂O₇:Eu²⁺, which is implying a higher luminescent efficiency of the former. All the samples absorb the ultraviolet (UV) light . Ca2MgSi₂O₇:Eu²⁺ emits blue –green emission.



Fig 4(a) : Excitation spectra of the sample $Ca2MgSi_2O_7:Ce^{3+}$ (b) Emission spectra of the sample $Ca2MgSi_2O_7:Ce^{3+}$.

(B) Chromaticity Diagram (CIE)

The chromaticity coordinates calculated from the emission spectra using the commission international de I'Eclaisage France in short CIE system are (0.30,0.33) for Ca₂MgSi₂O₇:Dy³⁺ (0.4 mol%) . Based on the standard CIE coordinate- color graph fig, we can study that the phosphor emits white light. Similarly. In addition, The CIE coordinates of Ca2MgSi₂O₇:Ce³⁺ is (0.17, 0.04). Based on the standard CIE coordinate color graph fig5, we can observed that this phosphor emit violet light. Luminescence colors of Ca2MgSi₂O₇:Eu²⁺ is placed in (0.179, 0.081). The emission spectrum of the sintered phosphors were converted to the CIE 1931 chromaticity using the photoluminescent data and the interactive CIE software (CIE coordinate calculator) diagram as shown in Fig. 5a–c.



 $\begin{array}{l} \mbox{Fig 5}: Chromaticity \ diagram \ of \ \ (a) \ Ca_2 Mg Si_2 O_7 : Dy^{3+} \\ phosphor \ \ (b) \ Ca2 Mg Si_2 O_7 : Ce^{3+} \ \ phosphor \ \ (\ c) \\ Ca2 Mg Si_2 O_7 : Eu^{2+} \ phosphor \ . \end{array}$

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