

# Investigation of Luminescence Properties of $\text{Eu}^{3+}$ Doped $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$ Phosphor

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**Abstract**— In the present work,  $\text{Eu}^{3+}$  doped  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$  phosphors were synthesized by a combustion technique and their structural and optical properties were investigated. The  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}^{3+}$  was further characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), and photoluminescence excitation and emission spectra (PL). The XRD pattern showed the crystalline nature of the prepared material. Under near-UV excitation (394 nm), the emission spectra were composed of intense bluish-green light emission peaking at 500 nm, yellow-orange light emission peaking at 585 nm, and red light emission peaking at 616nm showing white-light for human eyes. The emission intensity of red light reaches the maximum of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$  doped with 1mol%  $\text{Eu}^{3+}$  while for higher concentration 2 mol%  $\text{Eu}^{3+}$ , the emission intensity of bluish-green reaches the maximum.

**Keywords**—  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$ ; XRD; SEM; White-light; Combustion method; Luminescence.

## I. INTRODUCTION

Light-emitting diodes (LEDs) have recently attracted attention as novel sources for illuminating light. LEDs have several advantages over fluorescent lights, including a longer operating life, better energy efficiency and a mercury-free composition [1]. It is well known that white LEDs are mainly fabricated by combining blue LEDs with a yellow-emitting phosphor (YAG:  $\text{Ce}^{3+}$ ). However, the white light obtained has a poor colour rendering, because the yellow emission of YAG:  $\text{Ce}^{3+}$  lacks any red and blue-green emissions [2–4]. Recently, one solution to this problem has been to fabricate a white LED with high colour rendering by combining red, green and blue-emitting tricolour phosphors with irradiation by a near-UV LED. A more promising approach is to find a material that can produce white emission via the combination of emission in different colours from one kind of luminescence center. The development of white LEDs as a cost-competitive, energy-efficient alternative to conventional electrical lighting is very important for expanding LED applications toward general white lighting [5–7]. Phosphors activated with rare earth metal have been widely investigated in the past few decades on account of their technological importance [8]. In particular, phosphors for LED applications have received significant attention in recent years with the rapid development of white LEDs, which have such merits as high efficiency, long lifetime, and low power consumption [9].

Photoluminescence (PL) of europium has been extensively studied in different hosts [10-14].  $\text{Eu}^{3+}$  exhibits a red or orange luminescence, while  $\text{Eu}^{2+}$  strongly depends on the host and it may emit anywhere from UV to deep red region. Luminescence of  $\text{Eu}^{3+}$  has been used to obtain the red component of the full colour display devices [15-17]. The  $\text{Eu}^{3+}$  activated oxides have been extensively investigated due to their applications as red lamp phosphors [18, 19]. Silicates doped with rare earth ions have received great attention because of their potential applications in optical and laser devices.

In fact, silicates are also good hosts for the development of phosphors due to their suitable energy band structure, high chemical stability, easy preparation and low cost. In recent years, rare earth doped silicate phosphors, such as  $\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Dy}^{3+}$  [20],  $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Dy}^{3+}$  [21],  $\text{Ca}_3\text{Si}_2\text{O}_7$  [22] have been developed as the promising phosphors for white LEDs. It is interesting to develop novel materials in which the  $\text{Eu}^{3+}$  ion provides efficient emission on low-energy excitation. In this study, we describe the synthesis and fluorescence properties concerning the 5d–4f luminescence of the  $\text{Eu}^{3+}$  ion in novel complex silicate phosphors  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$ .

## II. MATERIALS AND METHOD

The powder phosphors  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}^{3+}$  was prepared by a combustion method. The following precursors: strontium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and lithium nitrate ( $\text{Li}(\text{NO}_3) \cdot \text{H}_2\text{O}$ ), europium nitrate ( $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), ammonium nitrate ( $\text{NH}_4(\text{NO}_3) \cdot \text{H}_2\text{O}$ ), silicon dioxide ( $\text{SiO}_2$ ) and urea ( $\text{CO}(\text{NH}_2)_2$ ) all in analytical purity were weighed according to the stoichiometric. The precursors were mixed and milled using a mortar and pestle, and a thick white paste was formed from water of crystallization present in the metal nitrates. The resulting paste was heated at  $500^\circ\text{C}$  in a muffle furnace. The process being highly exothermic and the liberated gases swell the mixture into large volume. The paste melted, under dehydration, and finally decomposed with the evolution of gases (oxides of nitrogen and ammonia). The mixture frothed and swelled, forming the foam that ruptured with a flame and glowed to incandescence. The voluminous combustion ash of the resulting  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}^{3+}$  was grounded to make fine powders. The obtained phosphor powders were annealed in air at  $850^\circ\text{C}$  for 2h. The influence of the initiating and annealing temperatures on the structural and the luminescent properties of the phosphors were investigated.

The structural evolution on heat treatment of the phosphor was studied using spectroscopic techniques. The XRD technique was used in order to identify the product and check their crystallinity. The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using a PAN-analytical diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5405 \text{ \AA}$ ) operating at 40Kv, 30mA. The photoluminescence (PL) excitation and emission spectra of the samples were recorded at room temperature by using a RF-5301PC SHIMADZU Spectrofluorophotometer (RF-5301 PC). Powder morphology was studied using SEM at STIC, Kochi, India (JEOL JSM-6390LV).

## III. RESULTS AND DISCUSSION

### A. Phase identification and morphology

In order to confirm the formation of the compound, X-ray diffraction pattern of the prepared samples were taken at room temperature, as shown in Fig. 1. The slow scan was performed in the  $2\theta$  range from  $10\text{--}80^\circ\text{A}$  with a scan step of 0.011. The average grain size can be estimated from the observed line broadening. Assuming that the particles are stress free, the size can be estimated from a single diffraction peak using Scherer's equation:  $D = 0.9 \lambda / \beta \cos(\theta)$ , where,  $D$  is the average grain size of the crystallites,  $\lambda$  is the wavelength of the incident X-rays,  $\theta$  be the Bragg angle and  $\beta$  is the diffracted full-width at half-maximum (in radian) caused by the crystallites. Using the XRD pattern, the average grain size of the concerned compound was calculated to be approximately  $1.2 \mu\text{m}$ . The sample produced well defined X-ray diffraction lines that confirm its crystalline nature. However for recorded XRD patterns no matching files are seen in the JCPDS library.

The particle size of the  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$  powder samples were determined by SEM as shown in Fig.2. The sample synthesized through combustion route, agglomerated and irregular structures with other fluffy shapes is obtained with non-uniform distribution (Fig.2). Although a small amount of particles can be observed occasionally in the figure, the interweaving particles are agglomerated so that the separate particles are not seen in the SEM image. In all these photographs the particles show the slightly bigger grains consist of tightly packed smaller particles.

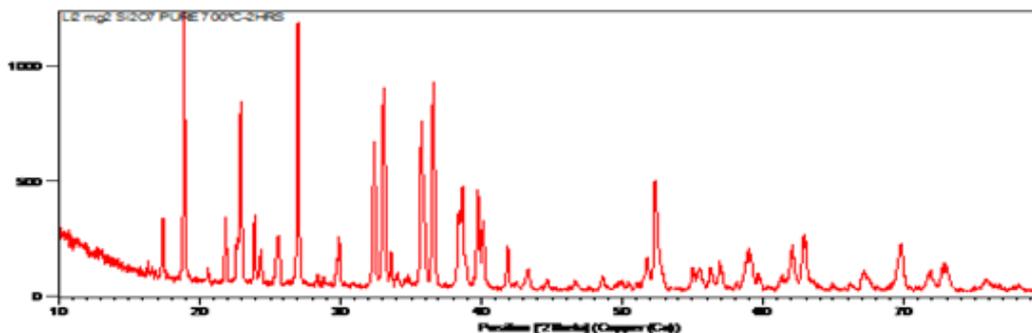


Fig.1 Powder XRD pattern of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}$  (1 mol%).

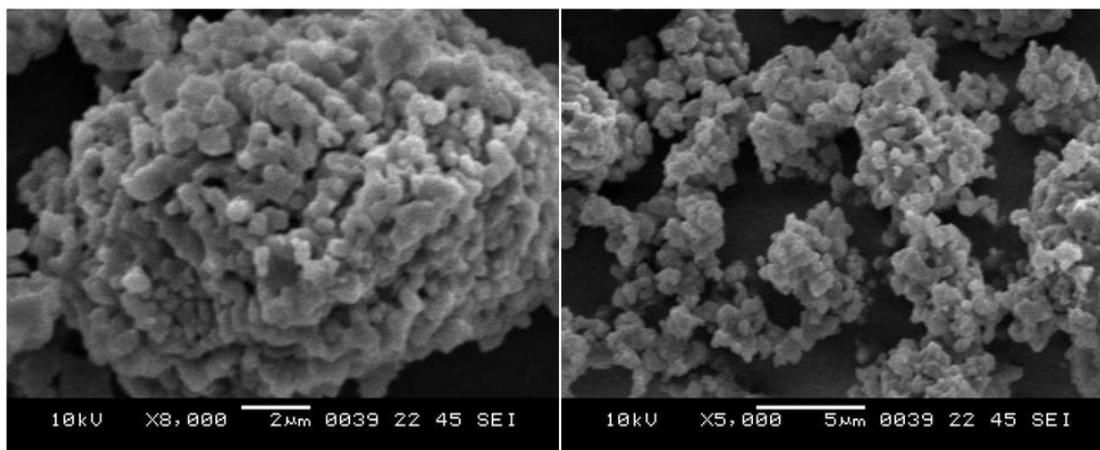


Fig. 2 SEM photographs of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}$  (1 mol%).

### B. Photoluminescence studies

PL spectra are useful in identifying the valence state of the Eu ion.  $\text{Eu}^{3+}$  or  $\text{Eu}^{2+}$  can be identified from the characteristic photoluminescence they exhibit. f-f transitions of  $\text{Eu}^{3+}$  are forbidden and  $\text{Eu}^{3+}$  PL is in general weak, unless there is excitation by charge transfer or energy transfer from a sensitizer. Figure 3 shows the PL emission spectra of  $\text{Eu}^{3+}$  ions in  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$  phosphor with different concentrations under the excitation 394 nm wavelengths of light. Two well resolved peaks are observed around 594 and 616 nm, which is assigned to due to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of  $\text{Eu}^{3+}$  ion. The emission spectra for the  $\text{Eu}^{3+}$  doped samples are composed of the broad emission band of host and the characteristic emission lines of  $\text{Eu}^{3+}$  with  $^5\text{D}_0$  configuration. A broadband is obtained in a large range of 450 - 570nm, peaking at about 500 nm in bluish green colour which is assigned to  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition of  $\text{Eu}^{2+}$  ion. The 594 nm line due to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  splits up into three components at 580, 587 and 594 nm (yellow-orange). The intensity of 594 nm line is very weak as compared to that of 616nm (red colour) line. The intensity of 616 nm line is two and half times more than 594nm line. The 616 nm lines due to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  also split up into two components at 616 and 627 nm. The splitting of energy levels depends on the relative contents of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$  and  $\text{Mg}_2\text{SiO}_4$  in fired powder. The maximum intensity of  $\text{Eu}^{3+}$  is observed at 1 mol% while it is at 2 mol% for  $\text{Eu}^{2+}$  in the host lattice. Variation in PL intensity with the different concentration of  $\text{Eu}^{3+}$  ion is shown in Fig.4. Excitation spectrum of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}^{3+}$  (1 mol %) shows three lines at 362, 383 and 394 nm, monitored at 616 nm. The emission spectra for 362 and 383 nm excitations are not shown here. It is thus seen that the sample contains Eu in trivalent as well as divalent form in this phosphor.  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$  exhibits both line and band emissions. Position of emission band of  $\text{Eu}^{2+}$  depends on red shift, which results from combination of crystal field and centroid shift [23].

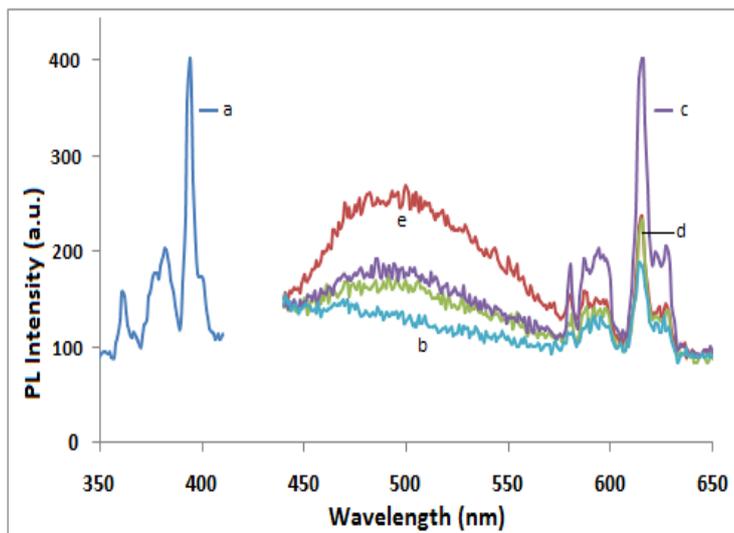


Fig. 3 PL Excitation ( $\lambda_{\text{emi}} = 616\text{nm}$ ) (a) and Emission spectra of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: x \text{Eu}^{3+}$  ( $\lambda_{\text{ext}} = 394\text{nm}$ ). b) 0.5, c) 1.0, d) 1.5 and d) 2.0 mol%.

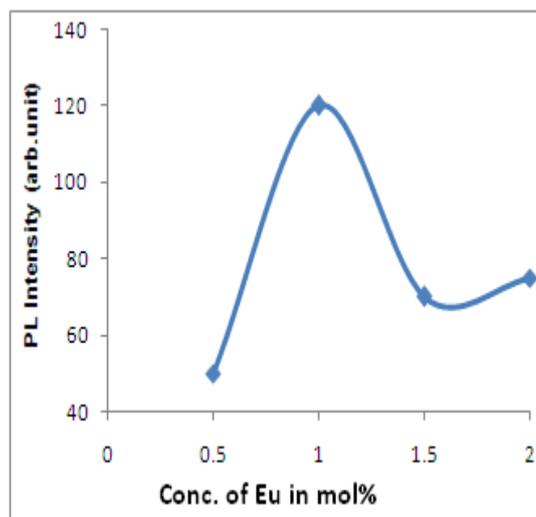


Fig.. 4 Effect of concentrations of  $\text{Eu}^{3+}$  ion on PL intensity of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: x \text{Eu}^{3+}$

The emission in the vicinity of 600 nm is due to the magnetic dipole transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ , which is insensitive to the site symmetry. The emission around 610 – 630 nm is due to the electric dipole transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ , induced by the lack of inversion symmetry at the  $\text{Eu}^{3+}$  site, is more stronger than that of the transition to the  ${}^7\text{F}_1$  state. Luminescence of  $\text{Eu}^{3+}$  ions in commercial red phosphors such as  $\text{YVO}_4$ ,  $\text{Y}_2\text{O}_3$  and  $\text{Y}_2\text{O}_2\text{S}$ , occupy the site that has no inversion of symmetry. The strong emission due to the electric dipole transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) in the materials is utilized for practical applications. Thus entire characteristics indicate that  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}^{3+}$  phosphor is a good candidate for white lighting devices applications.

#### IV. CONCLUSIONS

$\text{Eu}$  doped  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$  novel phosphor was synthesized by combustion process.  $\text{Eu}^{3+}$  emission lines are obtained at 594 and 616 nm along with a broad band peaking at 500nm. Both the peaks 594 and 616 nm, split due to crystal field and splitting depends upon the firing temperature. Emission of  $\text{Eu}^{3+}$  was found to be particularly useful as a red emitting lamp phosphor as it has good sensitivity and is quite well Hg free emission. Strong position of  $\text{Eu}^{3+}$  peak (616 nm) indicates that  $\text{Eu}^{3+}$  ions are mostly present at the site of centre of symmetry of crystal lattice.  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}^{3+}$  phosphors generate white light composed a blue band and a yellow emission band. With proper molar ratio of  $\text{Eu}$  concentration with the host  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7$ , warm white light can be generated. These results prove the potential of  $\text{Li}_2\text{Mg}_2\text{Si}_2\text{O}_7: \text{Eu}^{3+}$  phosphor candidate for multi-colors composed white LEDs.

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