

The Investigation of Structural and Photo-luminescent Properties of $\text{SrMgSiO}_4:\text{Eu}^{3+}$ Red Emitting Phosphor

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ABSTRACT

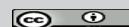
In this article, $\text{SrMgSiO}_4:\text{Eu}^{3+}$ red emitting phosphors were synthesized with different concentrations of Eu^{3+} ions by using solid state synthesis approach. The structure, morphology and luminescent properties of the phosphors were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and photoluminescence (PL) spectroscopy. The XRD analysis revealed that addition of dopant increased the crystallinity of the samples. The SEM images showed the samples have irregular in shapes. The photoluminescence emission spectra of prepared $\text{SrMgSiO}_4:\text{Eu}^{3+}$ phosphor was observed at 394 nm excitation wavelength. The optimum concentration of the dopant having highest luminescence intensity is found to be 0.5 mol %. The obtained PL results indicated that prepared phosphor is suitable as red phosphors for white LEDs.

Keywords: XRD, Photoluminescence, $\text{SrMgSiO}_4:\text{Eu}^{3+}$ phosphors, CIE coordinates

Since nineteenth century, inorganic phosphor materials have been serving as potential candidates in the field of lighting and display devices. Various types of phosphors were synthesized knowingly for different applications^[1-3]. Phosphors have been playing an essential role in phosphor converted LED (pcLED) technology to produce white light. Since phosphors efficiently yield the white light through proper colour combination in pcLEDs system which is now used in modern lighting technology. To accomplish good colour purity in pcLED devices phosphors with narrow band red emission are essential. At present, the wavelength conversion materials are still very important in the solid-state lighting revolution just like what they did in the fluorescent lamps before^[4]. The lanthanide ion Eu^{3+} is an effective luminescent center which exhibits intense red emission as a result of 4f-4f transition by occupying proper site symmetry in

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various host matrices. Further, Eu^{3+} is an excellent probe to analyze the site symmetry in host matrix. It has been incorporated in a variety of hosts such as $\text{LiAl}_5\text{O}_8:\text{Eu}^{3+[5]}$, $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{3+[6]}$, $\text{NaBaBO}_3:\text{Eu}^{3+[7]}$ to emit an intense red light which coming from $^5\text{D}_0-^7\text{F}_2$ transition. In this paper, we have reported the light emitting phosphors SrMgSiO_4 with different concentration of Eu^{3+} ions, synthesized by the well-known solid state reaction (SSR) method. The structural, morphological and luminescence properties of prepared phosphors doped with Eu^{3+} ions are also investigated and explained.

MATERIALS AND METHODS

The phosphors SrMgSiO_4 doped with Eu^{3+} ions were investigated in this work synthesized at a high temperature using conventional solid-state reaction method. SrCO_3 , MgO , SiO_2 and Eu_2O_3 were used as raw materials for preparation of the samples. The raw materials taken in appropriate stoichiometric ratios were ground manually for 1 hr in a mortar and pestle followed by sintering at 1050°C for 5 h. Boric acid (1 mol%) is mixed as a flux in the sample. The heating and the cooling rates were kept at $10^\circ\text{C}/\text{min}$. To show the effect of dopant concentration on structural and luminescent properties of prepared phosphors, different molar concentration of Eu^{3+} ions were mixed with SrMgSiO_4 . The phase purity of prepared samples was ascertained using a PANalytical X-ray diffractometer (Cu $\text{K}\alpha$ radiation $\lambda = 0.15406 \text{ nm}$) operated at 40 KV and 30 mA. The scanning was done in the range: $10^\circ < 2\theta < 80^\circ$. The surface morphology and size of particles were studied using a German make (Model: ZEISS-EVO 60 m) scanning electron microscope (SEM). For the verification of elemental composition, an Oxford Inca energy dispersive X-ray (EDX) spectrometer coupled with SEM was employed. The chemical bonding behavior of sample was analyzed using IR spectra measured with FTIR – 6300 spectrometer equipped with NRS-3300 laser (Jasco, Japan). The photoluminescence excitation (PLE) and photoluminescence (PL) spectra were recorded on RF-5301 PC spectrofluorophotometer (Shimadzu, Japan) with a Xe lamp as an exciting source. Time-resolved measurements (fluorescence decay times) were observed by using pico second time resolved (PSTR) fluorimeter (Make: Eddinburg Instruments, Model: Lifespec II).

RESULTS AND DISCUSSION

Structural analysis

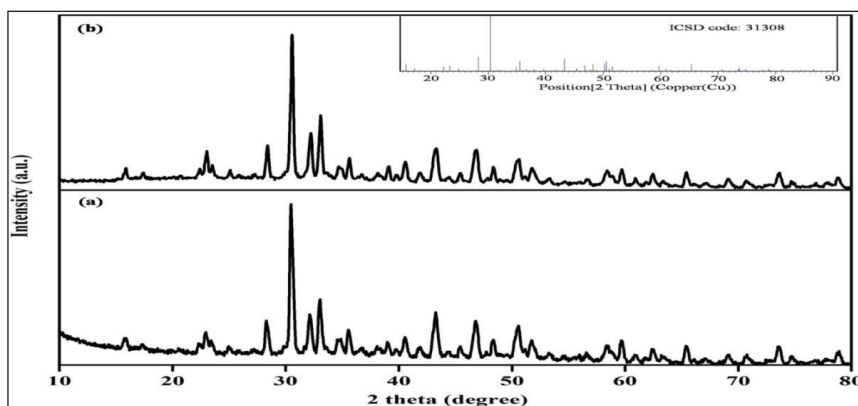


Fig. 1: XRD patterns of (a) undoped and (b) $\text{SrMgSiO}_4:\text{Eu}^{3+}$ (0.5 mol%) phosphors

Fig. 1 represents the XRD patterns of the prepared powder samples of un-doped and SrMgSiO₄:Eu³⁺ (0.5 mol %). A small quantity of the doped Eu³⁺ ions in the crystal does not affect the crystal purity and structure. The patterns were compared with those of the standard ICSD collection code: 31308 and it is well matched. The additional diffraction peaks of the Akermanite (silicates) impurity phases were also observed. Crystal structure refinement of the recorded XRD pattern was performed and was done considering the tetra-gonal unit cell and space group P-421/m. The refined lattice parameters were found as $a = b = 7.9960 \text{ \AA}$, $c = 5.1520 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and cell volume $V = 329.40 \text{ \AA}^3$ and calculated density = 3.71 g/cm^3 .

Fig. 2 depicts the SEM images of the un-doped SrMgSiO₄ and SrMgSiO₄:Eu³⁺ phosphors at magnification of 2.00 K \times . The images evidently indicate the presence of irregularly sized and shaped grains. The distribution of grain size is wide shown in Fig. 2. The smooth and shiny layer of the grains is investigative of the melting morphology fashioned by a solid state reaction at very high temperature.

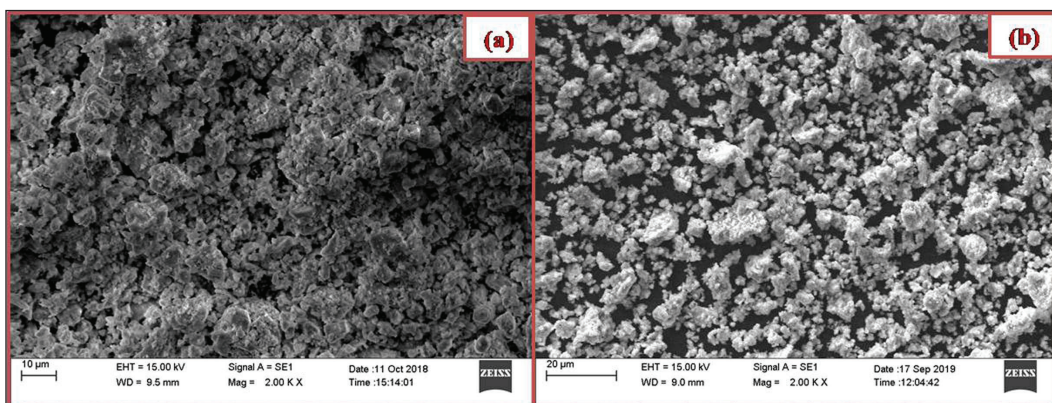


Fig. 2: SEM images of (a) un-doped and (b) SrMgSiO₄:Eu³⁺ (0.5 mol %) phosphors

Elemental diffraction spectroscopy (EDS) is used to analyze the chemical composition of the of the ingredient elements. Fig. 3 demonstrates the EDS patterns of the un-doped SrMgSiO₄ and SrMgSiO₄:Eu³⁺ phosphors. The EDS spectra illustrate strong peak of Sr, Mg, Si and O elements, along with the infinitesimal peak of dopant Eu³⁺ ions. The peaks corresponding to dopant Eu³⁺ ions in synthesized phosphors indicate that the successfully inclusion of Eu³⁺ ions in SrMgSiO₄ host matrix.

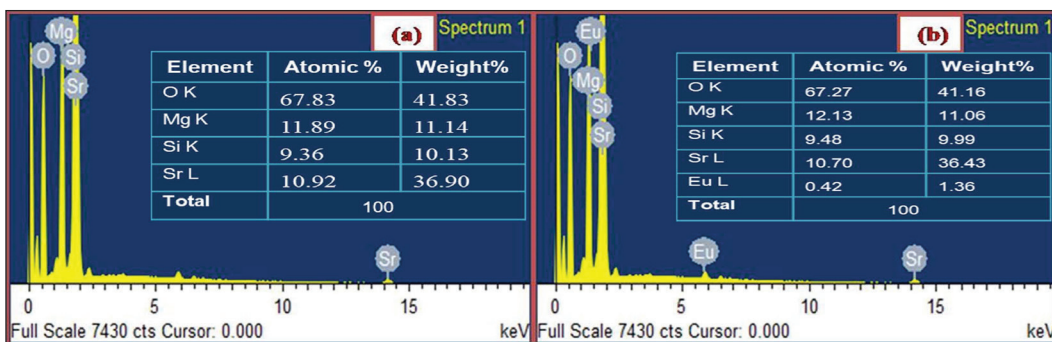


Fig. 3: EDX patterns of (a) un-doped (b) Eu³⁺ doped SrMgSiO₄ phosphors

The FTIR spectrum observed for the $\text{SrMgSiO}_4: \text{Eu}^{3+}$ (0.5 mol%) phosphors are demonstrated in Fig. 4. The FTIR spectrum reveals the positions of ions existing within the crystal lattice by their vibrations. The FTIR spectrum of Eu^{3+} ions doped SrMgSiO_4 phosphors was recorded in the frequency range of 4000 cm^{-1} and 400 cm^{-1} at room temperature. FTIR spectra supported the formation of a silicates structure by forming band at around 467 cm^{-1} . The characteristic band at 1008 cm^{-1} are owing to the Si-O-Si asymmetric stretching vibrational modes. Eu^{3+} ion is expected to replace Sr^{2+} site in the tetragonal structure of SrMgSiO_4 host matrix as the ionic radii of the Sr^{2+} (0.126 nm) and Eu^{3+} (0.112 nm) are almost same. During the formation of phosphor dopant Eu^{3+} ions might create distortion in host matrix resulting peak at 1400 cm^{-1} due to Sr^{2+} vibrations. A small peak originated at 1645 cm^{-1} corresponds to vibration modes assigned to Mg^{2+} ions^[8, 9].

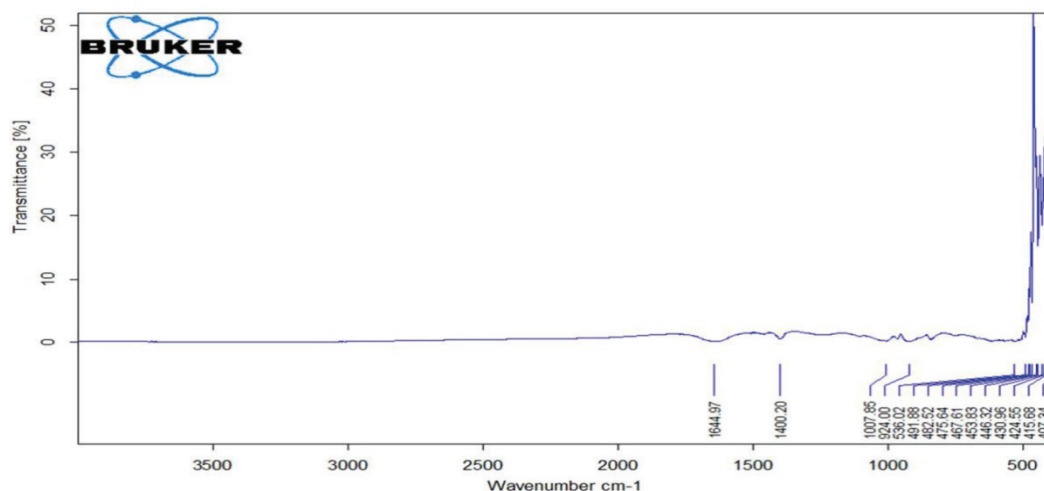


Fig. 4: FTIR spectrum of $\text{SrMgSiO}_4: \text{Eu}^{3+}$ (0.5 mol%) phosphor

Luminescent characteristics

The PL excitation and emission spectra of Eu^{3+} activated SrMgSiO_4 phosphors are represented in Fig. 5 and 6, respectively. In accordance with Fig. 5, the excitation spectrum comprises of four illustrious characteristic peaks centered at 343, 363, 382 and 394 nm which are all attributed to the intra-configurationally $4f-4f$ transitions of Eu^{3+} ions in this host lattice^[10]. The most high up peak is located at 394 nm which corresponds to the transitions ${}^6\text{H}_{15/2} \rightarrow {}^4\text{G}_{11/2}$. The emission spectra of Eu^{3+} doped SrMgSiO_4 phosphor were recorded under the excitation wavelength of 394 nm. It reveals two distinctive emission bands peaking at 594 nm and 616 nm which is coming from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electronic transitions of Eu^{3+} ions, respectively. The intense emission peak located at 616 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) is ascribed to the hyper-sensitive forced electric dipole (ED) transitions of Eu^{3+} which give the red colour in the display signals^[11, 12]. With the increasing of dopant concentration of Eu^{3+} ions, the electric dipole transition (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) is much stronger than that of the emission peak at 594 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) which is ascribed to magnetic dipole (MD) transitions^[13]. It is also observed that the PL intensity increases steadily with the increasing upto 0.5 mol% of dopant concentration of Eu^{3+} and beyond this concentration PL intensity starts diminishing. The drop in PL intensity is most probably due to concentration quenching. The highest PL

intensity under 394 nm excitation was obtained at 0.5 mol% of Eu³⁺ ions, as shown in Fig. 7. Further, the luminescence decay profile for the emission at 612 nm of Eu³⁺ in SrMgSiO₄: Eu³⁺ (0.5 mol%) phosphor is displayed in Fig. 8. The decay curve can be well fitted to a double-exponential function and decay times were calculated as 28.56 ns and 3308 ns, respectively

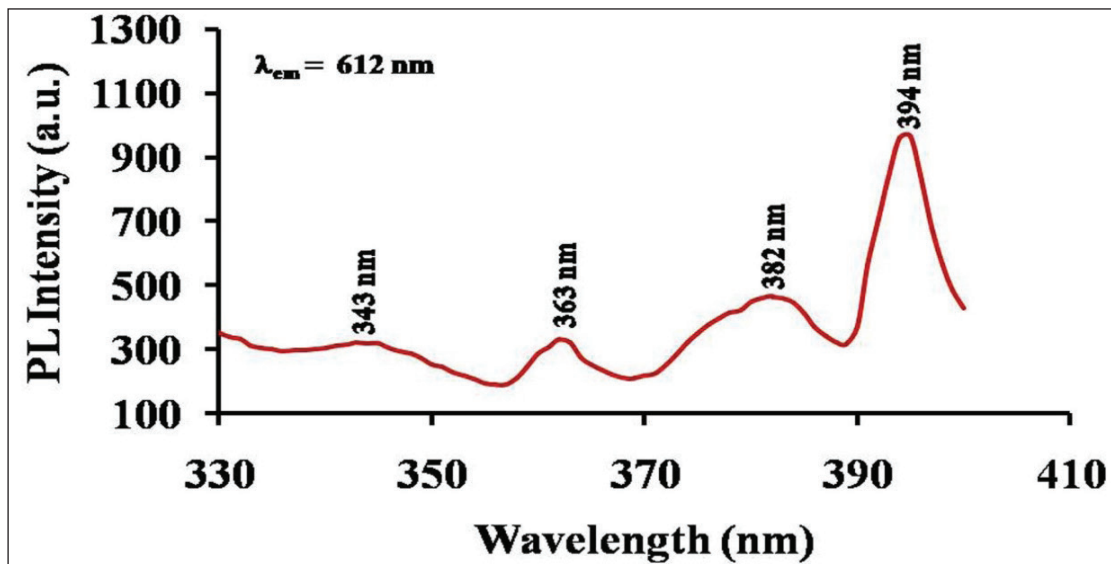


Fig. 5: PL excitation spectrum of SrMgSiO₄: Eu³⁺ (0.5 mol %) phosphor

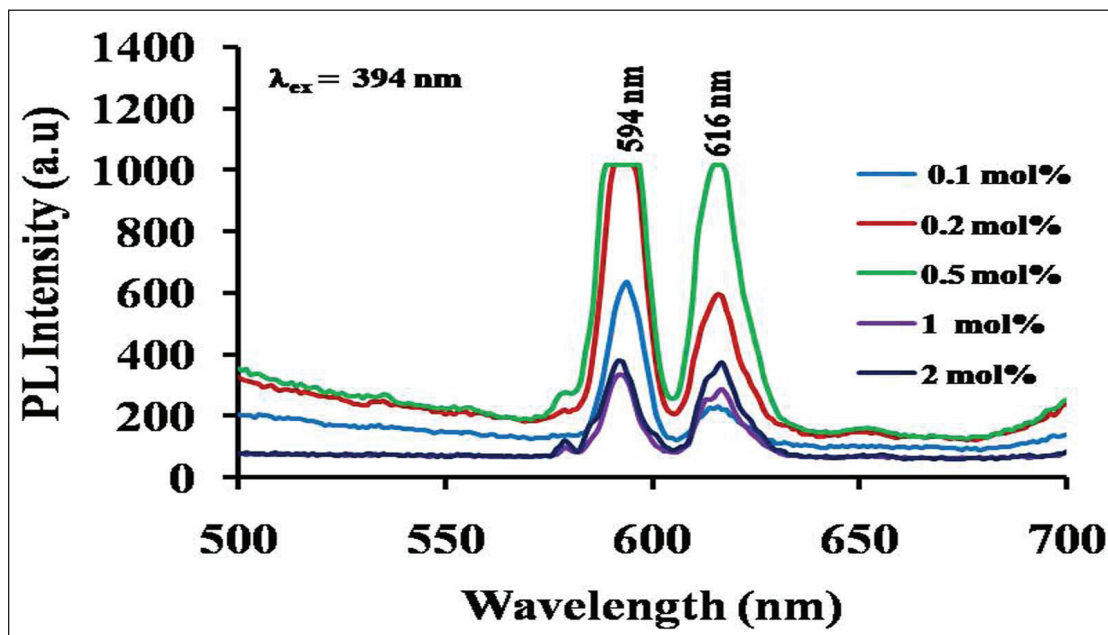


Fig. 6: PL emission spectra of SrMgSiO₄: Eu³⁺ phosphors

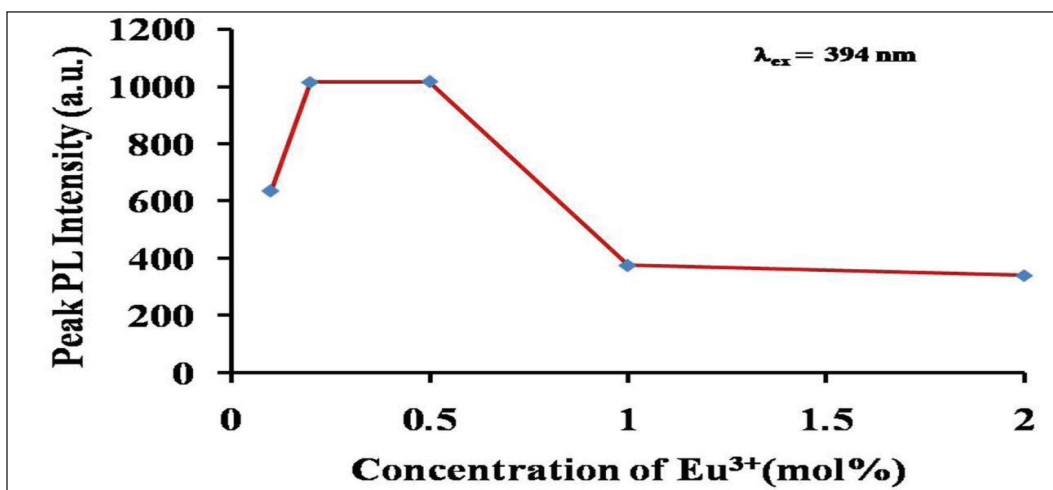


Fig. 7: Dependence of PL intensity on Eu^{3+} ions in $\text{SrMgSiO}_4:\text{Eu}^{3+}$ phosphor

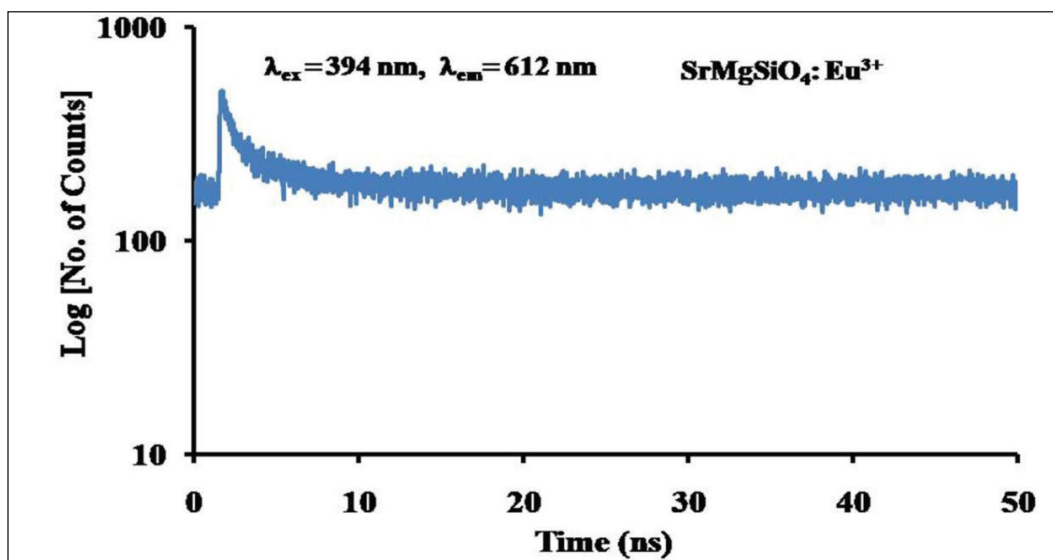


Fig. 8: Decay profile of $\text{SrMgSiO}_4:\text{Eu}^{3+}$ (0.5 mol %) phosphor

CIE chromaticity co-ordinates

In general, the colour of any light source can be represented on the (x, y) coordinate in this colour space. The CIE coordinates (x, y) was calculated to realize the effectiveness of the photoluminescence results of $\text{SrMgSiO}_4:\text{Eu}^{3+}$ phosphor, in the view of CIE chromaticity diagram as shown in Fig. 9. The chromaticity co-ordinates x and y were originated to be as $(x = 0.3584; y = 0.2937)$ for $\text{SrMgSiO}_4:\text{Eu}^{3+}$ phosphor, which falls into sunset cool white region. CIE 1931 chromaticity coordinates of synthesized phosphors

are acceptable for many optical device applications^[14].

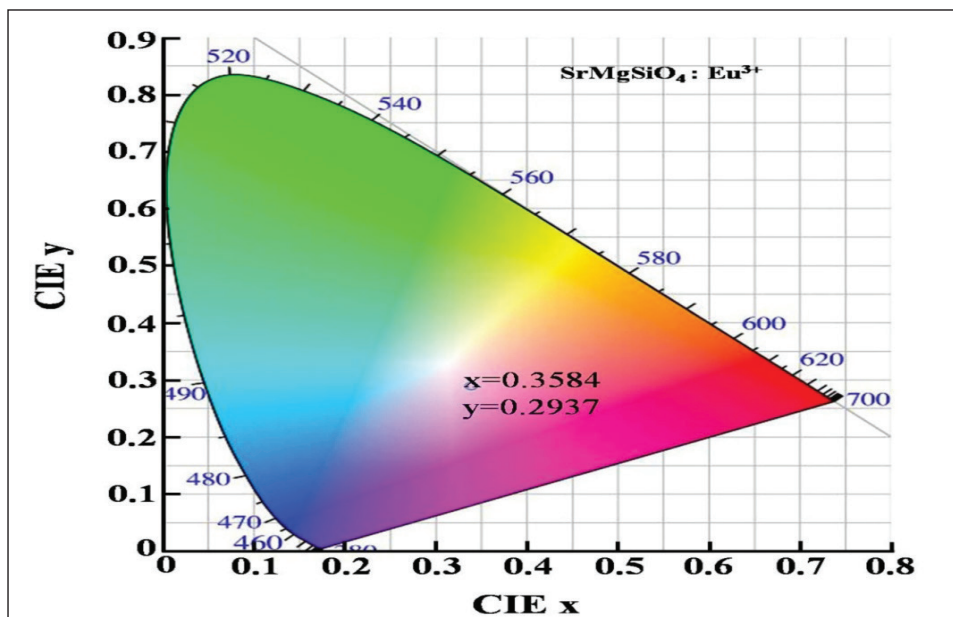


Fig. 9: CIE diagram of $\text{SrMgSiO}_4:\text{Eu}^{3+}$ (0.5 mol%) phosphor

CONCLUSION

In the present study, a novel Eu^{3+} activated SrMgSiO_4 phosphors have been successfully synthesized by SSR method. The structural properties of prepared phosphors $\text{SrMgSiO}_4:\text{Eu}^{3+}$ are analyzed by XRD, SEM, EDX and FTIR spectra. Luminescent properties of the phosphors are established by photoluminescence and decay profile techniques. The formation, phase purity and structure of prepared phosphor are confirmed by the XRD analysis. The SEM analysis describes surface morphology and average grain size in micrometer scale. The atomic and weight percentage of elements of prepared phosphors are confirmed by EDX measurement. The strong PL emission at 616 nm for the excitation of 394 nm is observed in phosphors. The result also indicates the concentration quenching was occurred at 0.5 mol%. The CIE coordinates of $\text{SrMgSiO}_4:\text{Eu}^{3+}$ (0.5 mol%) phosphor was computed to be ($x = 0.3584$; $y = 0.2937$) which falls into sunset red region. The entire results indicate that prepared phosphor appears to be a promising red components for white light emitting diodes.

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