

Synthesis and Photoluminescence properties of Sm^{3+} doped $\text{Sr}_2\text{MgSi}_2\text{O}_7$

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Abstract: The phosphors $\text{Sr}_{2-x}\text{MgSi}_2\text{O}_7:x\text{Sm}^{3+}$ ($x = 0.005, 0.01, 0.03, 0.05, 0.07$) were prepared by simple, time saving, economically modified solution combustion method using urea as fuel. XRD analysis confirms the phase formation of the phosphor. The spectral properties of the $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Sm}^{3+}$ were studied under near UV and electron excitation. The excitation spectra consists of a group of sharp transitions around 340–420 nm with a prominent peak at 403 nm. From the excitation spectra it is clear that phosphor could efficiently be excited by near-ultraviolet LEDs (375–405 nm). The emission spectra recorded at excitation wavelength 403 nm contains characteristic emission lines of Sm^{3+} ion at 567 nm and 600 nm (dominant one), due to transition from the excited state $^4G_{5/2}$ to the 6H_j ($j = 5/2, 7/2$) of Sm^{3+} ion. The optimal Sm^{3+} ion concentration was determined as $x = 1$ mole %. In our phosphor quenching behaviour is due to energy transfer among the nearest neighbour ions. The colour coordinates (0.526, 0.472) for PL from the CIE diagram corresponds to the shade of yellow-orange emission of the Sm^{3+} ion. Therefore, it is clearly a capable orange-red emitting phosphor for the yellow gap light emitting diodes.

Keywords: Photoluminescence, combustion route, concentration quenching

I. Introduction:

Recently, silicate-based phosphors have attracted much attention because of their many advantages compared with sulphide and aluminates phosphors [1–6], such as water resistance and colour variety. Additionally, the silicate host possesses chemical and physical stability, easy preparation and low cost. Therefore, the silicate host is of great interest for materials scientists in the application of long-afterglow phosphors as well as for phosphors for phosphor covered LEDs.

Luminescence of Eu^{2+} -doped alkaline earth silicates were studied as early as in Smith's work on $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$ in 1949 [7]. Later, Blasé reported luminescence from $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, $\text{Ba}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ and $\text{BaSrMgSi}_2\text{O}_7:\text{Eu}^{2+}$ [8, 9]. Barry reported luminescence from $\text{M}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ ($\text{M}=\text{Ca}, \text{Ba}, \text{Sr}$) and $\text{BaMg}_2\text{Si}_2\text{O}_7:\text{Eu}^{2+}$ [10–12]. Luminescence of $\text{CaMgSi}_2\text{O}_6:\text{Eu}^{2+}$ and $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ co-doped with and without Mn^{2+} was investigated by Lehman, and energy transfer from Eu^{2+} to Mn^{2+} was observed [13]. Solid-state lighting (SSL) has the potential to substantially improve energy efficiency in lighting [14–17]. The function of a phosphor in light emitting diodes (LEDs) for SSL is to absorb the primary ultraviolet (UV) or blue-emission from the LED chips and convert it into visible light. For this application, silicate-based phosphors activated with Eu^{2+} are very suitable [18, 19]. Recently Sm^{3+} doped orange-red phosphors are reported [20].

Generally, alkali-earth silicate phosphors were synthesized by solid-state reaction. $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, Er^{3+} [21], $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ [22], $\text{Sr}_{2-x}\text{Ca}_x\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x = 0, 1$) [23], $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ [24], $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ [25]. The synthetic temperature of such a method was high and the unreacted phases were appeared. Modified SSR method is also implemented which is quiet time consuming [26]. The said host is also prepared by combustion synthesis where ammonium nitrate and excess urea is used [27, 28].

We synthesized $\text{Sr}_2\text{MgSi}_2\text{O}_7$ doped with Sm^{3+} by time saving, low cost, low temperature, solution combustion method without ammonium nitrate.

II. Experimental

$\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Sm}^{3+}$ was prepared by the modified solution combustion synthesis method. The synthesis is based on the exothermic reaction between the fuel (urea) and oxidiser (metal nitrates). During this synthesis, the stoichiometric amounts of high purity starting materials, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (A.R.), $\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (A.R.), SiO_2 (A.R.), $\text{CO}(\text{NH}_2)_2$ (G.R.), HNO_3 and Samarium Nitrate were mixed thoroughly in agate mortar for about 5 minutes, so that the paste was formed. The prepared paste was kept in heating menthol till we got a clear and completely dissolved solution. As prepared solution was then transferred into the pre-heated furnace (700 °C) after warming it for 5 minutes the self heat generating redox reaction was completed and the fine powder of phosphor was finally obtained. This raw powder was sintered for 4 hrs in air at 1000°C and quenched to room temperature. During the combustion synthesis proper molar ratios of fuel and oxidizers depending on the moles

of precursors are very necessary for evacuation of unwanted various molecules so that fine powders of required product could be finally obtained.

The samples were subjected to XRD analysis using an X' Pert PRO advanced automatic diffractometer with Cu K α radiation ($\lambda = 1.540598 \text{ \AA}$) operated at 40 kV and 30 mA. The XRD data was collected in a 2θ range from 10^0 to 100^0 at room temperature. The measurements of photoluminescence (PL) over the range of 550–620 nm and photoluminescence excitation spectra (PLE) over 340–450 nm excitation range were carried out on Hitachi-F-7000 FL Spectrophotometer at room temperature. The spectral resolution of both excitation and emission spectra, width of the monochromatic slit was 1 nm, as well the measurement conditions such as PMT detector sensitivity and scan speed were kept constant from sample to sample in measurements.

The colour chromaticity coordinates were obtained according to Commission International de l'Éclairage (CIE) using Radiant Imaging colour calculator.

III. Results and discussion

3.1 XRD analysis

XRD patterns of the sample sintered at 1000 °C are shown in Fig.1. All the peaks can be indexed to Sr₂MgSi₂O₇ phase according to PDF 75-1736, which indicates that single-phase phosphor, was obtained, and the doped Sm³⁺ did not change the host crystal lattice. Sr₂MgSi₂O₇ has the tetragonal structure with P-421m (113) space group. The unit cell volume and lattice parameters of the matrix are 329.40 Å³, a=7.996 Å, b=7.996 Å, c=5.152 Å [29].

Fig.1: XRD pattern of Sr₂MgSi₂O₇

3.2 Photoluminescence

Fig.2 shows the room-temperature PL excitation and Fig.3 shows PL emission spectra of the Sr₂MgSi₂O₇:Sm³⁺. The excitation spectra consists of a group of sharp transitions around 340–420 nm with a prominent peak at 403 nm. From the excitation spectra it is clear that phosphor could efficiently be excited by near-ultraviolet LEDs (375–405 nm). The emission spectra recorded at excitation wavelength 403 nm contains characteristic emission lines of Sm³⁺ ion at 567 nm and 600 nm (dominant one), due to transition from the excited state ⁴G_{5/2} to the ⁶H_j (j = 5/2, 7/2) respectively. Therefore, it is clearly a capable orange–red emitting phosphor for the ‘yellow gap’ LEDs as mentioned previously [30]. The transitions of the Sm³⁺ ion are shown in fig.4 which reveals the probable transitions involved in this process. The interaction of Sr₂MgSi₂O₇:Sm³⁺ phosphor with different exciting wavelengths 403, 375, 360, 345 nm, leads to the transition of Sm³⁺ ions from the ground level ⁶H_{5/2} to the higher levels ⁴K_{11/2}, ⁴D_{5/2}, ⁴F_{9/2}, ³H_{7/2}, respectively. The Sm³⁺ ions from the higher states make non-radiative transition up to ⁴G_{5/2} level after that the transitions are radiative, as the energy gap between ⁴G_{5/2} and ⁶H_j (j = 5/2, 7/2, 9/2, 11/2) states is sufficient to give yellow-orange emission. To optimize the molar concentration of the Sm³⁺ ion, a series of samples were measured.

Fig.2: PL excitation at 600nm emission wavelength

Fig.3: PL emission at 404nm excitation wavelength

Fig.4: Energy level diagram of the Sm³⁺ ion in the Sr₂MgSi₂O₇ host lattice.

3.3 Concentration quenching properties

From fig.5, the PL intensity starts decreasing as the Sm³⁺ molar fraction increases beyond 1 mol%. Therefore, the optimal molar concentration was at $x = 0.01$. The decrease in intensity shows the occurrence of energy migration among Sm³⁺ ions at different sites in the lattice, resulting in concentration quenching. The probability of energy transfer between two activators is inversely proportional to the nth power of the distance between the activator ions. Thus, the probabilities of energy transfer increase with the increase in concentration of Sm³⁺ as the distance between the Sm³⁺ ions become small. Blasé suggested that the critical energy transfer distance (R_c) can be approximated by using equation(1) [31]:

$$R_c = 2 \left[\frac{3V}{4\pi x_c N} \right]^{1/3} \quad (1)$$

Where x_c is the optimal concentration, V is the volume of the unit cell, N is the number of cations in the unit cell. By taking the values of x_c , V and N to be 0.01, 329.4 Å³, 4 respectively, the critical energy transfer distance is approximated to be 25.05 Å.

The non-radiative energy transfer process between the Sm³⁺ ions may be described by three different methods: exchange interaction, radiation re-absorption or the multipolar interaction [32]. The exchange interaction is generally responsible for the energy transfer for the forbidden transition and the critical distance is about 5 Å. The second method (radiation reabsorption) comes into effect only when there is an overlap between the emission and the excitation spectra of the sensitizer and the activator, respectively. In the present study, the first two processes are not applicable. Therefore, the energy transfer process should be controlled by the

multipolar interaction. According to Dexter's theory [33], if the multipolar interaction occurs between the same activators, then the multipolar interaction can be determined from equation the emission intensity (I) per activator ion follows the equation(2).

$$\frac{I}{x} = K \left[1 + \beta(x)^{Q/3} \right]^{-1} \quad (2)$$

where x is the activator concentration, I/x is the emission intensity (I) per activator concentration (x), and K and β are constants for the same excitation condition for a given host crystal. Q=3 stands for energy transfer among the nearest neighbour ions, while Q=6, 8 and 10 stands for dipole–dipole, dipole–quadruple, and quadruple–quadruple interactions [29]. According to this method, the emission intensities of Sr₂MgSi₂O₇:xSm³⁺ were measured with doped Sm³⁺ contents of 0.5, 1, 3, 5 and 7 mol%, and the concentration dependence curves (log (I/x)~log x) are shown in fig.6 The linear fitting has been applied on the dependence of log I/x on log x and the slope is -1.2. The value of Q can be calculated as 3.6, which is close 3 and means that the quenching behaviour is due to energy transfer among the nearest neighbour ions.

Fig.5: Variation of the 600 nm PL emission peak as a function of Sm³⁺ concentration.

Fig.6: Plot of log(I/x) as a function of log(x) in Sr₂MgSi₂O₇:xSm³⁺ phosphors.

3.4 CIE chromaticity diagram

The CIE chromaticity diagram was calculated from the calculation program for the Sr₂MgSi₂O₇:0.01Sm³⁺ phosphor under 403 nm and electron excitation is displayed in fig.7. From the CIE diagram it can be found that the coordinates (0.526, 0.472) for PL, correspond to the shade of yellow-orange emission of the Sm³⁺ ion.

Fig.7: The CIE 1931 chromaticity diagram for Sr₂MgSi₂O₇:0.01Sm³⁺ phosphor under 403 nm excitation.

IV. Conclusion

In summary, we have successfully synthesized yellow-orange emitting Single phased Ba₂MgSi₂O₄:Sm³⁺ by using the low cost, time saving, combustion method without using Ammonium Nitrate. The emission spectra of these phosphors (under UV and electron excitation) show characteristic emission of the Sm³⁺ ion due to transitions from the excited state ⁴G_{5/2} to the ⁶H_j (j = 5/2, 7/2). The optimal Sm³⁺ ion concentration and its critical energy distance were determined to be x = 1 mol% and 25.05 Å, respectively. The value of Q can be calculated as 3.6 which indicate that the quenching behaviour is due to energy transfer among the nearest neighbour ions in the present phosphor. Phosphor could efficiently be excited by near-ultraviolet LEDs (375–405nm) and gives the emission in Orange –Red region and therefore it can be a promising phosphor for the ‘yellow gap’ LEDs.

References

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Figures:

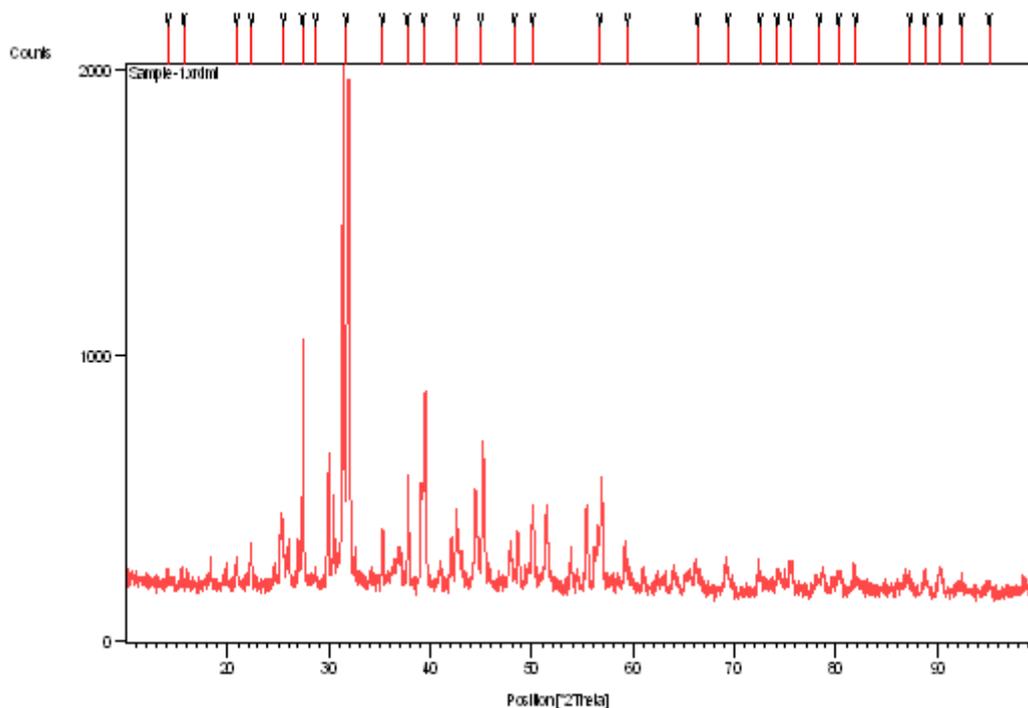


Fig.1: XRD pattern of Sr₂MgSi₂O₇

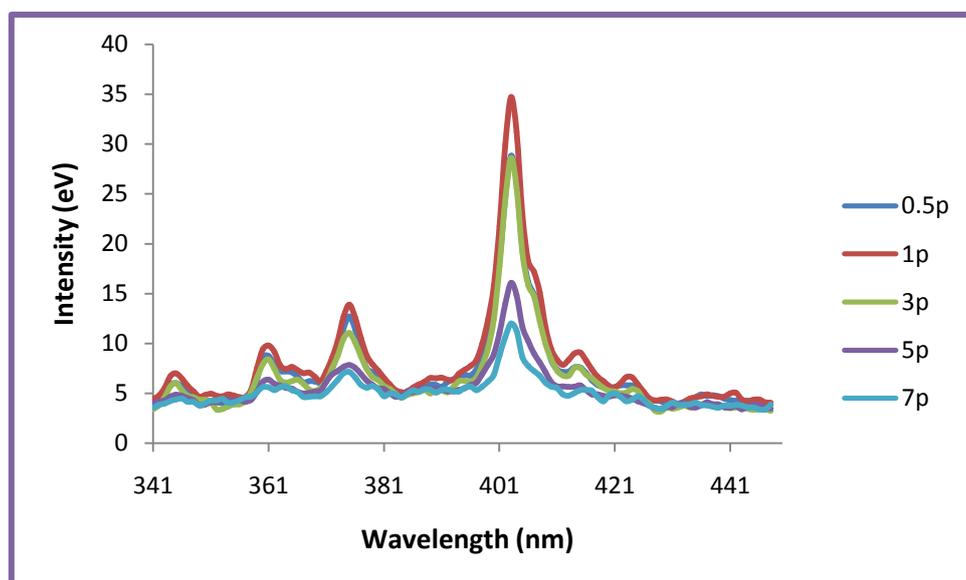


Fig.2: PL excitation at 600nm emission wavelength

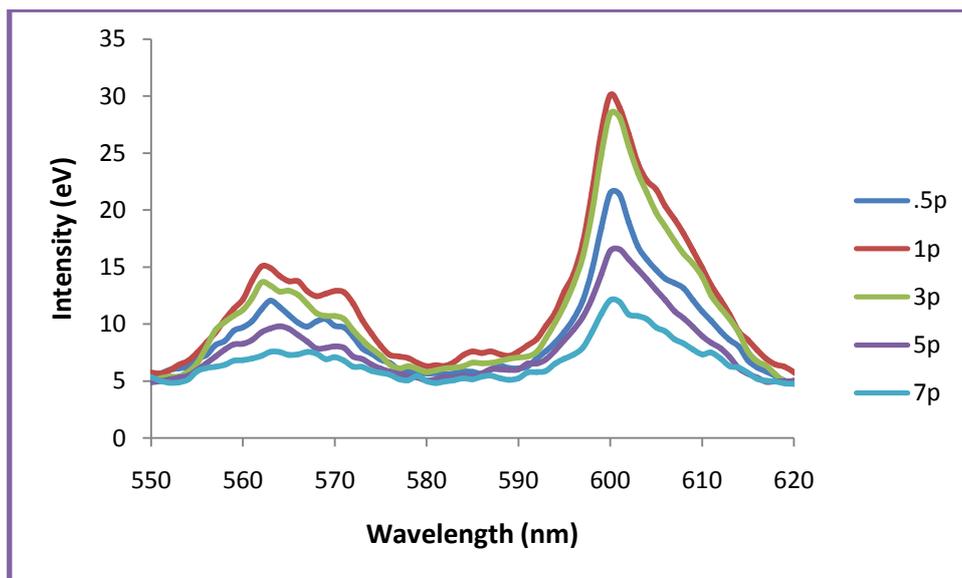


Fig.3: PL emission at 404nm excitation wavelength

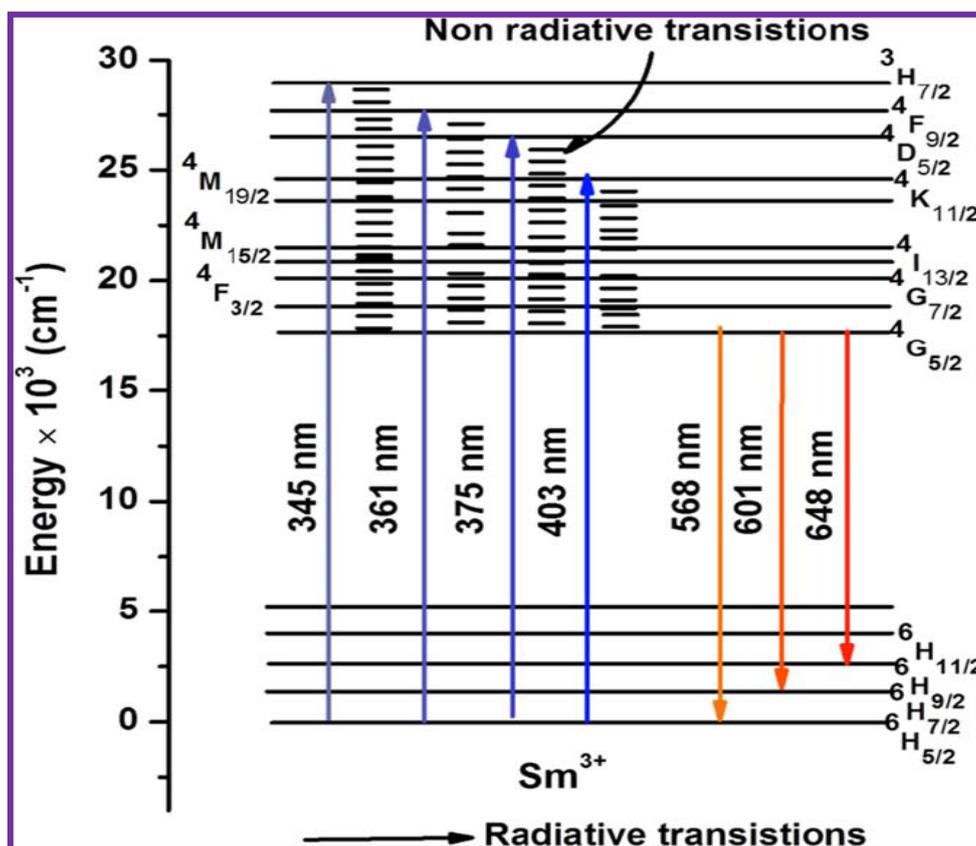


Fig.4: Energy level diagram of the Sm³⁺ ion in the Sr₂MgSi₂O₄ host lattice.

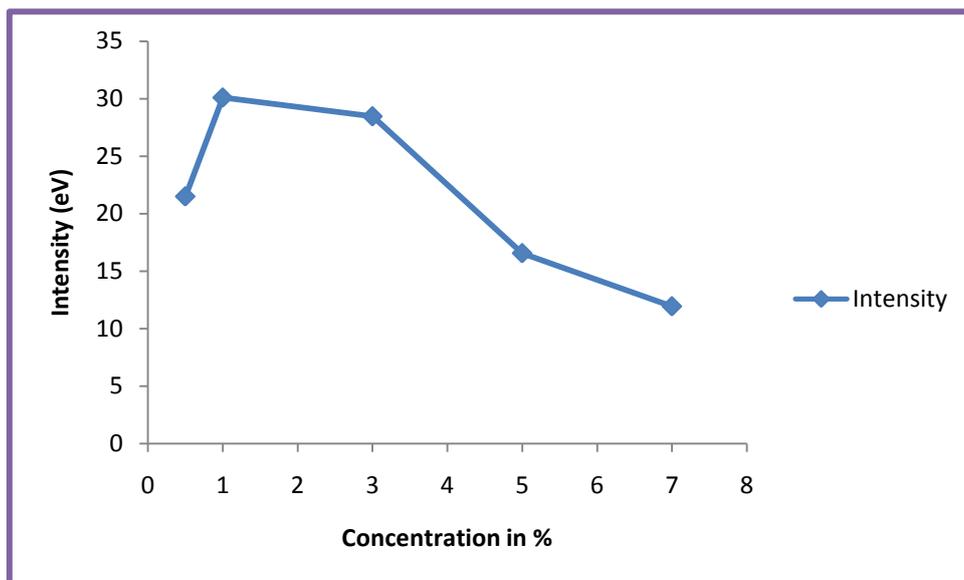


Fig.5: Variation of the 600 nm PL emission peak as a function of Sm³⁺ concentration.

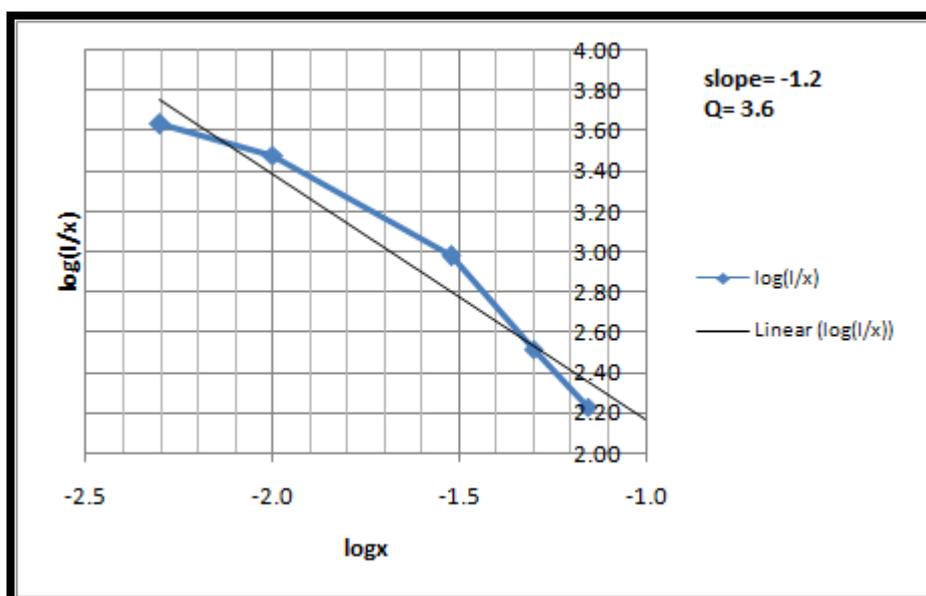


Fig.6: Plot of $\log(I/x)$ as a function of $\log(x)$ in Sr₂MgSi₂O₇:xSm³⁺ phosphors.

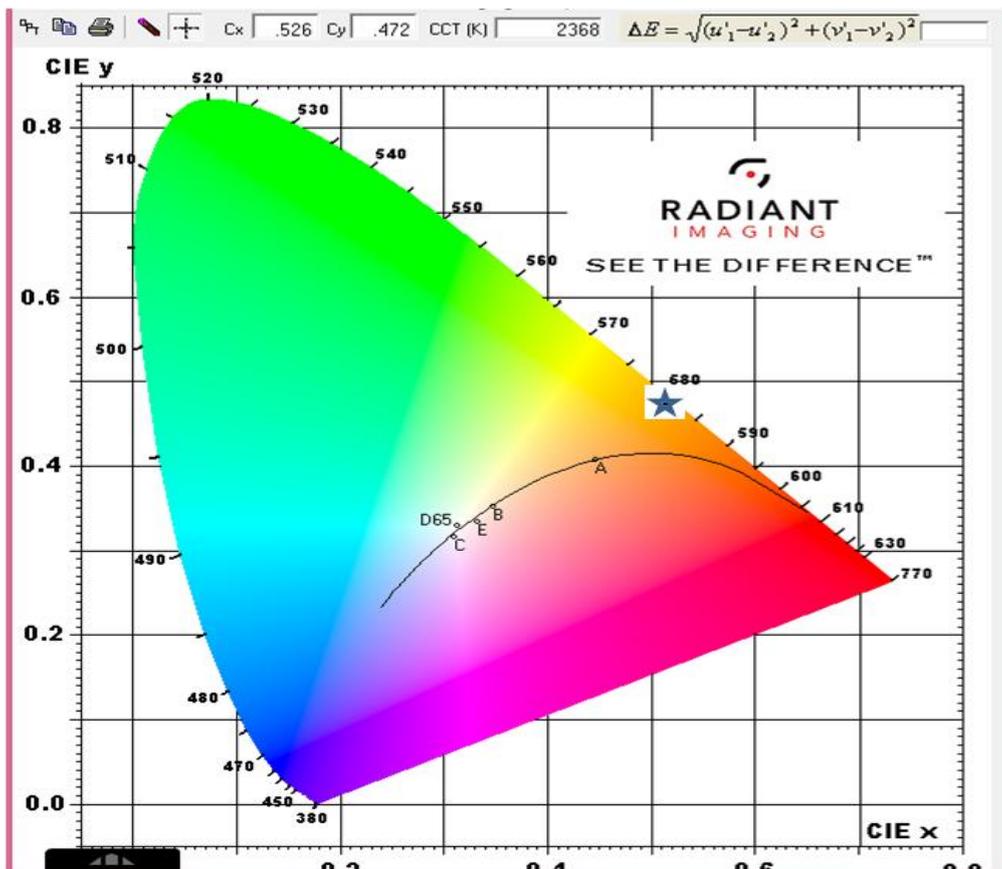


Fig.7: The CIE 1931 chromaticity diagram for Sr₂MgSi₂O₇:0.01Sm³⁺ phosphor under 403 nm excitation.