



# Luminescence of $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$ Doped with Samarium Phosphor

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## Abstract:

Photoluminescence study of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  sulphate phosphor, triggered by rare earth ion  $\text{Sm}^{3+}$  is investigated. The phosphor synthesized by cost effective wet chemical method was studied by powdered XRD, SEM and Photoluminescence characterization methods. The average crystallite size calculated by Scherrer formula is found to be ~34nm. PL excitation spectra of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  phosphor exhibit narrow bands in the near ultra violet (n-UV) range, and the PL emission spectra of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  phosphor shows narrow bands characteristic of  $\text{Sm}^{3+}$  ions in the visible orange region. Under 405nm excitation the emission peaks are obtained at 565nm, 598nm and 645nm can be attributed to the transitions  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$  ( $J=5/2, 7/2$  and  $9/2$ ) respectively within  $4f^5$  electronic configuration of  $\text{Sm}^{3+}$ . The calculated color chromaticity CIE coordinates for 1%  $\text{Sm}^{3+}$  activator in  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  host matrix, were **(0.323, 0.284)** which fall in the white light emission region. This phosphor may be useful for white light emitting phosphors in solid state lighting technology.

**Keywords:** Photoluminescence, white light, rare earth, wet chemical method

## 1. Introduction

The inorganic phosphors activated by rare earth ions possess a few attractive characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators. [1-4] Morphology characteristics of phosphors i.e. shapes and size of the powder particles, is one of the important parameters to use phosphors for a range of applications. The particle size of a phosphor affects the amount of phosphor particles needed to produce an optimal coating for a particular application. Phosphor having smaller particle size can provide equivalent coverage densities at lower powder weights than larger sized particles [5-6]. Hence phosphors in the nano size are gaining importance.

Rare earth activated phosphors can be divided into two classes- first is the broad band emitting owing to the 5d to 4f transition ( $\text{Eu}^{2+}$ ,  $\text{Ce}^{2+}$ ) and second is the narrow band emitting due to the transition between the 4f levels ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Nd}^{3+}$ , etc). The luminescence is more intense if the band gap between the excited state and the highest component of the ground state multiplet becomes larger. The halo-apatites are effective host lattices for luminescence and laser materials [7]. Several halide containing host materials have been studied as luminescence materials e.g.  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ . [8]





Ba<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu<sup>2+</sup> [9]., KZnSO<sub>4</sub>Cl, KMgSO<sub>4</sub>Cl, NaMgSO<sub>4</sub>F have been reported by Dhoble and co-workers [10] as good candidates as hosts for rare earth doped phosphors.

Phosphor converted white light emitting diodes (Pc-WLEDs) have gained more importance recently because of their applications such as flashlights, indicator lights, display backlighting and architectural lighting. [11, 12]. Until now major challenges in Pc-WLEDs have to be achieved for high luminous efficacy, high chromatic stability, brilliant color-rendering properties [13]. It is considered that NUV-LED+RGB phosphors is one of the best approaches to generate white light for both high luminous efficiency and high CRI.[14,15]

Literature survey reveals that the compound Na<sub>3</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl (cesanite) has not been studied yet as a phosphor material. Therefore in this paper we are reporting the luminescence characteristics of samarium doped Na<sub>3</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl phosphor prepared by wet chemical method.

## 2. Experimental

The phosphor Na<sub>3</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl: Sm<sup>3+</sup> was prepared by wet chemical method. For the preparation of Na<sub>3</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl:Sm, the initial raw material used were high purity Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and Sm<sub>2</sub>O<sub>3</sub> (all AR grade of 99.99% purity). The initial materials were weighed using the high precision (0.00001 gm) electronic monopan balance. The concentrations 'X' of Sm in the form of nitrate, (obtained by mixing with nitric acid) were mixed with host, (where X= 0.1, 0.2, 0.5, 1 and 1.5 mole %). The raw materials taken in stoichiometric ratio, were dissolved separately in distilled water and then mixed together to give desired compound.

The compound Na<sub>3</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl: Sm<sup>3+</sup> is prepared by heating in oven at 80° C for 10-12 hrs. The dried samples were then slowly cooled down to room temperature. The resultant mass was crushed to fine particle in crucible and this powder was used for further study. The photoluminescence (PL) emission spectra of the sample were recorded using fluorescence spectrometer (RF - 5301). Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

## 3. Results and Discussion

### Characterization

**X-ray diffraction:** Fig.1, shows the XRD pattern of Na<sub>3</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl phosphors. It shows good crystalline nature. In the XRD pattern starting compound or intermediate compounds lines are not observed, therefore, we consider that the compound is prepared successfully and the doped material have been effectively built into the host lattice. The average crystallite size as calculated by Scherrer formula is ~34nm.

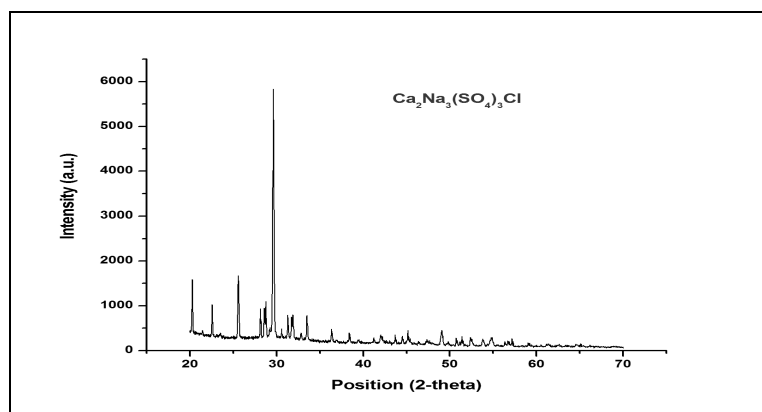
The Scherrer formula used is

$$D = \frac{K \cdot \lambda}{\beta \cos \theta} \text{-----(1)}$$

330

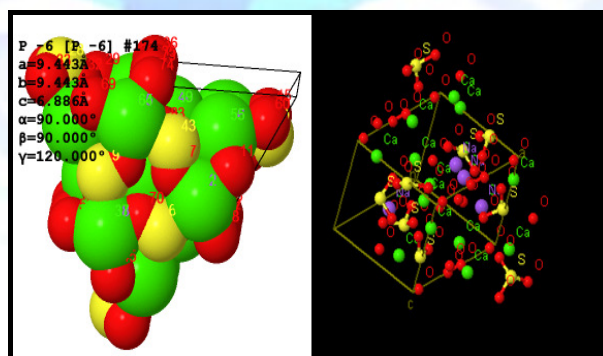


Where  $K = 0.94$ ,  $D$  is the crystallite size,  $\lambda$  is the wavelength of  $\text{CuK}\alpha$  radiation and  $\beta$  is the FWHM of the diffraction peak.



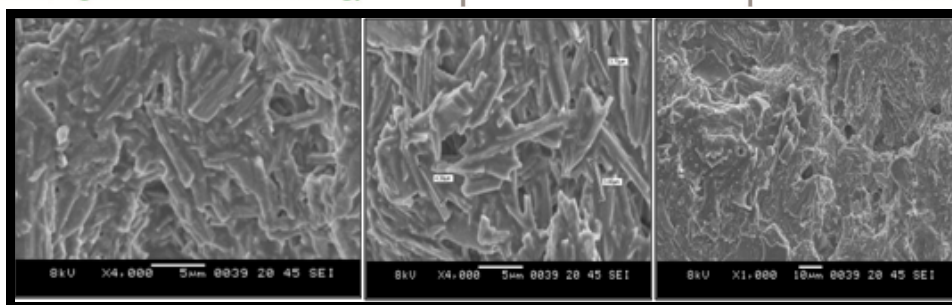
**Fig.1 XRD pattern of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  material**

Cesantite crystallizes in striated subhedral hexagonal prismatic crystal system, with space group  $P6_3/m$  [16]. The dimensions of Unit cell calculated are  $a = 9.456(1)$   $c = 6.195(1)$ ,  $Z = 2$  and  $V = 619.8 \text{ \AA}^3$ . It has an apatite like structure with ordering of Ca and Na in the two non equivalent cation sites, as in hedyphane. The apatite structure is well known for its ability to accommodate a wide variety of cations. The ionic radii of  $\text{Ca}^{2+}$ , and  $\text{Sm}^{3+}$  are,  $1.00 \text{ \AA}$  and  $0.958 \text{ \AA}$  respectively. Therefore  $\text{Sm}^{3+}$  ions may prefer to occupy  $\text{Ca}^{2+}$  sites in  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  host lattice. The crystal structure is similar to that shown in Fig. 2 below.



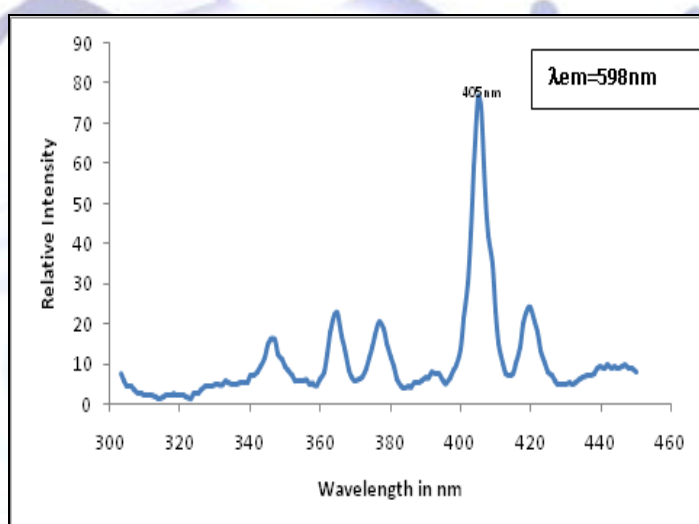
**Fig.2. Crystal structure of (Cesantite)**

**Scanning Electron Microscopy:** To study the morphological structure of phosphor prepared by wet chemical method, scanning electron microscopy has been performed. Fig. 3 shows the SEM micrograph of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  phosphor with different magnifications. The micrograph show that the phosphor consists of clustered structure of micro crystalline rod type structure. The lengths of these rod in the ranges from  $3\mu\text{m}$  to  $10\mu\text{m}$ .



**Fig.3 SEM micrograph showing surface morphology of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$**

**Photoluminescence of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$**  : Fig. 4 and Fig.5 show the excitation and emission spectra of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  phosphor doped with Samarium ions. The excitation spectrum was obtained by monitoring at 598nm wavelength which corresponds to the  $^4\text{G}_{5/2}$  to  $^6\text{H}_{7/2}$  transition within  $\text{Sm}^{3+}$  (Fig.4). The excitation band wavelengths 346, 365, 377, 405, 420 & 440nm correspond well to the electronic transitions from  $^6\text{H}_{5/2}$  to upper states within  $\text{Sm}^{3+}$ .



**Fig.4 Excitation spectra of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  at 598nm emission wavelength**

The emission spectra of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  was obtained by monitoring excitation wavelength at 405nm wavelength. The emission spectrum consists of three peaks characteristic of  $\text{Sm}^{3+}$  ions, which are at 565(green), 598(orange) and 645(red) nm. These three bands can be identified with the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$  ( $J=5/2, 7/2$  and  $9/2$ ) respectively. transitions within  $4f_5$  electronic configuration of  $\text{Sm}^{3+}$ . Among the emission lines, the transitions at 565nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ ) and 598nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ ) are having almost similar intensity, which correspond to green and near red emission of  $\text{Sm}^{3+}$ :  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  phosphor. The emission at 598nm due to  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$  ( $\Delta J=\pm 1$ ) is partly magnetic dipole (MD) and partly electric dipole (ED) nature emission band [17]. The other transition at 565nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ ) is purely MD natured and at 645nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ ) is purely ED natured, which is sensitive to crystal field. The intensity ratio of ED and MD transition has been used to measure the symmetry of the local environment of the trivalent 4f ions [18]. The asymmetry



nature increases with the increase in the intensity of ED transition. In  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  we have found that the intensity of  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$  (MD) transition is more than the  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$  (ED) transition, indicating the symmetric nature of  $\text{Na}_3\text{Ca}_2\text{Na}_3(\text{SO}_4)_3\text{Cl}$  host matrix. Energy level diagram representing the possible luminescence mechanism in  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  phosphor shown Fig.6.

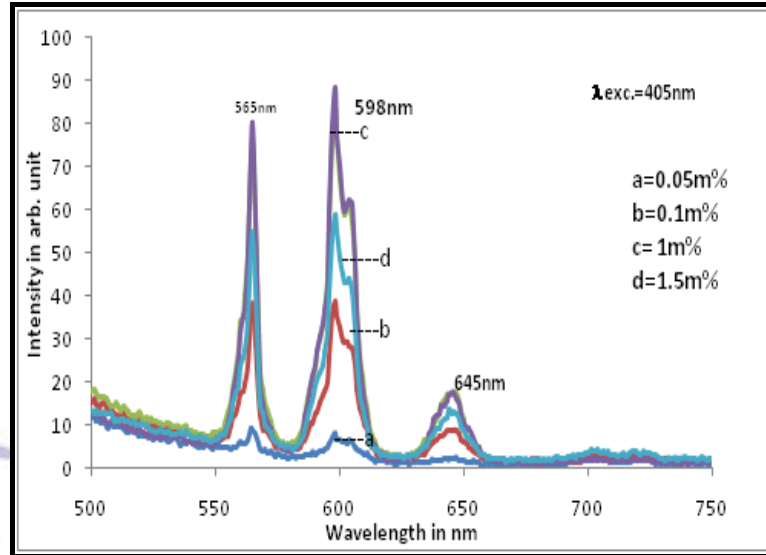


Fig.5 Emission spectra of  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  monitored at 405nm excitation wavelength

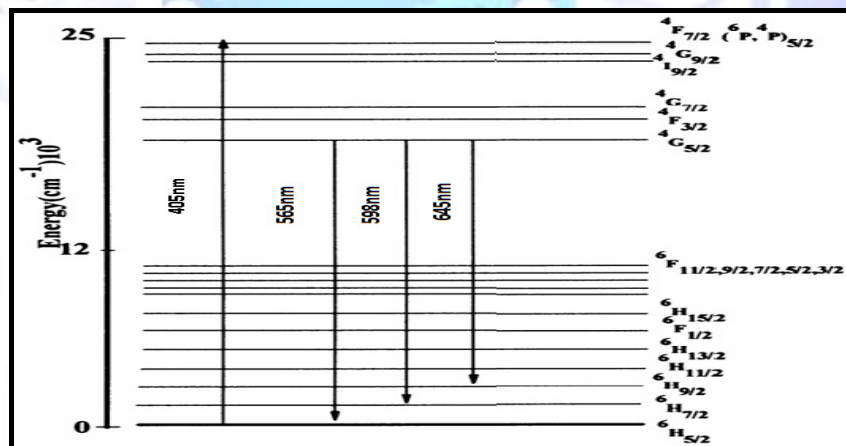


Fig.6 Energy level diagram representing the possible luminescence mechanism in  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  phosphor

The effect of concentration of dopant ions on the intensity of emission peaks in the host matrix  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  has also been studied (Fig. 7). It is found that initially with the increase of dopant ions  $\text{Sm}^{3+}$  in  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  phosphor, the intensity of emitted peaks increases upto 1mol%, but with further increase of dopant ions, at 1.5mol%, intensity decreases. This may be due to concentration quenching. The fall in emission intensity after a certain concentration is called concentration quenching, which is normally due to energy passage among rare earth ions. When the activator concentration exceeds  $x_c$  (critical concentration), energy transfer takes place, causing





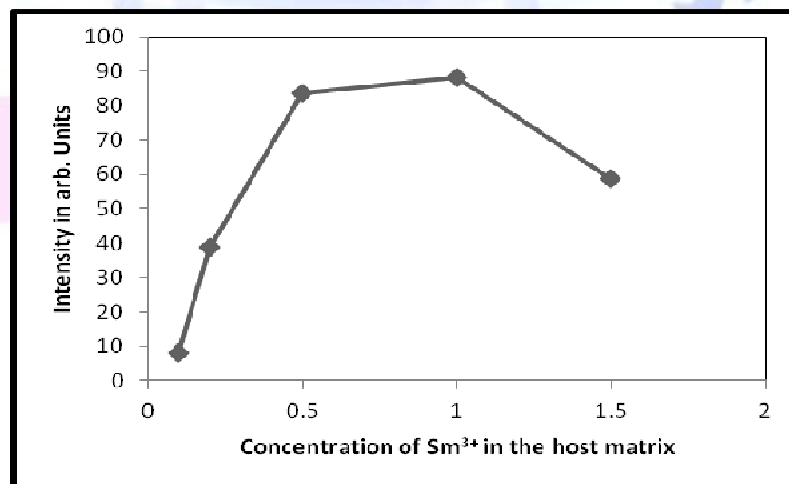
concentration quenching. According to Blasse[19] , the critical distance can be calculated using the equation,

$$R_c = 2 \left[ \frac{3V}{4\pi N_c Z} \right]^{\frac{1}{3}}, \quad (1)$$

where Z is the number of cations per unit cell, and V is the volume of the unit cell. Taking the value of V, N and  $X_c$  as  $619.8 \text{ \AA}^3$ ,  $Z=4$  ( Assuming  $\text{Sm}^{3+}$  ions occupy  $\text{Ca}^{2+}$  ions in the host) and 0.01, the calculated value of  $R_c$  is found to be approximately equal to  $29.4 \text{ \AA}$ . The process of energy transfer from one  $\text{Sm}^{3+}$  ion to another would be due to electric multipolar interaction which includes dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions[20]. The force of the multipole-multipole interaction can be understood from the change in the emission intensity if the energy transfer arises between the same sorts of activators. The emission intensity per activator ion can be expressed by the following equation (2)[21]

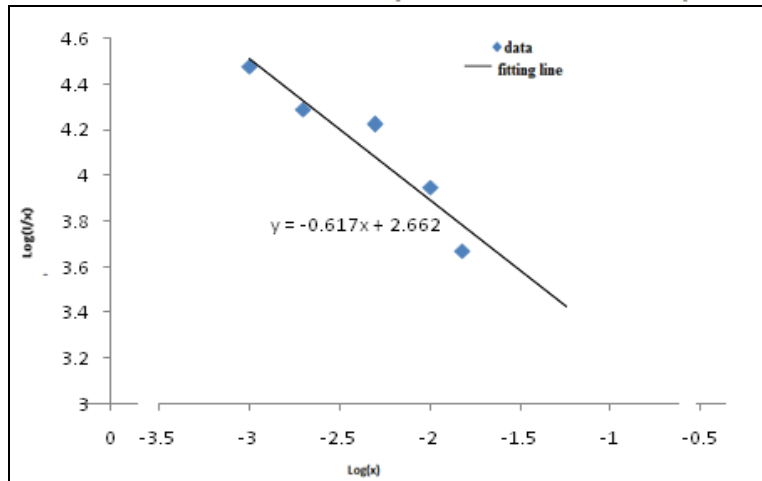
$$\frac{I}{x} = k \left[ 1 + (x)^\theta \right]^{-1}, \quad (2)$$

where I is the emission intensity, x is the activator concentration, k and  $\beta$  are constant for each interaction in the same excitation conditions for a given host,  $\theta$  is the index of electric multipole,  $\theta=3$  represents the energy transfer among nearest-neighbour ions, while  $\theta=6, 8$  and  $10$  for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interaction respectively [22]. The relationship of  $\log(I/x)$  versus  $\log(x)$ , shown in Fig. 8 is linear (fitted line  $y= -0.617x + 2.662$ ) and its slope approx. unity. The value of  $\theta$  is approximately equal to 3. This result indicates that the energy transfer among the nearest ions is the main mechanism of concentration quenching in  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}:\text{Sm}^{3+}$  phosphor.



**Fig. 7** Variation of maximum intensity at 598nm wavelength with concentration of  $\text{Sm}^{3+}$  ions in  $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{Cl}$  phosphor.

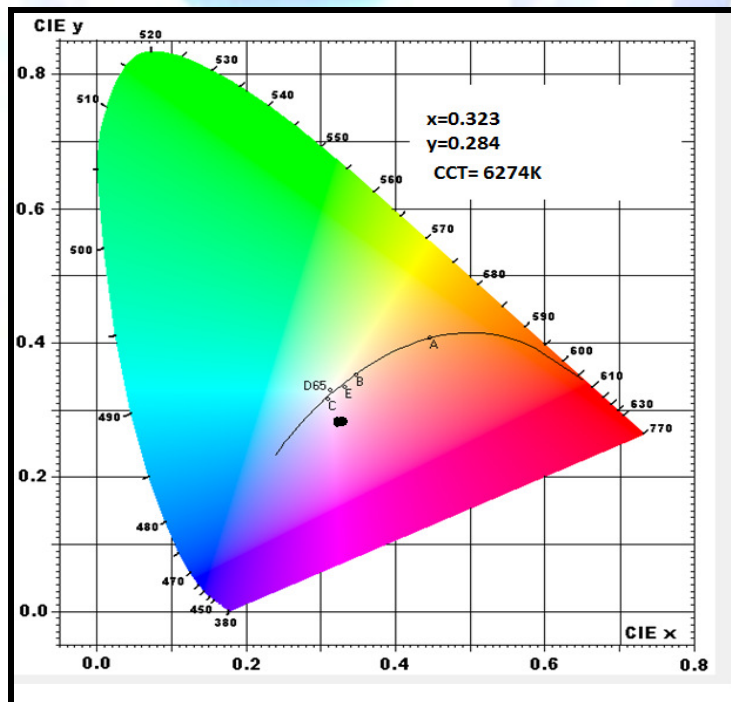




**Fig. 8** Logarithm of the emission intensity per activator ion( $\log(I/x_{Sm})$ ) as a function of  $\log(x_{Sm^{3+}})$  concentration

### CIE chromaticity coordinates

Considering the fact that the emission peaks of Samarium doped phosphors has three different colors green, orange and red, and the peak intensities for 565nm and 598nm is almost the same in  $Na_3Ca_2(SO_4)_3Cl:Sm^{3+}$  phosphor, we have calculated the CIE chromaticity coordinates for 1%  $Sm^{3+}$  doped  $Na_3Ca_2(SO_4)_3Cl$  from the spectral distribution, which are obtained as **(0.323,0.284)**. **Fig. 9** shows the CIE chromaticity coordinates (value of x and y) calculated from the emission spectra of 1% $Sm^{3+}$  doped  $Na_3Ca_2(SO_4)_3Cl$  phosphor . The chromaticity coordinates for standard white light are (0.33, 0.33). The chromaticity coordinates obtained in this case lie close to the standard value.



**Fig.9** CIE Chromaticity diagram for emission  $Na_3Ca_2Na_3(SO_4)_3Cl :Sm^{3+}$  under 405nm excitation



## 4. Conclusion

Thus we have successfully showed a simple and cost effective wet chemical method to synthesize  $\text{Sm}^{3+}$  doped  $\text{Na}_3\text{Ca}_2\text{Na}_3(\text{SO}_4)_3\text{Cl}$  nanophosphor. The resulted nanophosphor exhibited white light emission. The phosphor was characterized by XRD and SEM. The PL emission spectra showed green (565nm) and yellowish orange (598nm) and red (645nm) emission peaks when excited by 405nm wavelength which are due  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$  ( $J=5/2, 7/2$  and  $9/2$ ) respectively transitions within  $4f_5$  electronic configuration of  $\text{Sm}^{3+}$  ions. Concentration quenching has been investigated and it is found that energy transfer between nearest neighbours is the mechanism for concentration quenching. The calculated CIE chromaticity coordinates are (0.323, 0.284), which are close to standard white light chromaticity coordinates (0.33, 0.33). This study shows that the  $\text{Na}_3\text{Ca}_2\text{Na}_3(\text{SO}_4)_3\text{Cl} : 1\% \text{Sm}^{3+}$  phosphor is a good candidate for NUV based white light emitting phosphors technology.

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