Chapter 4

Spectroscopic and Luminescence Studies of doped and co-doped Y$_2$SiO$_5$ nanophosphors: chemical and green synthesis route
4.1. Spectroscopic and Luminescence studies of Dy$^{3+}$ doped Y$_2$SiO$_5$ nanophosphor : chemical synthesis route

4.1.1. Introduction

Luminescent nanoparticles have attracted great interest due to large surface to volume ratio and crucial importance of surface states in improvement of optical and luminescence features [1]. Due to their wide variety of applications, significant efforts have been made to produce the rare earth doped luminescent nanostructures such as phosphors [2], laser host materials [3], catalysts [4] and up-conversion materials [5]. The luminescence intensity was an important character for phosphor; improved performance of lighting and display requires high quality of phosphors for sufficient brightness. The luminescence properties depend on the activator concentration and crystallinity. Literature proved the influences of doping content of activator ion, grain size, morphology and agglomeration on luminescence efficiency [6-9].

LED technology has flourished for the past few decades. High efficiency, reliability, low power consumption and durability were among the key factors for the rapid development of the solid state lighting based on high brightness visible LEDs [10]. The currently used phosphors for near-UV/violet GaN-based LED were BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ for blue and Y$_2$O$_5$S:Eu$^{3+}$ for red. Dy$^{3+}$ doped phosphors [11, 12] were used as white-light-emitting materials. In this context, the search for stable, inorganic rare-earth-based phosphors with high absorption in the near-UV/blue spectral region is an attractive research task. The white LEDs have several advantages over the conventional incandescent and fluorescent lamps due to its high power efficiency, long life time, non-pollution and flexibility in design process [13-15].

As one of the activator ions in phosphors, Dy$^{3+}$ ion has been investigated in many hosts such as aluminates, phosphates and silicates because Dy$^{3+}$ plays an important role in the production of white light luminescent materials. Dy$^{3+}$ ions show two dominant bands in the emission spectrum such as yellow and blue bands. The yellow band corresponds to the hypersensitive transition of $^4F_{9/2} \rightarrow ^6H_{13/2}$ and the blue band corresponds to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition. With appropriate combination in Dy$^{3+}$ doped materials, the blue and yellow color light emission can be produced white light. Therefore, different host materials doped with Dy$^{3+}$ ion may be potential for white light emission [16-19]. Silicate nano phosphors show superior properties due to thermal stability, wide energy band gap, low cost, non-toxicity, chemical resistance,
high temperature strength, low thermal expansion and high conductivity, multi-color phosphorescence, high resistance to acid, alkali and oxygen. Among silicate phosphors, YSO doped with rare earth ions were studied extensively in display applications [20]. Over the past few years, the synthesis of inorganic nanoscale materials with specific morphologies attracted the phosphor developers. Silicate phosphors were synthesized by a variety of routes such as Solid-state reactions, Sol–Gel, Hydrothermal, Precipitation, Microwave techniques, etc. In the present studies, Y$_2$SiO$_5$:Dy$^{3+}$ nano phosphors were synthesized by low temperature combustion synthesis route [LCS]. This process provides molecular level of mixing and high degree of homogeneity, short reaction time that leads to reduction in crystallization temperature and prevents from segregation during heating [21-23]. The flux method was a well-known method used for single-crystal growth and improving of luminescent intensity, but it has rarely been applied to the synthesis of nanocrystalline materials. But addition of different fluxes like NaCl, KI, NH$_4$Cl, NH$_4$Br and NH$_4$F changes the crystallinity, structure and PL properties [20].

In the present work, Dy$^{3+}$ single doped Y$_2$SiO$_5$ phosphor were synthesized by solution combustion method using NaCl as flux. Structural characterization and photoluminescence studies were studied in detail.

4.1.2. Results and discussion

4.1.2.1. Powder X-ray diffraction (PXRD) studies

Fig 4.1.1 shows the PXRD patterns of Y$_2$SiO$_5$:Dy$^{3+}$ (1–9 mol %) calcined at 1000 °C, synthesized by solution combustion technique using urea and NaCl as fuel and flux respectively. All the X-ray diffraction peaks of the sample show a monoclinic phase with X1 type Y$_2$SiO$_5$ and was in good agreement with JCPDS card no. 41-0004 (with phase group $P2_1/c$ n.14) [20]. The lattice parameters and unit cell volume for monoclinic Y$_2$SiO$_5$ (X1) phase was estimated by using the equations (2.6) and (3.2.1). The estimated values of lattice parameters were found to be 3.78 Å and 414.84 Å$^3$ respectively. Further, no diffraction peaks from Dy$_2$O$_3$ or other impurities detected indicating that ions were homogeneously mixed and effectively doped in the host lattice in Y$^{3+}$ sites. The average crystallite size (D) was estimated from the line broadening in X-ray powder using Scherrer’s equation (2.8) [25] was found to be in the range 30-60 nm.
Fig 4.1.1. PXRD patterns of undoped and (1-9 mol %) Dy$^{3+}$ doped Y$_2$SiO$_5$ nanophosphor.

Further, strain present in the Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) nanoparticles prepared by combustion method was calculated using the W-H plots equation (2.9) [26]. The graph between ‘4sinθ’ (x-axis) and ‘βcosθ’ (y-axis) (shown in Fig.4.1.2). The slope of the line gives the strain and intercept of this line on y-axis gives grain size (D). The detailed values were given in Table 4.1.1.

**Table 4.1.1.** Estimated crystallite size and strain parameters of Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) nano phosphors.

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<th>Dy$^{3+}$ (mol %)</th>
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4.1.2.2 Morphological analysis. (SEM and TEM)

The surface morphology of pure, Dy$^{3+}$ (1–9 mol %) YSO nanophosphors prepared via combustion method were studied and shown in Fig.4.1.3. Combustion derived as formed YSO product showed highly porous, many agglomerates with an irregular morphology, large voids, cracks, pores and shape. Further, the dopant concentration does not influence the morphology of the sample.

**Fig 4.1.2.** W-H plots of un-doped and (1-9 mol %) Dy$^{3+}$ doped Y$_2$SiO$_5$. 
Fig. 4.1.3. SEM images of (a) pure Y$_2$SiO$_5$ and Y$_2$SiO$_5$:Dy$^{3+}$ (b & c) 1 mol %, (d - f) 5 mol %, (g - i) 7 mol %, (j - l) 9 mol % nanophosphors.
TEM studies were carried out to understand the crystalline characteristics of the nanoparticles. Fig. 4.1.4 (a-c) illustrates the TEM, HRTEM and SAED images of 5 mol % Dy$^{3+}$ doped YSO nanoparticles. The particles were observed to be irregular shaped, highly dispersed and the average size was found to be in the range 20-25 nm. The selected area electron diffraction (SAED) image provide distinct ring pattern which was evidence for the polycrystalline behavior of the as-prepared nanoparticles. Further, a well-defined lattice fringes obtained by high resolution TEM (HRTEM) pattern reveal the formation of highly crystalline nano phosphor [27].

![Fig. 4.1.4.](image)

**Fig.4.1.4.** (a) TEM, (b) HRTEM, (c) SAED images of Dy$^{3+}$ (5 mol %) doped Y$_2$SiO$_5$ nano phosphor.

### 4.1.2.3 UV-Visible absorption spectroscopy

The UV–Vis absorption spectra of Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) NPs were shown in the inset of Fig.4.1.5. The absorbance spectra of Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) NPs in transmission mode were recorded by distributing the particles uniformly in liquid paraffin, in the wavelength range of 200-800 nm. The sharp absorption peaks observed at 218 nm arises due to transition between valence band to conduction band. The weak absorption band at ~ 211 nm region was expected to arise from transitions involving extrinsic states such as surface traps / defect states / impurities [28]. These absorption peaks were slightly shifted towards higher wavelength region indicating the decrease in energy gap with increase in Dy$^{3+}$ concentration. Smaller sized particles were found to have high surface to volume ratio. This results in increase of defects distribution on the surface of nanomaterials. Thus, if the particle size was small; nanomaterials exhibit strong and absorption bands. In Y$_2$SiO$_5$: Dy$^{3+}$, the particles size was in nanometer which results in high surface to volume ratio as a result there was an increase in defects distribution on the surface of the nanomaterials.
Fig. 4.1.5. UV – Vis absorption spectra of Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) NPs.

For estimation of band gap in the nanomaterials, the absorbance spectra of Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) NPs in transmission mode were recorded by distributing the particles uniformly in liquid paraffin, in the wavelength range of 200-800 nm. For a direct band gap, the absorption coefficient near the band edge was given by Wood and Tauc’s relation [20]. This relation can be rearranged and written in the form

$$(\alpha h\nu)^2 = A^2 (h\nu - E_g)$$

From the Eq. (4.1.1) $\alpha h\nu = 0$ and $E_g = h\nu$. The energy gap was determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ and finding the intercept on the ‘$h\nu$’ axis by extrapolating the plot to $(\alpha h\nu)^2 = 0$. Fig. 4.1.6(a) shows the Wood and Tauc’s plot from which the direct band gap was obtained in the range of 5.21 – 5.73 eV. With increase in Dy$^{3+}$ concentration from 1 – 9 mol %, the band gap was found to decrease from 5.73 to 5.21 eV as shown in Fig 4.1.6(b). A reduction in $E_g$ for doped samples would arise neither from a quantum size effect nor from crystal structure variation but rather from surface traps states or point defects. A plausible explanation for the variations observed on the $E_g$ values can be related to the degree of structural order–disorder into the lattice, which is able to change the intermediary energy-level distribution within the band gap. The $E_g$ values mainly depend on the preparation methods and the experimental conditions. In particular, these key factors can favor on inhibit the formation of structural defects which are able to control the degree of structural order–disorder of the material and,
consequently, the number of intermediary energy levels within the band gap. It was observed that the absorption measurements were extremely sensitive to the changes in the lattice or variations on the structural order–disorder degree [29].

**Fig. 4.1.6.** (a) Wood and Tauc’s plots to find band gap (b) variation of Dy$^{3+}$ concentration with band gap for (1-9 mol%).
4.1.2.4. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of $Y_2SiO_5$: Dy$^{3+}$ (1-9 mol %) NPs were recorded in order to interpret the structures of the obtained samples shown in Fig. 4.1.7. The FTIR spectra were recorded in the range 500-4000 cm$^{-1}$ for $Y_2SiO_5$: Dy$^{3+}$ (1-9 mol %) NPs. The NPs exhibit peaks in the range locating at 496, 682, 721, 845, 971, 2107 and 2273 cm$^{-1}$. The 721 cm$^{-1}$ band can be assigned to characteristic metal–oxygen (Y–O) vibrations. The peak located at 496 cm$^{-1}$ was due to Si-O ($v_4$) and Si-O bending modes. The band at 682 cm$^{-1}$ was due to Si-O ($v_3$) stretching mode. The remaining peaks located at 845, 971, 2107 and 2273 cm$^{-1}$ can be associated to (Si-O-Si), $v_1$ (Si-OH), (CH & NO$_3$) and 2$v_3$ (Si-O) respectively. Slight deviation in vibrational frequencies and intensities of bands were observed with variation in concentration of Dy$^{3+}$ ions in $Y_2SiO_5$ matrix.

![FTIR spectra of $Y_2SiO_5$: Dy$^{3+}$ (1-9 mol %) nano phosphor.](image)

**Fig. 4.1.7.** FTIR spectra of $Y_2SiO_5$: Dy$^{3+}$ (1-9 mol %) nano phosphor.

4.1.2.5. Photoluminescence (PL) studies

Fig. 4.1.8 shows the excitation spectrum of $Y_2SiO_5$: Dy$^{3+}$ (5 mol %) nanophosphors with emission wavelength 575 nm. The spectra consists of series of excitation peaks at 388, 423, 451, 468 nm correspond to the electron transitions of Dy$^{3+}$ from the ground state $^6H_{15/2}$ to higher levels $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$, respectively [30].
Fig. 4.1.8. Excitation spectrum of $\text{Y}_2\text{SiO}_5: \text{Dy}^{3+}$ (5 mol %) emission at 575 nm.

The emission spectra of $\text{Y}_2\text{SiO}_5$: Dy$^{3+}$ (1-9 mol %) nanophosphor excited at 388 nm was shown in the Fig.4.1.9. The PL spectra consist of three main peaks in blue 485 nm, yellow 575 nm and red 636 nm region. Upon 388 nm wavelength excitation, Dy$^{3+}$ ions jumps resonantly to $^6\text{P}_{7/2}$ state and quickly releases non-radiatively to $^4\text{F}_{9/2}$ level. Radiative emission takes place from $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (485 nm, blue), $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (575 nm, yellow) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$ (636 nm, red). The blue emission corresponds to the magnetic dipole transition and the yellow emission belongs to the hypersensitive (forced electric dipole) transition with the selection rule $\Delta J = 2$ [31- 33]. The broad band suggests that the emission process was a typical multi phonon or multi level process (a solid system in which the relaxation occurs by several paths, involving the participation of numerous energy states within the band gap) [34]. It was observed that PL intensity increases upto 5 mol% Dy$^{3+}$ ions and above this intensity decreases due to concentration quenching as shown in Fig. 4.1.10 (a). The increase in PL intensity was due to cross relaxation between Dy$^{3+}$ ions, consequently with increasing Dy$^{3+}$ concentration the generation of luminescent centers increases as a result PL intensity enhances. The decrease of PL intensity may be due to creation of point defects due to imbalance charges.
As pointed out in Ref. [35, 36], the following cross relaxations may be responsible for the population decrease of $^4F_{9/2}$ multiplet: $^4F_{9/2} + ^6H_{15/2} \rightarrow ^6H_{9/2}(^6F_{11/2}) + ^6F_{3/2}$, $^4F_{9/2} + ^6H_{15/2} \rightarrow ^6H_{5/2} + ^6F_{7/2}$, and $^4F_{9/2} + ^6H_{15/2} \rightarrow ^6F_{1/2} + ^6H_{9/2}(^6F_{11/2})$. Due to the cross relaxations, Dy$^{3+}$ ions at the $^4F_{9/2}$ multiplet can be de-excited to the $^6H_{9/2}(^6F_{11/2})$, $^6H_{5/2}$, or $^6F_{1/2}$ multiplet, in the mean-while Dy$^{3+}$ ions at the ground state $^6H_{15/2}$ are excited to the $^6F_{3/2}$, $^6F_{7/2}$ or $^6H_{9/2}(^6F_{11/2})$ multiplet. Finally, all the Dy$^{3+}$ ions involved in the cross-relaxations can be de-excited to the $^6F_{9/2}$.
relaxations relax to the ground state nonradiatively and thus the luminescence related to the $^4F_{9/2}$ multiplet are quenched. It is clear that the increase rate of yellow emission is higher than that of blue emission until the Dy$^{3+}$ concentration is 5 mol%. The strong yellow emission corresponds to the hypersensitive transition of $^4F_{9/2} \rightarrow ^6H_{13/2}$ and so its intensity is strongly affected by the environment around Dy$^{3+}$ ions [37, 38]. Whereas the blue emission corresponding to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition is less sensitive. Generally, the yellow emission is dominant when Dy$^{3+}$ is located at a low symmetric site, whereas the blue emission is stronger when Dy$^{3+}$ is located at a high symmetric site [39, 40].

The energy transfer mechanism in phosphors was essential in order to obtain the critical distance ($R_c$) i.e. the critical separation between Dy$^{3+}$ and the quenching site was calculated according to the equation given by Blasse equation (3.2.4) [41]. For YSO: Dy$^{3+}$ nanophosphor the values of N, V and $X_c$ were 4, 289 Å$^3$ and 0.05 respectively. Using these parameters, the estimated ‘$R_c$’ was found to be 19.09 Å. According to Blasse theory [42], the nonradiative transfer between different Dy$^{3+}$ ions in YSO phosphor may occur by radiative re-absorption/exchange interaction/multipole–multipole interaction. Since ‘$R_c$’ is not less than 5 Å, exchange interaction is not responsible for nonradiative energy transfer process from one Dy$^{3+}$ ion to another Dy$^{3+}$ ion in this host. Therefore, multipolar interaction was used to explain the concentration quenching mechanism. Multipolar interaction involves several types of interaction such as dipole–dipole (d–d), dipole–quadropole (d–q), quadropole–quadropole (q–q) interaction. As a result, the energy transfer process of Dy$^{3+}$ in YSO phosphor would be due to multipolar interaction [43]. In order to determine the type of interaction involved in the energy transfer Van Uitert [44] equation (3.2.3). According to this equation, Q=3 for the energy transfer among the nearest neighbor ions, while Q=6, 8 and 10 for d–d, d–q and q–q interactions respectively [45]. Assuming that $\beta(X) Q/3 \gg 1$, equation (3.2.3) can be written as

$$\log \left( \frac{I}{x} \right) = k' - \frac{Q}{3} \log X; \ (K' = \log K - \log \beta) \quad \text{----------(4.1.2)}$$

The graph of log ($I/x$) vs. log x in Y$_2$SiO$_5$: Dy$^{3+}$ phosphor was shown in Fig.4.1.10 (b). The figure clearly shows that the relation between log ($I/x$) and log x was approximately linear and the slope was -0.93. The Q value obtained by the linear fitting using Eq. (4.1.2) was ~ 7.3, which was close to 8. This result indicates that the
dipole–quadrupole [23] interaction was the major mechanism for the concentration quenching of the emission of Dy$^{3+}$ ions in Y$_2$SiO$_5$ nano phosphor. The Commission International de l’Eclairage (CIE) chromaticity coordinates [46, 47] for Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) phosphors was calculated as a function of Dy$^{3+}$ concentration shown in Fig. 4.1.11(a). The CIE coordinates of white emission of Dy$^{3+}$ ions not only depend upon the asymmetric ratio but also on the higher energy emission levels. It was observed that in both the cases the CIE co-ordinates falls in white region which clearly represents both the phosphors can be used for white light emitting diodes (WLEDs) and solid state lighting devices.

Correlated color temperature (CCT) can be estimated by Plankian locus, which was only a small portion of the (x, y) chromaticity diagram and there exist many operating points outside the Planckian locus. If the coordinates of a light source do not fall on the Planckian locus, CCT was used to define the color temperature of a light source. CCT was obtained by transforming the (x, y) coordinates of the light source to (U’, V’) by using equations (3.2.6 and 3.2.7), and by determining the temperature of the closest point of the Planckian locus to the light source on the (U’, V’) uniform chromaticity diagram (Fig. 4.1.11(b)) [48, 49].

![Fig. 4.1.11. (a) CIE diagram of Y$_2$SiO$_5$:Dy$^{3+}$ (5 mol %) nanophosphors. (b) CCT diagram of Y$_2$SiO$_5$: Dy$^{3+}$ (5 mol %) nanophosphors.](image)

The average CCT of 5740 K was observed in Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) nanophosphors. Further it was observed that in both the cases coordinates falls on the Planckian locus. The CCT indicates white light emission can be achieved and
phosphors could be potentially used in white light emission displays and near ultraviolet pumped white LEDs [50].

4.1.3. Conclusions

Single-phased white light emitting phosphors $\text{Y}_2\text{SiO}_5$: Dy$^{3+}$ was prepared by the solution combustion method. Further, the calcinations temperature of $\text{Y}_2\text{SiO}_5$ was less (1000 °C) compared to solid state route. PXRD results of calcined samples at 1000 °C show pure monoclinic $\chi_1$ phase. The emission spectra of $\text{Y}_2\text{SiO}_5$: Dy$^{3+}$ was ascribed to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (485 nm, blue), $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (575 nm, yellow) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$ (636 nm, red) transitions of Dy$^{3+}$ ion, the most intense emission of Dy$^{3+}$ was recorded for the transition $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$. The CIE chromaticity coordinates for doped phosphors suggested that the emission color of the obtained phosphors indicates that the phosphors could be potentially used in white light emission displays and near ultraviolet pumped white LEDs.
References


[09] Yuyang He, Maiqun Zhao, Yanyan Song, Gaoyang Zhao, Xuan Ai *J. Lumin.* 131 (2011) 1144.


4.2 Spectroscopic and Luminescence studies of Eu$^{3+}$ co-doped Y$_2$SiO$_5$:Dy$^{3+}$ nanophosphors: chemical synthesis route

4.2.1. Introduction

Currently, in the field of luminescence, light emitting diodes (LEDs) lead over other conventional lighting devices (incandescent lamps, fluorescent lamps etc.) with its notable features such as low power consumption, long operation lifetimes, less pollution and wide applicability as lighting, displays etc. Today's most common method to produce white light was invented by Nichia Chemicals Co. in 1996, in which yellow phosphor (YAG: Ce) was coated on blue chip (InGaN). However, white LEDs made by this method show poor color rendering index (CRI) because of lack of red component. This problem could be overcome either by combining red, green and blue (RGB) LEDs or UV LED chip coated with RGB tricolor phosphor. These methods enable improvement of CRI but at the cost of complicating the fabrication technology (more components of RGB LED, requiring different driving current) or relatively low efficiency in the case of UV-excited tricolor phosphor LEDs. In addition, lack of efficient red emitting phosphor limits its applicability which makes these methods less popular [1-8].

It was found that Dy$^{3+}$ doped nanophosphors have received lot of interest in white light emitting because Dy$^{3+}$ ions emit two characteristic bands at 483 (\(^{4}F_{9/2} \rightarrow ^{6}H_{15/2}\), blue) and 574 nm (\(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\), yellow) [9, 10]. Changing the content of Dy$^{3+}$ and/or material composition, one can adjust its Y/B luminescence intensity ratio to a perfect value for white light emission [11]. For getting pure white light emission, Dy$^{3+}$/Ce$^{4+}$ [12], Dy$^{3+}$/Eu$^{3+}$ [13], and Dy$^{3+}$/Tm$^{3+}$ [14, 15] co-doped systems were investigated. In addition, the energy transfer phenomena between Tb$^{3+}$ and Dy$^{3+}$ [16, 17], Tm$^{3+}$ and Dy$^{3+}$ [15, 18], and Eu$^{2+}$ and Dy$^{3+}$ [19] were reported. To the best of our knowledge, no reports are available on generation of white light and energy transfer between Dy$^{3+}$ and Eu$^{3+}$ ions in Dy$^{3+}$/Eu$^{3+}$ co-doped Y$_2$SiO$_5$ (YSO).

Silicate family was an attractive class of materials among inorganic phosphors for wide range of applications due to their special properties such as water, chemical resistance and visible light transparency. Also, they show superior properties due to thermal stability, wide energy band gap, low cost, non-toxicity, chemical resistance, high temperature strength, low thermal expansion and high conductivity, multicolor phosphorescence, high resistance to acid, alkali and oxygen [20]. Among silicate
phosphors, Y\textsubscript{2}SiO\textsubscript{5} doped with rare earth ions were studied extensively in display applications [21]. Synthesis of crystalline Y\textsubscript{2}SiO\textsubscript{5} phosphor were challenging because of its high crystalline temperature [22]. Typically, solution combustion synthesis (SCS) involves a self-sustained reaction in solutions of metal nitrates and different fuels. Further, SCS contribute to the unique properties of the synthesized products. This technique is capable of producing ultra fine powders of silicates in shorter time and at a lower calcination temperature. This process provides molecular level of mixing and high degree of homogeneity, short reaction time that leads to reduction in crystallization temperature and prevents from segregation during heating [23].

In the present work, Dy\textsuperscript{3+} single doped Y\textsubscript{2}SiO\textsubscript{5} phosphor and Dy\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped phosphors with various Eu\textsuperscript{3+} ions concentrations were synthesized by solution combustion method. The energy transfer phenomenon from Dy\textsuperscript{3+} to Eu\textsuperscript{3+} in Y\textsubscript{2}SiO\textsubscript{5}:Dy\textsuperscript{3+}, Eu\textsuperscript{3+} phosphors was validated and the energy transfer mechanism was discussed in detail.

4.2.2. Results and discussion

4.2.2.1. Powder X-ray diffraction (PXRD) studies

Fig. 4.2.1 (a & b) shows the PXRD patterns of Y\textsubscript{2}SiO\textsubscript{5}:Dy\textsuperscript{3+} (1–9 mol %) and Y\textsubscript{2}SiO\textsubscript{5} : Dy\textsuperscript{3+} (5 mol %): Eu\textsuperscript{3+} (0.5- 5.5 mol %) calcined at 1000 °C for 3h, synthesized by solution combustion technique using urea and NaCl as fuel and flux respectively. All the X-ray diffraction peaks of the sample show a monoclinic phase with X1 type Y\textsubscript{2}SiO\textsubscript{5} and was in good agreement with JCPDS card no. 41-0004 [24] (with phase group P\textsubscript{2}1/C n.14). The lattice parameters and unit cell volume for monoclinic Y\textsubscript{2}SiO\textsubscript{5} (X1) was estimated using the equation (2.6) [25] and equation (3.2.1).The estimated values of lattice parameters were found to be 3.78 Å and 414.84 Å\textsuperscript{3} respectively. Further, no diffraction peaks from other impurities detected indicating that ions were homogeneously mixed and effectively doped in the host lattice in Y\textsuperscript{3+} sites. The average crystallite size (D) was estimated from the line broadening in X-ray powder using Scherrer’s equation (2.8) and the values were found to be in the range 25-50 nm.
Fig. 4.2.1. (a) PXRD patterns of undoped and (1-9 mol %) Dy$^{3+}$ doped Y$_2$SiO$_5$.

Fig. 4.2.1. (b) PXRD patterns of 5 mol % Dy$^{3+}$:Eu$^{2+}$ (0.5-5.5 mol %) doped.
Further, strain present in the Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) and Y$_2$SiO$_5$: Dy$^{3+}$ (5 mol %): Eu (0.5-4.5) nanoparticles prepared by combustion method was calculated using the W-H plots equation (2.9) [26]. The graph between ‘4sinθ’ (x-axis) and ‘βcosθ’ (y-axis) shown in Fig. 4.2.2 (a & b). The slope of the line gives the strain and intercept of this line on y-axis gives grain size (D). The detail values were given in Table 4.2.1.

![Graph showing W-H plots for different concentrations of Dy$^{3+}$ and Eu$^{3+}$ doped Y$_2$SiO$_5$](image)

**Fig. 4.2.2.** (a) W-H plots of un-doped and (1-9 mol %) Dy$^{3+}$ doped Y$_2$SiO$_5$. (b) W-H plots of 5 mol % Dy$^{3+}$: Eu$^{3+}$ (0.5-5.5 mol %) doped Y$_2$SiO$_5$.

**Table 4.2.1.** Estimated parameters of Y$_2$SiO$_5$: Dy$^{3+}$:Eu$^{3+}$ nano phosphors.

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</table>
4.2.2.2. Morphological studies

The surface morphology of pure, Dy$^{3+}$ (1–9 mol %) and Dy$^{3+}$ (5 mol %): Eu (0.5-4.5) Y$_2$SiO$_5$ nanophosphors prepared via combustion method was studied (Fig.4.2.3).

Fig.4.2.3. SEM pictures of pure (a-c), Dy$^{3+}$ (1–9 mol %), (d-i) and Dy$^{3+}$ (5 mol %): Eu (0.5-4.5) (j-o) Y$_2$SiO$_5$ nanophosphors.
Combustion derived as formed $Y_2SiO_5$ product showed highly porous, many agglomerates with an irregular morphology, large voids, cracks, pores and shape. Further, the dopant concentration does not influence the morphology of the sample [21].

TEM studies were carried out to understand the crystalline characteristics of the nanoparticles. Fig. 4.2.4 (a-c) illustrates the TEM, HRTEM and SAED images of 5 mol % $Dy^{3+}$ doped $Y_2SiO_5$ nanoparticles. The particles were observed to be irregular shaped, highly dispersed and the average size was found to be in the range 20-50 nm. The selected area electron diffraction (SAED) image provide distinct ring pattern which was evidence for the polycrystalline behavior of the as-prepared nanoparticles. Further, a well-defined lattice fringes obtained by high resolution TEM (HRTEM) pattern reveal the formation of highly crystalline nanophosphor [27]. Fig.4.2.5. show TEM, (b) HRTEM, (c) SAED patterns of $Y_2SiO_5$: $Dy^{3+}$ (5 mol %):$Eu^{3+}$ (3.5 mol %).

**Fig.4.2.4.** (a) TEM, (b) HRTEM, (c) SAED patterns of $Y_2SiO_5$: $Dy^{3+}$ (5 mol %)

**Fig.4.2.5.** (a) TEM (b) HRTEM (c) SAED patterns of $Y_2SiO_5$: $Dy^{3+}$ (5 mol %):$Eu^{3+}$ (3.5 mol %)
4.2.2.3. Photoluminescence (PL) studies

Fig. 4.2.6 shows the excitation spectra of $\text{Y}_2\text{SiO}_5$: $\text{Dy}^{3+}$ (5 mol %) and $\text{Y}_2\text{SiO}_5$:Dy$^{3+}$ (5 mol %): Eu$^{3+}$ (3.5 mol %) nanophosphors with emission wavelength 575 nm. The spectra consists of series of excitation peaks at 388, 423, 451, 468 nm correspond to the electron transitions of Dy$^{3+}$ from the ground state $^6\text{H}_{15/2}$ to higher levels $^4\text{I}_{13/2}$, $^4\text{G}_{11/2}$, $^4\text{I}_{15/2}$ and $^4\text{F}_{9/2}$, respectively [28].

![Excitation spectra of (5 mol %) Dy$^{3+}$ and 5 mol% Dy$^{3+}$:Eu$^{3+}$ (3.5 mol %) doped Y$_2$SiO$_5$ nanophosphors emission at 575 nm.](image)

The emission spectra of $\text{Y}_2\text{SiO}_5$: Dy$^{3+}$ (1-9 mol %) nanophosphor excited at 388 nm was shown in the Fig. 4.2.7. The PL spectra consist of three main peaks in blue 485 nm, yellow 575 nm and red 636 nm region. Upon 388 nm wavelength excitation, Dy$^{3+}$ ions jumps resonantly to $^6\text{P}_{7/2}$ state and quickly releases non-radiatively to $^4\text{F}_{9/2}$ level. Radiative emission takes place from $^4\text{F}_{9/2}$$\rightarrow$$^6\text{H}_{15/2}$ (485 nm, blue), $^4\text{F}_{9/2}$$\rightarrow$$^6\text{H}_{13/2}$ (575 nm, yellow) and $^4\text{F}_{9/2}$$\rightarrow$$^6\text{H}_{11/2}$ (636 nm, red). The blue emission corresponds to the magnetic dipole transition and the yellow emission belongs to the hypersensitive (forced electric dipole) transition with the selection rule $\Delta\text{J}=2$ [29-31]. It was observed that PL intensity increases up to 5 mol % Dy$^{3+}$ ions and above this intensity decreases due to concentration quenching. The increase in PL intensity was due to cross relaxation between Dy$^{3+}$ ions, consequently with increasing Dy$^{3+}$ concentration the generation of luminescent centers increases as a result PL intensity enhances. The
decrease of PL intensity may be due to creation of point defects due to imbalance charges.

**Fig. 4.2.7.** Emission spectra of 5 mol% Y$_2$SiO$_5$: Dy$^{3+}$: Eu$^{3+}$ (0.5-4.5 mol %) excited at 393 nm

Fig 4.2.7 shows the prominent emission peaks at 485, 583 and 612, 651, 688, 702 nm was observed from the PL spectra of Y$_2$SiO$_5$: 5 mol% Dy$^{3+}$, Eu$^{3+}$(x) (x= 0.5, 1.5, 2.5, 3.5, 4.5 and 5.5 mol%) phosphors excited at 393 nm. The peaks at 485, 583 and 688 nm corresponding to the transitions of Dy$^{3+}$ ions, and others are assigned to the transitions of Eu$^{3+}$ ions. It is clear that the introduction of Eu$^{3+}$ to the Y$_2$SiO$_5$: 5 mol% Dy$^{3+}$ added several regions of characteristic emissions located at red region 612 ($^5$D$_0$ $\rightarrow$ $^7$F$_2$), 651 ($^5$D$_0$ $\rightarrow$ $^7$F$_3$) and 702 nm ($^5$D$_0$ $\rightarrow$ $^7$F$_4$) [32]. With increase of Eu$^{3+}$ ions concentration the cross-relaxation between two neighboring Eu$^{3+}$ ions takes place and hence it quenches the emission intensity. The concentration quenching might be explained on the basis of following two factors: (i) the excitation migration due to resonance between the activators was enhanced when the doping concentration was increased, and thus the excitation energy reaches quenching centers, and (ii) the Eu$^{3+}$ concentration and reaches a maximum value at Eu$^{3+}$ concentration of 3.5 mol % accompanied by the intensity decrease of the Dy$^{3+}$ blue emission after 1.5 mol % of Eu$^{3+}$. The comparable emission intensities for blue, yellow and red emissions were achieved at 1.5 mol % Eu$^{3+}$ concentration. Further it was observed that the emission intensity of 3.5 mol % Eu$^{3+}$ was greater than that of 5 mol % Dy$^{3+}$ which clearly
explains energy transfer between the activators. Therefore the co-doped phosphors were highly efficient and white light was possible to be combined by properly designing the doping concentrations of Eu\(^{3+}\) and Dy\(^{3+}\) [35].

4.2.2.4. Energy transfer between Dy\(^{3+}\) and Eu\(^{3+}\) in Dy\(^{3+}\)/Eu\(^{3+}\) co-doped YSO nano phosphors.

To examine the energy transfer mechanism from Dy\(^{3+}\) to Eu\(^{3+}\) in Y\(_2\)SiO\(_5\), the concentration of the Dy\(^{3+}\) was fixed at the optimum doping of 5 mol % with a changing amount of Eu\(^{3+}\). It was obvious that the emission intensity of Dy\(^{3+}\) decreases gradually with the increasing Eu\(^{3+}\) concentration. In the interim, the characteristic emission of Eu\(^{3+}\) ions increases gradually, which further supports the occurrence of the energy transfer from Dy\(^{3+}\) to Eu\(^{3+}\) in Y\(_2\)SiO\(_5\) host.

The equivalent energy levels diagram and the probable optical transition which was involved in the energy transfer processes from Dy\(^{3+}\) to Eu\(^{3+}\) was described in Fig. 4.2.8. Upon excitation at 393 nm, the photon energy was absorbed by the host and was transferred to 4f shell of Dy\(^{3+}\) and Eu\(^{3+}\). Thus, the electrons of Dy\(^{3+}\) at \(^4\)F\(_{9/2}\) and Eu\(^{3+}\) at \(^5\)D\(_0\) excited state populates both from the nonradiative charge feeding and nonradiative transitions from higher excited states, then emit their characteristic light, respectively. On the other hand, the photon energy was absorbed by Dy\(^{3+}\) ions inducing the transitions from ground state to the metastable states that were low, and part of the excited electrons in these metastable excited states were repopulated into \(^4\)F\(_{9/2}\) level by multi phonon assisted nonradiative transitions [35]. The transitions from \(^4\)F\(_{9/2}\) to \(^6\)H\(_j\) (j = 15/2, 13/2, 11/2) were radiative and produce the emission lines of 485 nm and 583 nm, respectively. Huang and Lou et al. [36] proposed that concentration quenching in many cases was due to the energy transfer from one activator to another until an energy drop in the lattice was reached. As suggested by Blasse, the average separation R\(_{\text{Dy-Eu}}\) can be expressed by equation (3.2.4) [37]. In this equation N ; the number of Z ions in the unit cell, and V ; the volume of the unit cell. For Y\(_2\)SiO\(_5\) host, N = 4 and V = 289 Å\(^3\), Xc ; the total concentration of the doping content of the Dy\(^{3+}\) and Eu\(^{3+}\). Thus, the critical concentration R\(_{\text{Dy-Eu}}\) (Rc) was determined to be 15.76 Å when the 612 nm emission reaches to the maximum value at the Eu\(^{3+}\) doping concentration of 3.5% hence, the mechanism of exchange interaction was ineffective. As a result, the process of energy transfer of would be due to electric multipolar interaction. Partial energy level diagram of Dy\(^{3+}\) and Eu\(^{3+}\) ions are shown in the
Fig. 4.2.8. Multipolar interaction involves several types of interaction such as dipole-dipole (d-d), dipole-quadrupole (d-q), quadrupole-quadrupole (q-q) interaction.

The type of interaction involved in the energy transfer between Dy\(^{3+}\) and Eu\(^{3+}\) can be understood using Van-Uitert’s equation [38]. According Van-Uitert’s equation, Q=3 for the energy transfer among the nearest neighbor ions, while Q = 6, 8 and 10 for d-d, d-q and q-q interactions respectively [39, 40]. Assuming that β(X)\(^{0/3}\)>>1, From equation (4.1.2), the multipolar character (θ) can be obtained by plot log (I/X) vs log (X) as shown in Fig. 4.2.9 (a & b). The multipolar character Q for 5 mol% Dy\(^{3+}\): Eu\(^{3+}\) (0.5- 4.5 mol%) and Y\(_2\)SiO\(_5\): Dy\(^{3+}\) (1- 9 mol%) was calculated using equation (4.1.2) and found to be ~ 7.016 and 7.30 which was close to 8. Therefore, the in both the cases mechanism of interaction was due to dipole-quadrupole interaction.

The Commission International De I-Eclairage (CIE) chromaticity coordinates [34] for Y\(_2\)SiO\(_5\): Dy\(^{3+}\) (1-9 mol %) and Y\(_2\)SiO\(_5\): Dy\(^{3+}\) (5 mol %): Eu\(^{3+}\) (0.5- 4.5 mol %) phosphors was calculated as a function of Dy\(^{3+}\) concentration (Fig. 4.2.9 (a &b)). The CIE coordinates of white emission of Dy\(^{3+}\) ions not only depend upon the asymmetric ratio but also on the higher energy emission levels. It was observed that in both the cases the CIE co-ordinates falls in white region which clearly represents both the phosphors can be used for white light emitting diodes (WLEDs) and solid state lighting devices.
Fig. 4.2.9. (a) The relation between log(x) and log (I/x) in Y$_2$SiO$_5$: 5mol% Dy$^{3+}$:Eu$^{3+}$ (0.5-4.5 mol %) nanophosphors. (b) Relation between log(x) and log (I/x) in Y$_2$SiO$_5$:Dy$^{3+}$ (1-9 mol %) nanophosphors.

Correlated color temperature (CCT) can be estimated by Planckian locus, which was only a small portion of the (x, y) chromaticity diagram and there exist many operating points outside the Planckian locus. CCT was used to define the color temperature of a light source. CCT was obtained by transforming the (x, y) coordinates of the light source to (U’, V’) by using equations (3.2.6) and (3.2.7) [41, 42]. Fig. 4.2.11(a & b) shows the CCT diagram of Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) and Y$_2$SiO$_5$: Dy$^{3+}$ (5 mol %):Eu$^{3+}$ (0.5-4.5 mol %) nanophosphors. The average CCT values for Y$_2$SiO$_5$: Dy$^{3+}$ (1-9 mol %) and Y$_2$SiO$_5$: Dy$^{3+}$ (5 mol %):Eu$^{3+}$ (0.5-4.5 mol %) nanophosphors found to be 5740 and 4308 K respectively. Further, it was observed that in both the cases CCT falls on the Planckian locus and indicates warm white light emission and hence phosphors could be potentially used in white light emission displays and near ultraviolet pumped white LEDs [43].
**Fig. 4.2.10.** (a) CIE diagram of Y$_2$SiO$_5$:Dy$^{3+}$ (1-9 mol %) nanophosphor. [Inset (x,y) co-ordinate values]. (b) CIE diagram of 5 mol% Dy$^{3+}$: Eu$^{3+}$ (0.5-4.5 mol %) nanophosphor. [Inset (x,y) co-ordinate values].

**Fig. 4.2.11.** (a) CCT diagram of Y$_2$SiO$_5$:Dy$^{3+}$ (1-9 mol %) nanophosphor. (b) CCT diagram of 5 mol% Dy$^{3+}$: Eu$^{3+}$ (0.5-5.5 mol %) nanophosphor. (Inset: U', V' values used for the calculations of CCT)
4.2.3. Conclusions

Single-phased white light emitting $Y_2SiO_5$: Dy$^{3+}$ and YSO: 5mol% Dy$^{3+}$, (x) Eu$^{3+}$ were prepared by the solution combustion method. Further, the calcinations temperature of $Y_2SiO_5$ was less (1000 °C) when compared to solid state route. PXRD results of calcined samples at 1000 °C show pure monoclinic X1 phase. It was found that doping Eu$^{3+}$ can enhance the red emission of the sample. The energy transfer from Dy$^{3+}$ to Eu$^{3+}$ was observed through the combination of the PLE and PL spectra. The CIE chromaticity coordinates and CCT value for both doped and co-doped phosphors suggested that the emission color of the obtained sample can be tunable from white to reddish by simply adjusting the amount of Eu$^{3+}$ ions which indicates that the phosphors could be potentially used in white light emission displays and near ultraviolet pumped white LEDs.
References


4.3 Spectroscopic and Luminescence studies of Ce$^{3+}$ doped Y$_2$SiO$_5$ nano-phosphors using *calotropis gigantea* as fuel

**4.3.1. Introduction**

Many syntheses of nanoparticles have been developed in recent years to produce nanostructures that have a specific form and function relevant to a given application. The preparation of functionalized nanoparticles within a green context poses interrelated challenges in terms of maintaining product integrity such as structure, shape and size dispersity, functionality, purity, and stability while employing greener methods whenever possible. Many preparations of the building blocks of nanotechnology involve hazardous chemicals, low material conversions, high energy requirements, and difficult, wasteful purifications; thus, there are multiple opportunities to develop greener processes for the manufacture of these materials. Many of the green chemistry principles apply readily to the synthesis or production of nano scale materials. Green chemistry provides a number of advantages in process development and manufacturing as well as product design. Some progress toward greener nano synthesis has already been made. For example, a more efficient and less hazardous synthesis of metal nanoparticles has been developed, producing greater amounts of particles, in less time, under milder conditions, while using less hazardous reagents than the traditional preparation. Metal nanoparticles have been synthesized using intact organisms, such as living plants and microorganisms. The potential of plants as biological materials for the synthesis of nanoparticles is not yet to be fully explored. Nanoparticles are a topic of extensive research due to their unique applications in many areas, especially in the area of luminescence (i.e., nanophosphors) [1–7].

In current years, white light-emitting diodes (WLEDs) have attracted a lot of attention in the solid state lighting, because of their high efficiency, energy saving, long lifetime, safety and environmental protection[8,9]. The governing technique to obtain white light is combine ultraviolet (UV) LED chip with tricolor phosphors [10]. Y$_2$SiO$_5$: Ce$^{3+}$ is a blue emitting phosphor and has been studied by many physicists in order to understand the luminescent behavior for application in the lighting industry (such as field emission displays, FEDs). From the literature it is found that Y$_2$SiO$_5$:Ce$^{3+}$ has two different monoclinic crystal structures. A low temperature (synthesized at temperatures less than 1190 °C) X1 phase (much weaker luminescent intensity [11], with space group P$_{21}$c) and a high temperature (synthesized at temperatures above 1190 °C with a melting temperature at 1980 °C)
X2 phase (space group B_{2/c}). In each of these two phases there are two possible Y^{3+} sites in the Y_{2}SiO_{5} matrix [12, 13]. These two sites are attributed to the difference in coordination numbers (CN). During the preparation method of Y_{2}SiO_{5}: Ce^{3+} the activator Ce^{3+} (radius of 0.106nm) can easily substitute for Y^{3+} (radius of 0.093nm) thus also resulting in the two different crystallographic sites. The notations A1 and A2 are given to the two sites in the X1 phase with CN of 9 and 7. B1 and B2 are denoted for the X2 phase with CN of 6 and 7. A1 with the CN of 9 means that there are 8 oxygens bonded to yttrium and silicon and only 1 that is bonded to only yttrium. CN of 7 means that 4 oxygens are bonded to yttrium and silicon and 3 are bonded to only yttrium. Both B1 and B2 have two oxygen atoms that are only bonded to yttrium [14, 15]. The phosphor used in this study is the X1 phase as indicated by the XRD results (not shown here) and emission spectra [16]. Luminescence in Y_{2}SiO_{5}: Ce^{3+} occurs due to characteristic transitions (in the Ce^{3+} ion itself). Y_{2}SiO_{5} has a wide bandgap of about 7.4eV (insulator) so doping it with an activator such as Ce^{3+} creates an energy level structure inside the wide band gap where the 5d to 4f transition takes place. Splitting of the 4f energy level into the \(^2\text{F}_{5/2}\) and \(^2\text{F}_{7/2}\) energy levels is due to the 4f1 electron in Ce^{3+} [17, 18].

Among these methods, solution combustion synthesis has an edge over other methods as it is considered as simple, instantaneous, single-step and energy saving [18]. Most of the wet chemical routes utilize high temperatures and many of the reactants, starting materials; stabilizers and solvents used in these methods are toxic and potentially hazardous. Therefore, plant based bio-mediated synthetic routes are almost hazard-free and at the same time economically viable and environmental friendly. We already have reported the potential application of Euphorbia tirucalli green mediated route for the synthesis of Eu^{3+} doped Gd_{2}O_{3} NSs, Phyllanthus acidus bio-mediated route for the synthesis of Fe doped ZrO_{2} photocatalysts and Calotropis bio-mediated route for the synthesis of Eu^{3+} activated La(OH)_{3} and La_{2}O_{3} red nanophosphors [19-21]. Hence, for sustainable development of nanotechnology, ecofriendly approaches and green routes should be rapidly explored [22]. In view of this, Calotropis gigantea (C. gigantea) has been chosen as plant latex in present investigation. It belongs to Apocynaceae a large shrub growing with cluster of waxy flowers that are either lavender or white in color. The plant contains cardiac
glycosides, β-sitosterol, madrine, saponins, alkaloids, tannins, trisecharoides and flavonols [23].

Based on the above discussions, the present investigation explores bio-mediated synthesis of \( \text{Y}_2\text{SiO}_5: \text{Ce}^{3+} \) (0.5 - 7 mol %) red nanophosphors by utilizing \( \text{C. gigantea} \) latex as fuel and NaCl as flux for the first time. Emissions of Ce\(^{3+}\) ions can be tuned in the blue spectral regions due to the \( ^5\text{D}_0 \to ^7\text{F}_2 \) transitions which would be useful to obtain white-light emission. Further, the nanophosphors were characterized by PXRD, SEM, TEM, FTIR, Raman and UV-Visible spectroscopic techniques, and the CIE coordinates and CCT values were investigated in detail.

4.3.2. Results and discussion

4.3.2.1. Powder X-ray diffraction (PXRD)

Fig.4.3.1. Shows the PXRD patterns of \( \text{Y}_2\text{SiO}_5: \text{Ce}^{3+} \) (0.5-7 mol %) synthesized nanophosphors calcined at 1000°C by solution combustion technique using \( \text{Calotropis gigantea} \) as fuel. All the PXRD patterns of the samples matched with the monoclinic phase of X1 type \( \text{Y}_2\text{SiO}_5 \) having a phase group \( \text{P}2_1/\text{c} \ n. 14 \) and are in good agreement with JCPDS card no. 41-0004 [24]. As the concentration of Ce\(^{3+}\) ions in \( \text{Y}_2\text{SiO}_5 \) increases, no shift in diffraction peaks and no secondary phases were detected indicating that Ce\(^{3+}\) ions are homogeneously mixed and effectively doped in the host lattice in \( \text{Y}^{3+} \) sites. With increase in the concentration of Ce\(^{3+}\) ion from 0.5 to 7 mol %, the intensity of the diffraction peaks increases and crystallization proceeds along (013) plane (Fig. 1b). The lattice parameters and unit cell volume for monoclinic phase were estimated using the equation (3.2.1). The estimated lattice parameters were found to be 3.76 Å and 53.15 Å\(^3\) respectively. When the particle size was less than 100 nm, appreciable broadening was observed in the X-ray diffraction patterns. The observed line broadening can be used to calculate the average particle size of the phosphor [25]. The average crystallite size is estimated using Scherrer’s equation (2.8) and W-H plots equation (2.9) [20].
The average crystallite size (D) was estimated in accordance with Scherrer’s formula using full width at half maximum (FWHM) data $D = \frac{k\lambda}{\beta\cos\theta}$. Where $k$; constant (shape factor, about 0.90); the X-ray wavelength (0.15418 nm); the full width at half maximum (FWHM) of the diffraction line and the diffraction angle. The FWHM can be expressed as a linear combination of micro strain and the crystallite size. The effects of microstrain and crystallite size on the FWHM can be expressed by the Williamson–Hall (W-H) plots:

$$\beta\cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin\theta$$

where ‘$\beta$’; the measured FWHM (in radians), ‘0’; the Bragg angle of the peak, ‘$\lambda$’; the X-ray diffraction wavelength, ‘$\varepsilon$’; the strain associated with the NPs. The above equation represents a straight line between $4\sin\theta$ (X-axis) and $\beta\cos\theta$ (Y-axis) of the nanophosphors.

Fig. 4.3.2 shows the W-H plots of $Y_2SiO_5$: $Ce^{3+}$ (0.5-7 mol %) nanophosphors, the slope of line give the strain ($\varepsilon$) and intercept (0.9$\lambda$/D) of this line on Y-axis gives crystallite size (D). The crystallite size of $Y_2SiO_5$: $Ce^{3+}$ (0.5-7 mol %) nanophosphors were found to vary from 33-36 nm and 32-36 nm by Scherrer’s and W-H plots method respectively shown in Table 4.3.1.
The small variation in the values were due to the fact that in Scherrer’s formula, strain component was assumed to be zero and observed broadening of diffraction peak was considered as a result of reducing grain size only. The strain was continues to increase with increase in Ce$^{3+}$ion concentration.

**Table 4.3.1.** Estimated crystallite size (Scherrer’s formula and W – H method) and strain $Y_2SiO_5$: Ce$^{3+}$ (0.5 - 7 mol %) nanophosphors.

<table>
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<th>Strain x10$^{-3}$</th>
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4.3.2.2. Morphological studies

Fig 4.3.3 shows SEM images of $Y_2SiO_5$:Ce$^{3+}$ (0.5-7 mol %) nanophosphors. The surface morphology of $Y_2SiO_5$:Ce$^{3+}$ nanophosphors exhibit irregular shape. As the concentration of Ce$^{3+}$ increases, agglomeration of the particles also increases. No change in the shape of NPs was observed with increase in dopant concentration. The agglomeration of particles was generally depends on reaction rate, impurities, charges on the particles etc.

Fig. 4.3.3. SEM images of (a) pure $Y_2SiO_5$ and $Y_2SiO_5$:Ce$^{3+}$ (b & c) 1 mol %, (d - f) 3 mol %, (g - i) 5 mol %, (j - l) 7 mol %, nanophosphors.
4.3.2.3 FTIR analysis

The FTIR spectra of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ (0.5-7 mol %) nanophosphors were recorded in order to interpret the structures of the obtained nanophosphors (Fig. 4.3.4).

![FTIR spectra](image)

**Fig. 4.3.4.** FTIR spectra of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ (0.5 - 7 mol %) nanophosphors

The effect of substitution of dopant and the phase formation of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$, FTIR spectra for different mol concentration was recorded. The YSO: $\text{Ce}^{3+}$ exhibit peaks in the range locating at 682, 721, 845, 971, 2107 and 2273 cm$^{-1}$. The 560 and 713 cm$^{-1}$ band can be assigned to characteristic metal–oxygen (Y–O) vibrations. The band at 680 cm$^{-1}$ was due to Si–O ($v_3$) stretching mode. The remaining peaks located at 830, 887, 960, 1050, 2100 and 2291 cm$^{-1}$ can be associated to (Si-O-Si), $v_1$(Si-OH), (CH & NO$_3$) and 2$v_3$(Si-O) respectively. Slight deviation in vibrational frequencies and intensities of bands were observed with variation in concentration of $\text{Ce}^{3+}$ions in $\text{Y}_2\text{SiO}_5$ matrix.

4.3.2.4. UV-Visible absorption analysis

UV–Vis absorption spectra of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ (0.5 -7 mol %) nanophosphors were shown in inset Fig.4.3.5. The absorbance spectra of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ (0.5 -7 mol %) NPs in transmission mode were recorded by distributing the particles uniformly in liquid.
paraffin, in the wavelength range of 200-800 nm. The absorption spectrum shows prominent absorption peak at 205, 277 and 368 nm. The weak absorption band at nearly 350 nm region was expected to arise from transitions involving extrinsic states such as surface traps / defect states / impurities [19].

Another absorption peak observed at 368 nm was due to $5d-4f$ absorption transition of Ce$^{3+}$. These absorption peaks were slightly shifted towards higher wavelength region indicating the decrease in energy band gap with increase in Ce$^{3+}$ ion concentration. Smaller sized particles were found to have high surface to volume ratio. This results in increase of defects distribution on the surface of nano materials. Thus, if the particle size was small; nano materials exhibit strong and absorption bands [20]. In Y$_2$SiO$_5$: Ce$^{3+}$ NPs, the particles size was in nanometer which results in high surface to volume ratio as a result there was an increase in defects distribution on the surface of the nano materials.

For estimation of band gap in the nano materials, the absorbance spectra of Y$_2$SiO$_5$: Ce$^{3+}$ (0.5 -7 mol %) NPs in transmission mode were recorded in the wavelength range of 200-800 nm. For a direct band gap, the absorption coefficient near the band edge was given by equation 4.1.1 (Wood and Tauc’s relation) [28]. Fig.4.3.6 shows the Wood and Tauc’s plot from which the direct band gap was obtained in the range of 4.87 eV.
A reduction in $E_g$ for doped samples would arise neither from a quantum size effect nor from crystal structure variation but rather from surface traps states or point defects. A plausible explanation for the variations observed on the $E_g$ values can be related to the degree of structural order–disorder into the lattice, which is able to change the intermediary energy-level distribution within the band gap. The $E_g$ values mainly depend on the preparation methods and the experimental conditions. In particular, these key factors can favour or inhibit the formation of structural defects which are able to control the degree of structural order–disorder of the material and consequently, the number of intermediary energy levels within the band gap. It was observed that the absorption measurements were extremely sensitive to the changes in the lattice or variations on the structural order–disorder degree [29].

### 4.3.2.5. Photoluminescence studies

Fig. 4.3.7 presents the RT excitation spectrum of $Y_2SiO_5: Ce^{3+}$ (5 mol %) nanophosphors by monitoring the emission wavelength at 433 nm. The narrow peaks located at wavelength range 360 – 500 nm can be assigned to the $f$-$f$ transitions of $Ce^{3+}$ ions. The $f$-$f$ transitions of $Ce^{3+}$ ions at 388 ($^5D_3 \rightarrow ^7F_6$) 433 nm ($^5D_3 \rightarrow ^7F_4$) and 488nm ($^5D_4 \rightarrow ^7F_6$) Among these transitions, $^5D_3 \rightarrow ^7F_4$ is the most intense peak which finds the application in commercially available near UV GaN – based LED chips [30].
Fig. 4.3.7. PL excitation spectrum of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ (5 mol %) nanophosphor

Fig. 4.3.8. PL emission spectrum of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ (0.5 - 7 mol %) nanophosphors ($\lambda_{\text{ex}} = 370$ nm)

Fig. 4.3.8 shows the PL emission spectra of $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ (0.5 - 7 mol %) nanophosphors at 370 nm excitation. It was obviously seen that maximum emission intensity of the $\text{Y}_2\text{SiO}_5$: $\text{Ce}^{3+}$ phosphor appears at 1 mol %. When the $\text{Ce}^{3+}$ doping concentration was higher than 1 mol%, the luminescence intensity reduces contrarily owing to the concentration quenching effect. The dopant concentration that determines the average distance between the two neighboring activator ions has a
great impact on the PL efficiency in RE$^{3+}$ ions doped nano crystals. High doping concentration of Ce$^{3+}$ ions in Y$_2$SiO$_5$ nanocrystals may bring about deleterious cross relaxations between the adjacent Ce$^{3+}$ ions, resulting in the quenching of excitation energy and there by fewer luminescence of Ce$^{3+}$ ion. Therefore, the optimum dopant concentration of Ce$^{3+}$ in Y$_2$SiO$_5$: Ce$^{3+}$ phosphor was about 1 mol %. The concentration quenching occurs due to the energy transfer from one activator to the neighboring ion. The critical distance for energy transfer ($R_c$) in Y$_2$SiO$_5$: Ce$^{3+}$ was estimated from the structural parameters namely unit cell volume (V), total Ce$^{3+}$ sites per unit cell (N) and critical concentration ($X_c$) energy transfer from one activator to the neighboring ion using an equation (3.2.4). For the Y$_2$SiO$_5$: Ce$^{3+}$ system, N = 4, V = 53.15 Å$^3$ and $X_c = 0.01$. The $R_c$ of Ce$^{3+}$ ions in Y$_2$SiO$_5$ were found to be 7.98 Å. When critical energy distance between Ce$^{3+}$ ion in Y$_2$SiO$_5$ is greater than 5 Å, the overlapping between excitation and emission spectra decreases. The energy transfer between Ce$^{3+}$ ion take places due to electric multipolar interaction which can be determined by the equation (3.2.3). In this equation $X$; Ce$^{3+}$ ion concentration, k and b; constants, $Q = 6, 8$ and $10$ for dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions. The value of $Q$ is determined by plotting log $(X)$ versus log $(I/X)$ (Fig. 4.3.10) which gives a linear graph having a slope = -0.9642 and intercept = 7.1. The $Q$ value is close to 3 indicates that the concentration quenching in Y$_2$SiO$_5$ is due to exchange of interaction.

![Fig.4.3.9. Variation of PL Intensity with Concentration](image_url)
Fig. 4.3.10. Plot of log (I/X) Vs log x of Y$_2$SiO$_5$: Ce$^{3+}$ (0.5 - 7 mol %) nanophosphors.

Fig. 4.3.11. CIE chromaticity diagram (Inset: Chromaticity coordinates of Y$_2$SiO$_5$: Ce$^{3+}$ (0.5-7 mol %) nanophosphors.

Fig. 4.3.11. illustrates the CIE chromaticity diagram estimated from 1931 CIE (International Commission on Illumination) system of Y$_2$SiO$_5$: Ce$^{3+}$ (0.5 - 7 mol %) nanophosphors. The location of CIE coordinates were marked with star in red region. The CIE co-ordinates of Y$_2$SiO$_5$: Ce$^{3+}$ (0.5 - 7 mol %) nanophosphors were tabulated.
in inset Fig. 4.3.9. CIE color coordinates were found to be (0.147, 0.036) which lies in strong red yellow region. To identify technical applicability of this yellow emission, CCT is determined from CIE coordinates (Fig. 4.3 12).

The CCT specify color appearance of the light emitted by a light source, relating its color to the color of light from a reference source when heated to particular temperature. However, lamps with a CCT rating below 3000 K was usually considered as “warm” light source, while those with a CCT above 4000 K is “cool” in appearance. In the present study, the average CCT of $Y_2SiO_5$: Ce$^{3+}$ (0.5 -7 mol %) at 370 nm excitation was found to be 1770 K which lies well within the vertical daylight Thus, the phosphor could be highly useful candidate in white light emitting diodes.

![Diagram](image)

**Fig 4.3.12.** CCT chromaticity diagram (Inset: Chromaticity coordinates) of $Y_2SiO_5$: Ce$^{3+}$ (0.5 - 7 mol %) nanophosphors
4.3.3. Conclusions

In conclusion, a novel Ce³⁺ ion incorporated Y₂SiO₅ nanophosphors were synthesized by eco-friendly and cost effective green mediated route using Calotropis gigantea latex as a fuel and NaCl as a flux. The dependence of Ce³⁺ ion concentration on the phase structure, morphology and luminescence properties of the samples has been investigated in detail. The PL emission spectrum excited under 370 nm showed prominent spectral lines owing to efficient energy transfer between host and Ce³⁺ ions. When the sample containing 1 mol % Ce³⁺, the sample exhibited the strongest emission intensity. Further, the phosphor showed excellent CIE chromaticity coordinates (0.147, 0.036), and average CCT value 1770 K. Hence, this phosphor can find potential application in fabrication of near ultraviolet excited white light emitting diodes.
References


4.4 Spectroscopic and Luminescence studies of Sm$^{3+}$ co-doped Y$_2$SiO$_5$:Ce$^{3+}$ nanophosphors using calotrops gigantea as fuel

4.4.1. Introduction

*Calotrops gigantea* (Crown flower) belongs to family *Apocynaceae*. It is a large shrub growing to 4 m (13 ft) tall. It has clusters of waxy flowers that are either white or lavender in colour. Each flower consists of five pointed petals and a small, elegant "crown" rising from the centre, which holds the stamens. The aestivalation found in colotrops is valvate i.e sepals or petals in a whorl just touch one another at the margin, without overlapping. The plant has oval, light green leaves and milky stem. The latex of *Calotrops gigantea* contains cardiac glycosides, fatty acids, and calcium oxalate.

Since the beginning of civilization, human beings have worshiped plants and such plants are conserved as a genetic resource and used as food, fodder, fibre, fertilizer, fuel, febrifuge and in every other way [1]. *Calotrops gigantea* is one such plant [2]. In ancient ayurvedic medicine the plant *Calotrops gigantea* is known as “Sweta Arka” and *Caotrops procera* as “Raktha Arka”. Both of them are often similar in their botanical aspects and also have similar pharmacological effects [3]. In previous studies the phytochemical constituents in the various parts of *Calotrops gigantea* especially in the leaves such as Usharin, gigantin, calcium oxalate, alpha and beta-calotropoel, beta-amyrrin., fatty acids, hydrocarbons, acetates and the benzoates, a mixture of tetracyclic triterpene compounds, terols, giganteol and giganteol are also found to be present [4-6], Cardenolide calotropin [7], alpha-amyrrin, beta-amyrrin, taraxasterol, beta-sitosterol, alpha-amyrrin methylbutazone, beta-amyrrin methylbutazone, alpha-amyrrin acetate, beta-amyrrin acetate, taraxasteryl acetate, lupeol acetate B, gigantursenyl acetate A, gigantursenyl acetate B [8, 9] flavonol glycoside, akundarol, uscharidin, calotropin, frugoside, calotroposides A to G [10] are responsible for many of its activities. The following cardenolides are also described in the literature: calactin, calotoxin, calotropagenin, proceroside, syriogenine, uscharidin, uscharin, uzarigenin and voruscharin [11-18]. Due to the presence of these components, the plants are resistant to phytopathogens and insects mainly in leaves where the latex circulates abundantly. The milky latex of the plant is rich in lupeol, calotropin, calotoxin, and uscharidin, the latex protein.
4.4.2 Results and discussion

4.4.2.1 Powder X-ray diffraction (PXRD)

Fig. 4.4.1 shows the PXRD patterns of 1000 °C calcined for 3 hr solution combustion synthesized \( \text{Y}_2\text{SiO}_5: \text{Ce}^{3+} \) (1 mol\%) and \( \text{Y}_2\text{SiO}_5: \text{Ce}^{3+}(1.0 \text{ mol\%}):\text{Sm}^{3+} \) (0.2–1 mol\%) nanophosphors. The diffraction peaks corresponded to monoclinic phase with \( \text{X1} \) type \( \text{Y}_2\text{SiO}_5 \) having a phase group \( \text{P2}_1/\text{C} \) n.14 and are in good agreement with JCPDS card no. 41-0004[19]. The particle size was estimated from the XRD peaks by using Debye Scherer’s equation (2.8) [20], \( D = 0.9 \lambda / \beta \cos \theta \) where 0.9 is the shape factor; \( \lambda \) is the wavelength of X-rays and \( \beta \) is full width at half maximum (FWHM) and \( \theta \) is Bragg’s angle. Further, full-width at half-maximum (FWHM) was expressed as a linear combination of lattice strain and crystalline size [21].

![PXRD pattern of \( \text{Y}_2\text{SiO}_5: \text{Ce}^{3+} \) (1.0 mol\%):\Sm^{3+} (0.2–1 mol\%) nanophosphors.](image)

By plotting \( 4\sin \theta \) along x-axis and \( \beta \cos \theta \) along y-axis we get a straight line which is shown in Fig 4.4.2. The slope of the line give the strain evolved due to incorporation of dopant ions and the intercept \((0.9k/D)\) gives the particle size. The particle size estimated by W-H plot equation (2.9) and was found to be in the range 36-38 nm which was approximately equal to the particle size estimated by the Scherrer’s formulae [22]. The particle size and strain component estimated by using Scherrer’s
and W-H plot methods were tabulated in Table. 4.4.1 and it is observed that the particle size increases and strain decreases as $\text{Sm}^{3+}$ co-dopant ion concentration increases.

![Diagram of Y$_2$SiO$_5$:Ce$^{3+}$ (1.0 mol%):Sm$^{3+}$ (0.2–1 mol%) nanophosphors.

**Fig.4.4.2.** W-H plots of Y$_2$SiO$_5$:Ce$^{3+}$ (1.0 mol%):Sm$^{3+}$ (0.2–1 mol%) nanophosphors.

**Table.4.4.1.** Estimated particle size values of Y$_2$SiO$_5$:Ce$^{3+}$ (1.0 mol%):Sm$^{3+}$ (0.2–1 mol%) nanophosphors.

<table>
<thead>
<tr>
<th>Y$_2$SiO$<em>5$:Ce$^{3+}$$</em>{0.1}$:Sm$^{3+}$ (mol %)</th>
<th>Average Particle size $d$ (nm)</th>
<th>Strain x10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scherrer’s Method</td>
<td>W-H Method</td>
</tr>
<tr>
<td>0.0</td>
<td>34</td>
<td>36</td>
</tr>
<tr>
<td>0.2</td>
<td>36</td>
<td>37</td>
</tr>
<tr>
<td>0.4</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>0.6</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td>0.8</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>1.0</td>
<td>36</td>
<td>38</td>
</tr>
</tbody>
</table>
4.4.2.2 Morphological analysis

The structural, topological and surface features of the nanophosphors could be studied in detail by SEM micrographs. The surface morphology of combustion derived $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$ (1 mol%) and $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$ (1.0 mol%):Sm$^{3+}$ (0.2, 0.6 and 1 mol %) nanophosphors were recorded and shown in Fig.4.4.3 (a-l).

Fig.4.4.3. SEM micrographs of $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$ (1.0 mol%):Sm$^{3+}$ (0.2, 0.6, 1 mol %) nanophosphors.

Initially without adding Sm$^{3+}$ co-dopant ion in $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$ nanophosphors the micrograph showed flakes like structure and with further addition of Sm$^{3+}$ co-dopant
ion showed the formation of non-uniform dumble shaped nanoparticles which are fused together of the surface of the flakes. This shows that there is some effect on of co-dopant ion on $Y_2SiO_5:Ce^{3+}$ nanophosphors during the synthesis. Generally, flaming reaction involves liberation of large amount of gases. The pores and voids may be attributed to the large amount of gases escaping out of the reaction mixture during combustion [23].

4.4.2.3 Fourier transform infrared spectroscopy (FTIR)

FTIR spectrum of $Y_2SiO_5:Ce^{3+}$ (1.0 mol%):$Sm^{3+}$ (0.2–1 mol%) nanophosphors is shown in Fig.4.4.4 The absorption in the range 1280–1760 cm$^{-1}$ is due to absorption of $H_2O$ and NO$_3$ groups the peak at 1040 cm$^{-1}$ originates due to absorption of Si–O–Si asymmetric stretching vibrations. The water in the silicate lattice gives rise to characteristic sharp bands in the third region of these spectra. Inorganic silicates have a characteristic, strong band centred on 1100 cm$^{-1}$ that in some cases appear as multiple bands.

![FTIR spectra of $Y_2SiO_5:Ce^{3+}$ (1 mol%):$Sm^{3+}$ (0.2-1 mol%) nanophosphors.](image-url)
In our case, the band noticed at 1040 cm\(^{-1}\) of dried gel sample transformed into four well differentiated absorption peaks of SiO\(_4\) at 1012, 934, and 880 cm\(^{-1}\) in calcinated sample, suggesting the formation of well-crystallized silicate. New absorption peak at 563 cm\(^{-1}\) is due to bonding vibrations of Y–O bonds [24].

**4.4.2.4 UV-visible spectroscopy**

The UV–visible absorption spectra of Y\(_2\)SiO\(_5\): Ce\(^{3+}\) (1 mol %) nanophosphor and Y\(_2\)SiO\(_5\):Ce\(^{3+}\) (1.0 mol%):Sm\(^{3+}\) (0.2, 0.6 and 1 mol%) nanophosphor is as shown in the Fig.4.4.5. The spectra show a broad absorption bands at 232 and 278 nm. The maximum absorption at 232 nm in the absorption spectra may be due to the transition of electrons from valence band to the conduction band. The weak absorption at 278 nm may be due to the presence of extrinsic states such as surface traps or defect states or impurities available for transition [25]. The intensity and broadness of the absorption band also depends on the size of the particle. Smaller is the size of the particles, broader and stronger will be the absorption band. Because the defect concentration on the surface of the nanophosphor material increases as particle size decreases due to high surface to volume ratio [26]. Further, the optical energy band gap of the Y\(_2\)SiO\(_5\):Ce\(^{3+}\) (1 mol%) and Y\(_2\)SiO\(_5\):Ce\(^{3+}\) (1.0 mol%):Sm\(^{3+}\) (0.2, 0.6 and 1 mol%) nanophosphor was determined by using Wood and Tauc relation \( \alpha(h\nu) = k(h\nu – E_g)^{1/n} \) [27], where \( h\nu \) is the energy of the photon, \( \alpha \) is the optical absorption co-efficient, \( k \) is the constant and \( n = 2 \) and \( 1/2 \) for direct allowed and indirect transitions respectively. The energy band gap value is determined by plotting \((\alpha E)^2\) vs \( E \) and extrapolating the linear region of the curve as shown in Fig.4.4.6. The energy band gap value estimated was found to be in the range 6.12-6.27eV which are in good agreement with the \( E_g \) values reported in the literature[28]. The change in the \( E_g \) value with increase of Sm\(^{3+}\) co-dopant ion concentration in Y\(_2\)SiO\(_5\):Ce\(^{3+}\) nanophosphor may be due to the change in the structural order or disorder produced in the lattice which may affect the distribution of energy level with in the band gap. Also \( E_g \) values depends on the various factors such as synthesis techniques and experimental conditions which acts as a controlling aid for the arrangement of atoms in the lattice and avoids defects in the phsophors materials.
Fig 4.4.5. Absorption spectrum of $Y_2\text{SiO}_5\text{:Ce}^{3+}$ (1 mol%): Sm$^{3+}$ (0, 0.2, 0.6, 1 mol%) nanophosphors.

Fig 4.4.6. Energy band gap diagram of $Y_2\text{SiO}_5\text{:Ce}^{3+}$ (1 mol%): Sm$^{3+}$ (0, 0.2, 0.6, 1 mol%) nanophosphor
4.4.2.5 Photoluminescence

The structural, compositional, impurities and defects present in the phosphors could be identified by in detail photoluminescence studies on phosphor materials. Initially, $Y_2SiO_5:Ce^{3+}$ (1 mol %) nanophosphor was excited and its emission spectra was recorded. The emission spectra showed a high intense broad blue emission band centered at 444 nm. This broad emission spectra corresponds to $5d^1 \rightarrow 4F^1$ transition of $Ce^{3+}$ ions [29, 30]. For further, different concentrations of $Sm^{3+}$ ions were co-doped into $Y_2SiO_5:Ce^{3+}$ (1 mol %) nanophosphor. Fig.4.4.7 (a) shows the excitation spectra recorded at 601 nm for 0.8 mol% $Sm^{3+}$ co-doped $Y_2SiO_5:Ce^{3+}$ (1 mol %) nanophosphor. The excitation spectra consist of broad emission bands at 367, 404 and 468 nm. Fig.4.4.7 shows the emission spectrum recorded at 404 nm. The spectra consists of sharp emission peaks at 566, 601 and 654 nm which were attributed to typical $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions of $Sm^{3+}$ ions, respectively [31]. On comparing the intensity of $Sm^{3+}$ co-doped $Y_2SiO_5:Ce^{3+}$ (1 mol %) nanophosphor with $Y_2SiO_5:Ce^{3+}$ (1 mol %) nanophosphor the intensity of the emission peaks remained almost same. This shows that there is no significant transfer of non-radiative energy from $Ce^{3+}$ ions to $Sm^{3+}$ ions [32-34].
Fig 4.4.8. PL emission spectra of $Y_2SiO_5:Ce^{3+}$ (1 mol%):$Sm^{3+}$ (0-1 mol%) nanophosphors

Fig.4.4.9. shows the variation of Co - dopant $Sm^{3+}$ ion concentration in the present $Y_2SiO_5: Ce^{3+}$ (1 mol%) nanophosphor. Initially, with increase of $Sm^{3+}$ ion concentration the emission peak intensity increases up to 0.8 mol% with further increase in Co-dopant ion concentration the peak intensity decreases. This phenomenon of decrease of intensity with Co-dopant ion concentration is called concentration quenching [35]. Concentration quenching is caused by the migration of excitation energy between the emission ions or energy migration to quenching centers where the excitation energy is lost by non-radiative transition. Consequently in low dimensional arrangements the rare earth ions shows critical concentration. That is at lower co-dopant ion concentrations the luminescence centres are separated and the probability of transfer of energy between the co-dopant ions is very small. As a result when the concentration reaches certain extent (0.8 mol%) there is a easy exchange of energy from one luminescence centre to another due to which non-radiative energy tranfer process increases. The cross-relaxation process occurred between the two energy levels could be easily estimated by estimating the critical distance ($R_c$) by using the Blasse’s equation (3.2.4) [37]. In this equation $V$; the volume of the unit cell, $X_c$ ; the critical concentration of the co-dopant ion, and $N$; the number of units per unit cell. In this case, $N = 7$, $X_c$ and $V=1.65$ Å respectively. Therefore, the critical distance of $Sm^{3+}$ co-dopant ion in $Y_2SiO_5:Ce^{3+}$ (1 mol %) nanophosphor is found to
be 8.257 Å. If $R_c$ value is greater than 5Å the energy transfer between Eu$^{3+}$ ions takes place due to electric multipolar interaction and is estimated by using the equation (3.2.3). In this equation $X$; the concentration of Eu$^{3+}$ ions concentration, $k$ & $\beta$; constants, $Q = 6$, 8 and 10 for dipole – dipole, dipole – quadrupole and quadrupole – quadrupole interactions [36, 37]. By plotting log $(X)$ Vs log $(I/X)$ the value of the intercept was found to be 7.38 as shown in Fig. 4.4.10. Hence, the value of $Q$ is nearly equal to 8, therefore quenching takes place due to dipole – quadrupole interactions.

**Fig 4.4.9.** Variation of PL intensity with Sm$^{3+}$ co-dopant ion concentration in Y$_2$SiO$_5$:Ce$^{3+}$ (1 mol%) nanophosphors

**Fig. 4.4.10.** Variation of log $X$ vs log $(I/x)$
The Commission International De I-Eclairage (CIE) chromaticity coordinates for $Y_2SiO_5:Ce^{3+} (1 \text{ mol\%})$ phosphors was estimated and plotted as shown in Fig. 4.4.11. The $Y_2SiO_5:Ce^{3+} (1 \text{ mol\%})$ nanophosphor was lying in the blue region and could be used as a blue LED, when $Sm^{3+}$ co-dopant ion was added into $Y_2SiO_5:Ce^{3+} (1 \text{ mol\%})$ nanophosphor the color co-ordinate values shifted to white region. This shows that by adding $Sm^{3+}$ co-dopant ion in $Y_2SiO_5:Ce^{3+} (1 \text{ mol\%})$ nanophosphors
could be tuned for WLED applications. The color correlated temperature (CCT) for $Y_2SiO_5:Ce^{3+}(1.0 \ \text{mol}\%) :Sm^{3+}(0.2-1 \ \text{mol}\%)$ nanophosphor is shown in Fig.4.4.12. The CCT value was estimated by using McCamy empirical formula [38]. The average CCT value is found to be 5011 K.

4.4.3. Conclusion

$Y_2SiO_5:Ce^{3+}(1.0 \ \text{mol}\%):Sm^{3+}(0.2 - 1 \ \text{mol}\%)$ nanophosphors were prepared by Solution combustion technique. The obtained samples were subjected to 1000 °C calcination temperature for 3 hr. The PXRD results showed the formation of monoclinic $X1$ phase nanophosphors. The particles size estimated by Debye Scerr’s and W-H plot methods were slightly varying due to ignorance of strain component in Debye Scherrer’s formulae. The SEM micrographs showed flakes with non uniform dumble shaped nanoparticles which are fused together on the surface of the flakes. The FTIR spectra shows the characteristic peaks at 1012, 934, and 880 cm$^{-1}$ corresponding to SiO$_4$ bonds and 563 cm$^{-1}$ corresponding to of Y–O vibration bonds. The UV-vis absorption spectrum shows absorption bands at 348 and 378 nm. The energy band gap value increases with increase in $Sm^{3+}$ co-dopant ion concentration which is due to the change in the structural order or disorder produced in the lattice which may affect the distribution of energy level with in the band gap. The PL spectra monitored at 404 nm shows characteristic emission peaks at 566, 601 and 654 nm corresponding to $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions of $Sm^{3+}$ ions, respectively. 0.8 mol% $Sm^{3+}$ co-doped $Y_2SiO_5:Ce^{3+}(1.0 \ \text{mol}\%)$ nanophosphor showed maximum PL intensity with further increase of $Sm^{3+}$ co-dopant ion concentration the PL intensity decreases. The decrease in PL intensity is due to migration of excitation energy between the emission ions or energy migration to quenching centers where the excitation energy is lost by non-radiative transition. The $Y_2SiO_5:Ce^{3+}(1.0 \ \text{mol}\%)$ nanophosphor was lying in the blue region and could be used as a blue LED, when $Sm^{3+}$ co-dopant ion was added into $Y_2SiO_5:Ce^{3+}(1.0 \ \text{mol}\%)$ nanophosphor the color coordinate values shifted to white region. This shows that by adding $Sm^{3+}$ co-dopant ion in $Y_2SiO_5:Ce^{3+}(1.0 \ \text{mol}\%)$ nanophosphors could be tuned for WLED applications. The average CCT value estimated by McCamy empirical formula is found to be 5011 K. CIE chromaticity CCT values suggest that $Y_2SiO_5:Ce^{3+}(1.0 \ \text{mol}\%):Sm^{3+}(0.2 - 1 \ \text{mol}\%)$ nanophosphors are promising material optical display applications and for WLEDs.
References


