CHAPTER 5

Effect of Annealing on the Structural, Optical and Emissive Properties of SrWO$_4$:Ln$^{3+}$ (Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) Nanoparticles

5.1 Introduction

Rare earth doped tungstates have a scheelite type tetragonal structure with general formula AWO$_4$ (A=Sr, Ca, Ba) and their space group is I4$_1$/a. They have been studied widely due to their several applications in catalysts, scintillation detector, $w$-LEDs, photoluminescent devices, optics fiber, solar cell, fluorescent lamps and more [1-8]. Improvement of the luminescence properties of scheelite based phosphors has become a primary focus in the luminescent materials science. Tungstate has broad and intense absorption bands due to charge transfer (CT) from oxygen to metal in the near-UV region. Inorganic hosts such as strontium tungstates (SrWO$_4$) have been well known for a long time for its strong visible luminescence in blue and green region at room temperature under UV excitation. Due to its higher thermal and chemical properties, it can be conveniently activated with rare earth ions in order to develop active media for solid state lasers [9] and phosphors technologies [10, 11,12].

Rare earth doped SrWO$_4$ has attracted much interest and has been synthesized by solid state reaction[13], Czochralski technique[14], Pechini method[15], hydrothermal method[16], co-precipitation method[17] and solvothermal method[18]. However, these methods require high temperature which results in agglomeration of optically active lanthanides ions. This clustering results in reduction of luminescence intensity. To overcome this drawback polyol method is used with ethylene glycol as capping agent as well as reaction medium. Polyol method has great potential for manufacturing high quality nanoparticles economically. EG prevents the agglomeration of the nanoparticles[19].
In this chapter, a series of SrWO$_4$:Ln$^{3+}$ ($Ln^{3+}$ = Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) nanocrystals were successfully synthesized through a polyol method using ethylene glycol as capping agent. In order to increase the crystallinity the as-prepared samples were annealed at 800 °C. The prepared nanophosphors were well analyzed by means of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Raman, UV-Vis spectroscopy, DSC/TGA, Photoluminescent (PL) spectra as well as the life time decay. The CIE values are found to increase on annealing the samples at 800 °C. Additionally, we systematically investigate the structural and luminescent properties of different lanthanide ions in SrWO$_4$ host. The effect of annealing temperature on the structural and photoluminescence emission intensity were also investigated. The SrWO$_4$:Ln$^{3+}$ ($Ln^{3+}$ = Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) phosphors show their characteristic emission under ultraviolet excitation due to the efficient energy transfer from $WO_4^{2-}$ group to rare earth ions.

Our results show that the prepared nanophosphors can be used as potential candidates for phosphor applications.

5.2 Experimental Details

5.2.1 Material Synthesis

The nanoparticles of SrWO$_4$ doped with Ln$^{3+}$ ($Ln^{3+}$ = Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) were prepared using ethylene glycol (EG) as both capping agent and reaction medium at 150 °C. Strontium nitrate (Sr(NO$_3$)$_2$, AR), Europium oxide (Eu$_2$O$_3$, 99.99%, Sigma Aldrich), Dysprosium oxide (Dy$_2$O$_3$, 99.99%, Sigma Aldrich), Samarium oxide (Sm$_2$O$_3$, 99.99%, Sigma Aldrich) and Sodium tungstate dihydrate (Na$_2$WO$_4$.2H$_2$O, AR) were used as sources of Sr$^{2+}$, Eu$^{3+}$, Dy$^{3+}$, Sm$^{3+}$ and $WO_4^{2-}$, respectively. In a typical synthesis procedure of 2 at.% Dy$^{3+}$ - doped SrWO$_4$ nanoparticles, 1.150 g of Sr(NO$_3$)$_2$ and 0.020 g of Dy$_2$O$_3$ were dissolved in concentrated nitric acid (HNO$_3$). The mixture was heated at 80 °C to remove the excess of acid and the process of removal of excess of acid was repeated five times after addition of deionized water (5 ml). To this aqueous solution of Sr(NO$_3$)$_2$ (1.150 g) was added followed by 50 ml of
EG. The pH of the solution was adjusted to 9 using urea. The resulting solution was then stirred for 1 hour. This solution together with the aqueous solution of 1.829 g of Na$_2$WO$_4$. 2H$_2$O is then transferred to a two neck round bottom flask and was heated upto 150 °C for 3 hours under refluxing condition in a condenser until precipitation was complete.

The white precipitate so obtained was collected by centrifugation and washed 5 times in methanol to remove excess of EG and finally it was washed with acetone and dried at 90 °C for 2 hours in vacuum oven to yield the final white product. Finally, the as prepared samples were divided in 2 parts. One part of the sample was annealed at 800 °C in an ambient atmosphere at a heating rate of 2 °C min$^{-1}$ for 2 hours in an alumina crucible and the other part was left untreated.

5.2.2 Characterizations

The structures of the final products were characterized by X-ray diffraction (XRD) using Bruker D8 Advance X-ray diffractometer (Cu Kα 1 irradiation, $\lambda = 1.5406$ Å) radiation at 40 KV and 40 mA at $4^\circ(2\theta)/$min scanning rate. All patterns were recorded over the angular range $10^\circ \leq 2\theta \leq 80^\circ$ with a step size of $\Delta 2\theta = 0.02$. The morphology and particle size of the as prepared powders were characterized by scanning electron microscopy (FESEM, JSM-6700, model JEOL, Japan). Simultaneous DSC/TGA spectra were recorded using NETZSCH STA 449 $F1$. DSC and TG analyses were carried out using 10 mg of the sample at a heating rate of 10 °C min$^{-1}$ up to 1000 °C, in nitrogen atmosphere under a flow of 60 cm$^3$ min$^{-1}$. Infrared spectra were recorded on a Fourier transform infrared (FT-IR) spectrophotometer of Shimadzu (model 8400 S) with a resolution of 2 cm$^{-1}$ and in the range 400-4000 cm$^{-1}$. For IR measurement the samples were mixed with KBr (Sigma Aldrich, 99.99 %) in 1:5 ratios and this mixture was placed in a sample holder and the spectra were recorded. UV-vis spectra were recorded using UV-2700 Double beam spectrophotometer in the reflection mode. For UV-vis measurement the samples were dispersed in the methanol and then the spectra were taken. The Raman spectra of the...
as prepared and annealed samples were measured with Renishaw micro-Raman spectrometer attached with 633 nm laser as an excitation source.

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were recorded. Lifetime decay was recorded with Edinburg instrument F-920 equipped with 100 W µs flash xenon lamp as the excitation source.

5.3 Results and discussions

5.3.1. Crystallinity, phase purity and structure

The crystallinity and phase purity of the rare-earth ions doped SrWO$_4$ powders were first investigated by XRD. Fig. 5.1(a-c) show the XRD patterns of the as-prepared as well as annealed samples of 2 at.% Ln$^{3+}$ (Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) -doped SrWO$_4$, and the standard data for tetragonal SrWO$_4$ (JCPDS 08-0490), respectively. It can be seen that the XRD patterns for all the samples can be well indexed to a pure scheelite tetragonal structure (I 4$_1$/a space group), which are in good agreement with the values of the standard card (JCPDS 08-0490). No other impurities related with the doped components can be observed in the XRD patterns, which suggest that the rare-earth ions have been uniformly incorporated into the host lattice of SrWO$_4$. The calculated lattice parameters of as-prepared 2 at.% Dy$^{3+}$ -doped SrWO$_4$ are $a = 5.444$ Å, $c = 11.952$ Å, $V = 354.30$ Å$^3$ and 800 ºC annealed samples are $a = 5.430$ Å, $c = 11.952$ Å, $V = 354.24$ Å$^3$. For as-prepared 2 at.% Eu$^{3+}$ -doped SrWO$_4$ are $a = 5.429$ Å, $c = 11.954$ Å, $V = 352.47$ Å$^3$ and 800 ºC annealed samples are $a = 5.415$ Å, $c = 11.954$ Å, $V = 350.57$ Å$^3$. For as-prepared 2 at% Sm$^{3+}$ -doped SrWO$_4$ are $a = 5.427$ Å, $c = 11.981$ Å, $V = 352.92$ Å$^3$ and 800 ºC annealed samples are $a = 5.437$ Å, $c = 11.901$ Å, $V = 351.83$ Å$^3$. They all are in good agreement with the standard data of $a = 5.416$ Å, $c = 11.951$ Å and $V = 350.66$ Å$^3$ for pure tetragonal SrWO$_4$ (JCPDS 08-0490).
The peak broadening can be used to estimate the average crystallite sizes by the Scherrer formula,

\[ D = \frac{(0.89)\lambda}{\beta \cos \theta} \]  \hspace{1cm} (5.1)

Where, \( D \) is the average crystallite size, \( \lambda \) is the wavelength of the X-rays (0.15405 nm), and \( \theta \) and \( \beta \) are the diffraction angle and full-width at half maximum (FWHM) of the peak in the XRD pattern, respectively. The average crystallite sizes determined from the highest intense peak (112) using the Scherrer formula for the as-prepared and 800 °C annealed samples for \( \text{SrWO}_4: \text{Dy}^{3+} \) are found to be \(~54\) and \(71\) nm, for \( \text{SrWO}_4: \text{Eu}^{3+} \) \(~41\) and \(57\) nm, for \( \text{SrWO}_4: \text{Sm}^{3+} \) \(~43\) and \(62\) nm, respectively.
5.3.2. Rietveld refinement analysis

The Rietveld analysis was performed on as-prepared as well as 800 ºC annealed crystalline 2 at.% Dy\(^{3+}\) doped SrWO\(_4\) samples (Fig. 5.2(a) and (b)) using the fullprof package [20] and assuming a I\(_4\)/a space group for a scheelite type tetragonal structure. In this scheelite type tetragonal structure, positions of the respective atoms are Sr: (4b: 0, 0.25, 0.0625), W: (4a: 0, 0.025, 0.125) and O: (16f: x, y, z) with angles (α=β=γ=90°). Pseudo-Voigt function was used to model the peak profiles and six coefficient polynomial was used to describe the background.

![Rietveld plots](image)

**Fig. 5.2** Rietveld plots of 2 at. % Dy\(^{3+}\) doped SrWO\(_4\) samples (a) as-prepared and (b) annealed at 800ºC

The values of \(R_{wp}\), \(R_p\) and \(\chi^2\) are shown in Table 5.1. The rietveld analysis shows that the samples are in crystalline phase and no phase mixture was observed which confirm the results obtained by conventional XRD. Rietveld plots of 2 at.% Eu\(^{3+}\) and Sm\(^{3+}\)-doped SrWO\(_4\) as-prepared and 800 ºC annealed samples are shown in Fig 5.3(a)-(c) and (b)-(d), respectively.
Table 5.1
Coefficients of the Rietveld refinement for as-prepared and 800 °C annealed SrWO$_4$:Ln$^{3+}$
($\text{Ln}^{3+} = \text{Dy}^{3+}$, $\text{Eu}^{3+}$ and $\text{Sm}^{3+}$) samples

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Fig. 5.3 (a and b) Rietveld plots of as-prepared and 800 °C annealed Eu$^{3+}$-doped SrWO$_4$ samples. (c and d) Rietveld plots of as-prepared and 800 °C annealed Sm$^{3+}$-doped SrWO$_4$ samples
5.3.3 SEM Study

The morphology of as-prepared and 800 °C annealed SrWO$_4$:2Sm$^{3+}$ was studied using SEM. SEM image (Fig. 5.4 (a) and (b)) shows that the morphology of nanoparticles is nearly spherical in shape and the particle size is about 40-60 nm in diameter which is well consistent with the size calculated by Scherrer’s formula from the XRD patterns.

![SEM micrographs of SrWO$_4$:Sm$^{3+}$](image)

**Fig. 5.4** SEM micrographs of SrWO$_4$:Sm$^{3+}$ (a) as-prepared and (b) annealed at 800 °C for 2 h.

The similarity between the sizes derived from XRD and SEM suggests that the particles are well crystalline. On annealing, nucleation and crystal growth continued [21]. This may be the reason for irregular shapes and agglomerated particles in case of samples annealed at 800 °C (Fig. 5.4(b)).

5.3.4 DSC/TGA Study

Fig. 5.5 shows the simultaneous DSC/TGA curves along with DTG curves of ASP 2 at.% Dy$^{3+}$ doped SrWO$_4$ nanoparticles. The sample was measured in the temperature range of 35 to 1000 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The TG analysis in Fig. 5.5 presents a weight loss of 4.62% from 50-400 °C, 1.90% in the range 400-600 °C and no appreciable loss are observed beyond 600 °C. The mass loss till 300 °C is attributed to complete dehydration of the powders while the mass loss till 600 °C is due to the evaporation of organic constituents like EG. There are two exothermic peaks in the DTG curve in the vicinity of 48°C and 598 °C which correspond to evaporation of water molecules, decomposition of organic molecules and phase formation of SrWO$_4$: Dy$^{3+}$, respectively.
Fig. 5.5 Simultaneous DSC/TGA character of as-prepared 2 at.% Dy$^{3+}$-doped SrWO$_4$

To study the heat flow as a function of temperature in the inert gas (N$_2$) atmosphere associated with transitions in SrWO$_4$:Dy$^{3+}$ ASP sample DSC was recorded (Fig. 5.5). The curve shows both exothermic and endothermic peaks. The peak around 239$^\circ$C represents the mass loss due to the evaporation of organic compounds like ethylene glycol and methanol. Whereas, the large and sharp endothermic DSC (Differential Scanning Calorimetry) peak at about 599 ºC indicate the phase formation of SrWO$_4$:Dy$^{3+}$. These results show that the prepared nanophosphors are thermally stable and can be used in lightning and display devices.

5.3.5 FT-IR study

The FTIR spectra of the as-prepared and 800 ºC annealed nanoparticles of 2 at.% Dy$^{3+}$-doped SrWO$_4$ in the wavenumber range of 400–4000 cm$^{-1}$ are shown in Fig. 5.6. The FTIR spectra of Eu$^{3+}$ and Sm$^{3+}$-doped SrWO$_4$ are shown in Fig. 5.7 (a) and (b), respectively. It can be seen that all samples show approximately similar vibrations modes of strontium tungstate, this confirmed the phase purity of phosphors.
The bands at 1631 and 3475 cm$^{-1}$ correspond to H–O–H bending and O–H stretching vibrations. These are characteristic vibrations of water molecules which are physically adsorbed from air on the surface of nanoparticles [22]. The peaks are absent in case of annealed samples due to the evaporation of water molecules from the surface of the nanoparticles on annealing. The strong peak at 830 cm$^{-1}$ can be assigned to $\nu_3$ asymmetric stretching vibration originating from the W–O stretching vibration in $WO_4^{2-}$ tetrahedron. And the weak absorption peak at 675 cm$^{-1}$ can be assigned to bending vibration of W–O. The 1200 cm$^{-1}$ vibration is due to the N–O band from HNO$_3$ used in the sample preparation. In the as-prepared sample peaks are
observed at 2247 and 2920 cm$^{-1}$ indicating C–H stretching vibration from EG molecules on the surface of SrWO$_4$:Dy$^{3+}$ nanoparticles. The IR spectra of SrWO$_4$:Eu$^{3+}$ and SrWO$_4$:Sm$^{3+}$ show the same profile (Fig. 5.7 (a) and (b)).

The FT-IR results also confirm that the obtained SrWO$_4$:Ln$^{3+}$ (Eu$^{3+}$, Dy$^{3+}$ and Sm$^{3+}$) phosphors possess single-phase scheelite structure.

5.3.6 Micro Raman study

Fig. 5.8 shows Raman spectra at 633 nm in the frequency ranging from 100 to 1100 cm$^{-1}$ for SrWO$_4$:Ln$^{3+}$ (Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) nanoparticles synthesized by the polyol method and treated at 800 ºC. At room temperature these compounds show well known Raman bands at ~ 104, 131, 188, 334, 371, 797, 836 and 920 cm$^{-1}$ and weak bands near 264 and 405 cm$^{-1}$.

![Fig. 5.8 Room temperature Raman spectra of (a) SrWO$_4$:Dy$^{3+}$, (b) SrWO$_4$:Eu$^{3+}$ and (c) SrWO$_4$:Sm$^{3+}$ nanophosphors processed by the polyol method and treated at 800ºC.](image)

The Raman peak at 920 cm$^{-1}$ could be assigned as $v_1$ of the $W−O$ symmetric stretching while the peak at 334 cm$^{-1}$ is assigned as $v_2$ of the $W−O−W$ symmetric bending. The peaks at 836 and 797 cm$^{-1}$ are designated as $v_3$ of the $W−O$ anti-symmetric stretching, and peaks at 371 and 405 cm$^{-1}$ are designated as $v_4$ of the $W−O−W$ anti-symmetric bending [23,24]. External peak modes are localized in the range from 104 to 131 cm$^{-1}$ which corresponds to the stretching and flexion mode of Sr – O. Free rotation modes of $WO_4^{2−}$ are visible at 188 and 264 cm$^{-1}$. According
to literature data [25], all Raman modes observed for SrWO$_4$:Ln$^{3+}$ (Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) obtained in this work are characteristics of the tetragonal structure.

5.3.7 UV-vis spectroscopy

The optical band gap energy was estimated by the method proposed by Wood and Tauc [26]. According to them the optical band gap is associated with the absorbance and incident photon energy by the following equation:

$$\alpha h \nu = k (h \nu - E_g)^{1/2}$$  \hspace{1cm} (5.2)

Where, $k$ is a constant, $h$ is the Planck’s constant, $\nu$ is the frequency and $E_g$ is the optical band gap. The band gap energy $E_g$ can be obtained from an extrapolation of the straight-line portion of the $(\alpha h \nu)^2$ versus $h \nu$ plot to zero absorption coefficient value. Fig. 5.9(a) and (b) provide the estimated band gap 5.34 eV and 4.50 eV for ASP and 800 °C annealed 2 at.% Sm$^{3+}$-doped SrWO$_4$ nano-particles, respectively.

![Fig. 5.9 Variation of $(\alpha h \nu)^2$ vs photon energy (in eV) curve for (a) as-prepared and (b) 800 °C annealed 2 at.% Sm$^{3+}$-doped SrWO$_4$](image)

The band gap calculations for as-prepared and 800 °C annealed Eu$^{3+}$-doped SrWO$_4$ nanoparticles are estimated to be ~ 4.25 and 4.00 eV and for Sm$^{3+}$-doped SrWO$_4$ are 5.32 and 4.32 eV, respectively and shown in electronic supplementary information Fig. 5.10 (a)-(c). The band gap energy clearly shifts to a lower energy on annealing the samples (Fig. 5.9). This red shift in band gap energy can be associated to quantum confinement effect in nano-size particles due to structural defects [27].
5.3.8 Photoluminescence Study

The PL excitation and emission spectra were used to study the luminescence properties of all the samples. The excitation spectrum ($\lambda_{em} = 613$ nm) of as-prepared 2 at. % Eu$^{3+}$-doped SrWO$_4$ phosphors is shown in Fig. 5.11 (a). It consists of an intense broad band at 270 nm. This broad band is due to the combination of Eu-O charge transfer band and W-O charge transfer band but their exact position cannot be located due to their merged occurrence between 250-320 nm. The possible reason for this occurrence can be explained as follows [28, 29]:

This broad band is occurred when the electrons from 2p state of oxygen (near valence band) are transferred to the 4d state of tungstate (near conduction band) by absorbing the photons after excitation and finally the comeback of electrons to lower energy states again by radiative transitions.
Fig. 5.11 Excitation (blue curve) and emission (red curve) spectra of (a) as-prepared and (b) 800 °C annealed 2 at. % Eu$^{3+}$-doped SrWO$_4$ nanoparticles

At the longer wavelengths the f-f forbidden transitions of Eu$^{3+}$ can be assigned to $^7F_0 \rightarrow ^5D_4$ (361), $^7F_0 \rightarrow ^5G_2$ (380), $^7F_0 \rightarrow ^5L_6$ (393), $^7F_0 \rightarrow ^5D_3$ (415) and $^7F_0 \rightarrow ^5D_2$ (464), respectively. The emission spectrum of as-prepared SrWO$_4$:Eu$^{3+}$ sample was obtained by exciting it at 364 nm (Fig. 5.11 (a)), which shows a strong transition line of $^5D_0 \rightarrow ^7F_2$ (613 nm) due to electric dipole transition and few weak lines at $^5D_0 \rightarrow ^7F_0$ (532 nm), $^5D_0 \rightarrow ^7F_1$ (590 nm, magnetic dipole transition), $^5D_0 \rightarrow ^7F_3$ (651 nm) and $^5D_0 \rightarrow ^7F_4$ (700 nm). The $^5D_0 \rightarrow ^7F_2$ (613 nm) transition showed its dominance in emission spectrum, which suggests that Eu$^{3+}$ ions have occupied the non inversion sites in SrWO$_4$ lattice [30,31-35]. Similar spectra for excitation and emission are shown by SrWO$_4$:Eu$^{3+}$ nanoparticles annealed at 800 °C (Fig. 5.11 (b)). On annealing the samples at 800 °C due to decrease in non-radiative rates and removal of –OH molecules from the surface of the nanoparticles, the luminescence intensity increases upto ~ 2 times.

Fig. 5.12 (a) depicts the PL excitation and emission spectra of as-prepared 2 at.% Dy$^{3+}$-doped SrWO$_4$. The excitation spectrum was monitored at 572 nm. It consists of a broad band centered at 247 nm and sharp lines extended to visible range. The broad band is due to energy transfer from WO$_4^{2-}$ to Dy$^{3+}$ and the sharp lines are due to f-f transitions of Dy$^{3+}$ 4f configuration [36]. In the emission spectrum under 350 nm (Fig. 5.12 (a)), the intensity of $^6F_{9/2} \rightarrow ^6H_{13/2}$ (572 nm) of yellow luminescence
is dominant over $^4F_{0/2} \rightarrow ^6H_{15/2}(475, 484 \text{ nm})$ of blue luminescence which shows that Dy$^{3+}$ ions occupied the sites without inversion centre in the SrWO$_4$ host lattice, which is very similar to the case of Eu$^{3+}$. The intensity of f-f transition lines is greater than the broad band due to efficient energy transfer from the $WO_4^{2-}$ groups to Dy$^{3+}$ ions in SrWO$_4$:Dy$^{3+}$.

The trivalent samarium ion is very unique and has gained much attention due to its orange red luminescence and higher excitation wavelength ($\lambda_{\text{exc}} = 405 \text{ nm}$) which can be used for sensitization in the bio-medical diagnosis. The excitation spectrum ($\lambda_{\text{em}} = 642 \text{ nm}$) of as-prepared SrWO$_4$:Sm$^{3+}$ is shown in Fig. 5.13 (a); a broad band with a maximum at 254 nm can be observed. This is assigned to the charge transfer from oxygen ligands to the central tungstate atom with in $WO_4^{2-}$ groups and also to Sm-O charge transfer band. Upon excitation at 405 nm, the intense narrow peaks observed in the orange red region in the luminescence spectrum due to transitions from $^4G_{5/2} \rightarrow ^6H_{5/2}(561 \text{ nm})$, $^4G_{5/2} \rightarrow ^6H_{7/2}(605 \text{ nm})$, $^4G_{5/2} \rightarrow ^6H_{9/2}(642 \text{ nm})$ and $^4G_{5/2} \rightarrow ^6H_{11/2}(704 \text{ nm})$, which can be assigned to an energy transfer from the $WO_4^{2-}$ to sm$^{3+}$ ions. The emission spectra of Sm$^{3+}$ ions is dominated by the orange red emission peak at $^4G_{5/2} \rightarrow ^6H_{7/2}(642 \text{ nm})$, which is due to electric dipole transition. Fig. 5.13 (b) shows the excitation and emission spectra of 800 ºC annealed samples of 2 at.% Sm$^{3+}$-doped SrWO$_4$. On annealing the SrWO$_4$:Sm$^{3+}$ phosphors, the luminescence intensity increase upto $\sim$ 3 times.
Excitation (brown curve) and emission (orange-red curve) spectra of (a) as-prepared and (b) 800 °C annealed 2 at.% Sm$^{3+}$-doped SrWO$_4$ nanoparticles

5.3.9 CIE Study

Fig. 5.14 shows the corresponding CIE (Commission Internationale de l’Eclairage 1931 chromaticity) coordinates positions, which show the different emission colors for the as-prepared and 800 °C annealed SrWO$_4$:Dy$^{3+}$, SrWO$_4$:Eu$^{3+}$ and SrWO$_4$:Sm$^{3+}$, respectively. On annealing the samples at 800 °C, the value of CIE coordinates shift to darker colors. Thus, the color coordinates also depend on the annealing temperature [11].

It can be seen that on annealing the phosphor, in case of Dy$^{3+}$ doped SrWO$_4$, the color perception changes from green-yellow (presented by point a1, x = 0.32 & y = 0.33) to dark yellow (presented by point a2, x = 0.41 & y = 0.35). For Eu$^{3+}$ doped...
SrWO$_4$, the color perception changes from red ($b_1$, $x = 0.62$ & $y = 0.38$) to dark red ($b_2$, $x = 0.66$ & $y = 0.34$). For Sm$^{3+}$ doped SrWO$_4$, on annealing the phosphor the color perception changes from orange-red ($c_1$, $x = 0.47$ & $y = 0.37$) to dark orange-red ($c_2$, $x = 0.52$ & $y = 0.39$) (Fig. 5.14). The calculated CIE color coordinates for all samples are listed in Table 5.2.

Table 5.2  
CIE values for as-prepared and 800 $^\circ$C annealed SrWO$_4$:Ln$^{3+}$ (Ln$^{3+}$ = Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) samples

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5.3.10 Lifetime study

The life time decay curves of 2 at.% Sm$^{3+}$-doped SrWO$_4$ samples were recorded under 355 nm excitation by monitoring the emission of orange red band at 642 nm. The decay curves were fitted with monoexponential equation. The mono-exponential decay fit is expressed as:

$$I = I_0 e^{-t/\tau}$$  \hspace{1cm} (5.3)

Where, $I_0$ and $I$ are intensities at zero time and at time $t$, respectively, and $\tau$ is the lifetime for the transition.

The mono-exponential fitting of as-prepared and annealed at 800 $^\circ$C 2 at.% Sm$^{3+}$ doped SrWO$_4$ phosphor under 355 nm excitation are shown in Fig. 5.15 (a) and (b). The lifetime value of annealed sample (0.456 ms) (Fig. 5.15 (b)) is greater than the as-prepared sample (0.405 ms) (Fig. 5.15 (a)).
This may be due to increase in particle size and reduction in surface defects after annealing. The lifetime values of as-prepared and 800 °C annealed SrWO₄:Dy³⁺ and SrWO₄:Eu³⁺ are listed in Table 5.3.

**Table 5.3**
Parameters obtained after mono-exponential fit to the decay data of as-prepared and 800 °C annealed SrWO₄:Dy³⁺ and SrWO₄:Eu³⁺ samples.

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<tr>
<th>Name</th>
<th>Sample</th>
<th>Excitation (nm)</th>
<th>( \tau ) (ms)</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrWO₄:Dy³⁺</td>
<td>ASP</td>
<td>350</td>
<td>0.51</td>
<td>0.9955</td>
</tr>
<tr>
<td>SrWO₄:Dy³⁺</td>
<td>800 °C</td>
<td></td>
<td>0.66</td>
<td>0.9967</td>
</tr>
<tr>
<td>SrWO₄:Eu³⁺</td>
<td>ASP</td>
<td>350</td>
<td>0.65</td>
<td>0.9986</td>
</tr>
<tr>
<td>SrWO₄:Eu³⁺</td>
<td>800 °C</td>
<td></td>
<td>0.76</td>
<td>0.9946</td>
</tr>
</tbody>
</table>

5.4 Conclusion:

In summary, rare-earth ion (Dy³⁺, Eu³⁺ and Sm³⁺) doped SrWO₄ synthesized successfully at low temperature by polyol method under urea hydrolysis using ethylene glycol as capping agent. The samples are annealed at 800 °C in order to increase the crystallinity. Both XRD and SEM results indicate that these phosphors have better crystallinity and show uniform morphologies and particle size, meanwhile
the particles of the phosphors become agglomerated on annealing. The obtained SrWO$_4$:Ln$^{3+}$ (Ln$^{3+}$ = Dy$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$) nanophosphors show strong emissions of different colors of the Ln$^{3+}$ ions, respectively. The decay curves of all the samples can be well fitted with a mono-exponential function. These nanophosphors can exhibit potential applications in the fields of display devices and light emitting diodes (LEDs).
References:


