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Luminescence properties of Eu^{3+} doped Li_2SrSiO_4 phosphor

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Abstract. The modified solid-state reaction method has been used in this work to prepare Eu^{3+} doped Li_2SrSiO_4. PL spectroscopy was used to investigate photoluminescence (PL) properties of the sample. X-ray powder diffraction study was used to confirm the crystalline nature and phase purity of the sample. The particle size of prepared material ranges from 37 to 56 nm was observed from XRD. From PLE and PL spectrum the excitation and emission spectra of photoluminescence for Eu^{3+} doped Li_2SrSiO_4 were recorded. The prepared Eu^{3+} doped Li_2SrSiO_4 phosphor might have application in solid state lighting.

1. Introduction

Solid state lighting has made significant growth in the contemporary digital era that significantly impacts daily life. The use of phosphors in traditional lighting and display techniques has been a key and technologically significant component for many decades [1]. Currently, rare earth doped phosphor proved its 100% efficiency in the solid-state lightinglike fluorescent tube, LEDs, X-ray imaging, color television [2]. All these applications are based on high efficiency, sharpness and many other luminescent properties of rare earth ions. The solid-state lighting demonstrates themselves as the most emerging technology in the current condition. It also demonstrates excellent efficiency, energy saving, environmental protection, and maintenance due to their diverse qualities and uses [3], absence of mercury, quick response etc.

The superior optical and electronic properties are originated from 4f shell of rare- earth ions. When the various hosts doped with Eu^{3+} ion having electronic configuration [Xe] $4f^7 5d^0 6s^2$, it was observed that it is one of the promising rare earths which gives red emission and UV absorption [4]. Artificial light can be produced and improved by using silicate-based phosphors. The silicates have wide applications due to its several merits as eco- friendly nature, facial synthesis, excellent long-term stability, crystal structure, brightness, w-LEDs, high efficiency Si solar cells, PDPs, Green emitters etc. [5-7]. Optical properties Eu^{3+} doped orthosilicate phosphors, like Ba_2SiO_4 and $BaZnSiO_4$, are investigated earlier. Since Sr^{2+} ion has an effective ionic radius is similar to Eu^{3+} ionic radii, the charge compensation mechanism occurred here. The synthesis method and luminescent properties of Li_2SrSiO_4: Eu^{3+} phosphor is reported in this paper.

2. Experimental Details

In present study, the modified solid-state reaction method was used to prepare Eu^{3+} doped Li_2SrSiO_4 phosphor. The Precursors: Lithium Carbonate [Li_2CO_3], Strontium Carbonate [Sr_2CO_3], Silicon dioxide [SiO_2] and Europium Oxide [Eu_2O_3] all in the analytical purity, were used in desired stoichiometric ratio. For the preparation of sample stoichiometric amount of Li_2CO_3, Sr_2CO_3, SiO_2

and Eu_2O_3 are crushed in mortar pestle for half-an-hour and transferred in silica crucible. The mixture then placed in the furnace. The sample were preheated at 500 ^{0}C for 3 hrs for sufficient diffusion and infiltration of the starting materials then again crushed and transferred in a silica crucible, and placed in a furnace for annealing at 850^{0}c for 5hrs. After cooling the mixture is again crushed and ready for further study.

The powder X-ray diffraction study using a PAnalytical diffractometer with Cu Kα radiation (λ = 1.5405AU) was carried out to check the phase and purity of the prepared sample. The range of XRD data was kept from 10 to 70^0. The scanning electron microscopy (SEM) (JEOL JSM 6360 LV) was used to examine the surface morphology of the sample. The photoluminescence studies were carried out by a Spectro fluorophotometer (Shimadzu RF-5301PC) equipped with a 150W Xe lamp.

3. Results and Discussion

3.1. X-ray diffraction

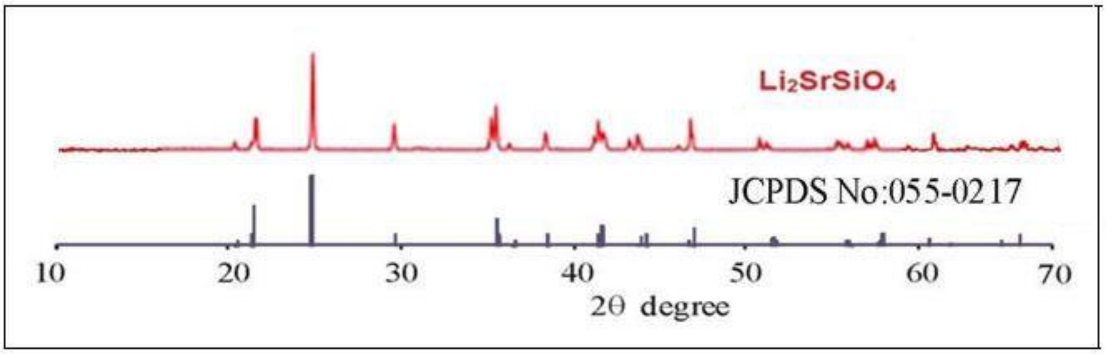

Figure 1. X-ray diffraction (XRD) of Li_2SrSiO_4 with standard JCPDS file.

Figure 1 shows the X-Ray diffraction pattern of prepared Li_2SrSiO_4 phosphor. All the XRD peaks in the pattern were well matched with the standard JCPDS card for Li_2SrSiO_4 (No. 055-0217). The crystal structure of the sample belongs to $P3_{121}$ space group and no peaks from impurities was occurred. The particles' average crystallite size (D) was estimated by Scherer's formula, $D = 0.9\ \lambda / \beta \cos\theta$ for different peaks and was found to be about 50.48 nm. The grain size, micro strain and dislocation density related to Li_2SrSiO_4 are shown in the table 1.

3.2. SEM Analysis

Morphology of Eu^{3+} doped Li_2SrSiO_4 was studied using SEM images with high (figure 2a) and low-magnification (figure 2b), as shown in figure 2. The images reveal the several nanoparticles are present within the grains. As observed from SEM micrograph, particles show irregular morphological distribution due to agglomeration of small particles.

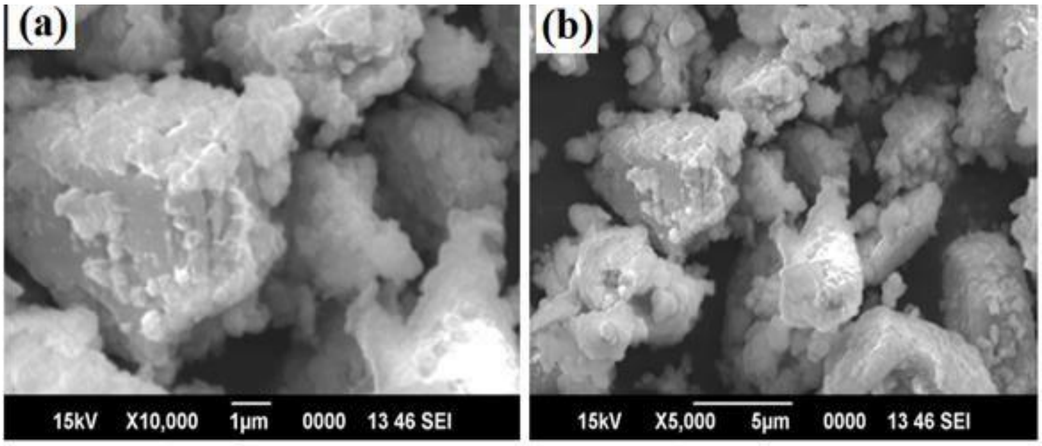

Figure 2. SEM images (a) high and (b) low magnification of Li_2SrSiO_4: Eu phosphor.

Table 1: Structure parameter of Li_2SrSiO_4

Position (2θ)	FWHM (β2θ)	Grain size D (nm)	Strain (ε)*10^{-4}	Dislocation Density (ρ)*10^{14}
21.9143	0.0029	48.7	7.1	4.2
25.2356	0.0029	49.0	7.0	4.1
30.0225	0.0029	49.5	7.0	4.0
35.7000	0.0026	56.0	6.1	3.2
35.9994	0.0026	56.0	6.2	3.2
38.8882	0.0026	56.5	6.1	3.1
42.0222	0.0026	57.1	6.0	3.0
42.2987	0.0040	37.1	9.3	7.2
44.3243	0.0035	42.7	8.1	5.4
47.3677	0.0029	52.2	6.6	3.6

3.3. PL-Spectroscopy

The trivalent Eu^{3+} ion emits characteristic orange-red light with multiple narrow linesas a result of the 4f→4f transition. The electronic transition of Eu^{3+} shows redistribution of electrons within 4f sub-shell due to which luminescence spectrum is somewhat influenced by surrounding ligands of Li_2SrSiO_4 host [8]. Figure 3 presents the PLE and PL spectra of Li_2SrSiO_4: 0.015 Eu^{3+} phosphor obtained by monitoring the excitation at 253 nm. The excitation spectrum consists highest intensity

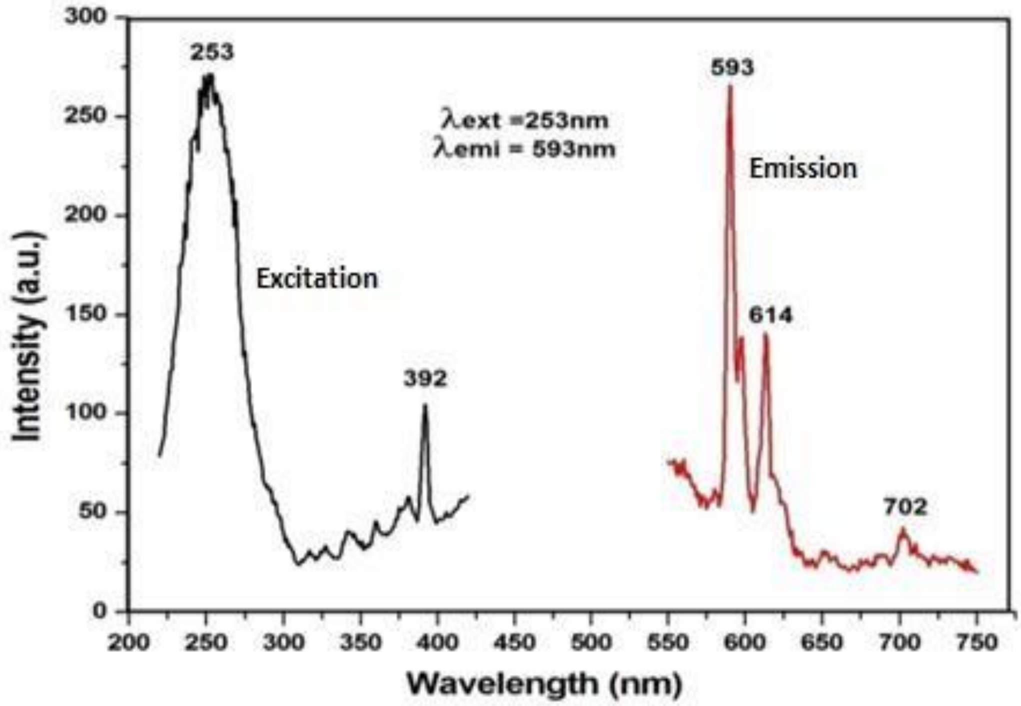

Figure 3. PL excitation and emission spectrum of Li_2SrSiO_4: $0.015Eu^{3+}$.

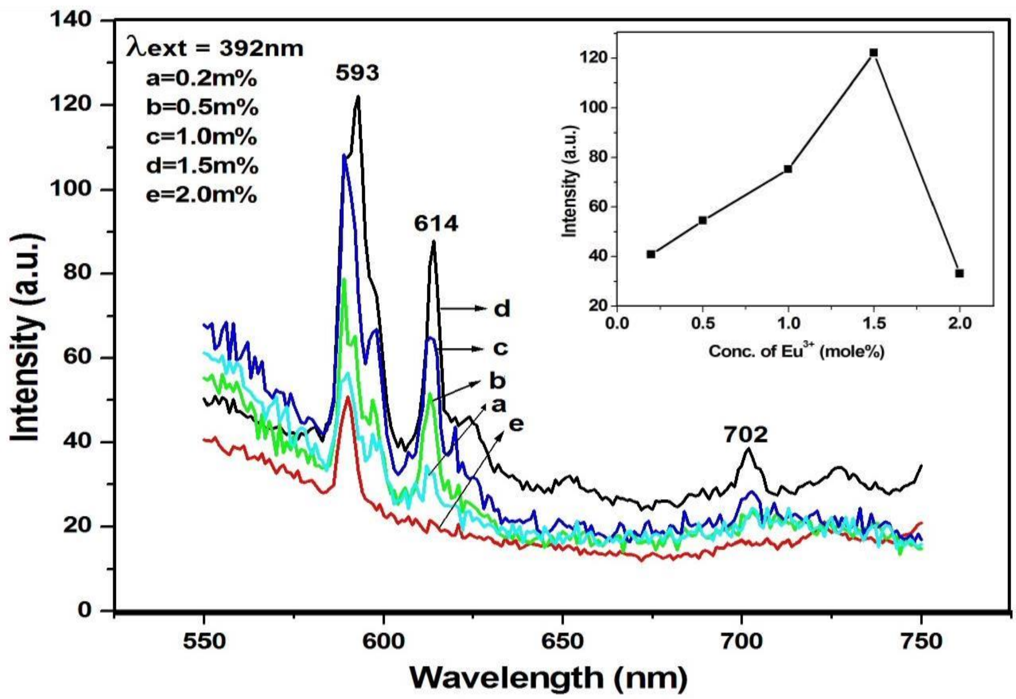

Figure 4. Emission spectra of Li_2SrSiO_4: xEu^{3+} phosphor monitored at λ_{ext} = 392 nm.
(Inset: Variation of emission intensity with concentration of Eu^{3+} in Li_2SrSiO_4.

peak at 253 nm and a characteristics sharp peak of Eu^{3+} at 392 nm which is due to f-f transition. The nature of the emission spectrum excited at 253 and 392 nm are identical, only difference is in intensity. The emission intensities of Eu^{3+} at 253 nm excitation are maximum. At 392 nm excitation, emission spectra with various concentration of Eu^{3+} doped Li_2SrSiO_4 phosphor is shown in figure 4. The transition of Eu^{3+} ions belong to the emission peaks at 593, 614 and 702 nm are mainly due to $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, and $^5D_0 \rightarrow ^7F_4$ respectively, with maximum intensity at 593 nm [9]. In addition, reddish-orange emission is stronger than red emission, indicating that the inversion site in host lattice occupied by large number of Eu^{3+} ions. The ratios of peak emission intensity corresponding to $^5D_0 \rightarrow ^7F_1$ (592 nm) and $^5D_0 \rightarrow ^7F_2$ (614 nm) transitions for 253 nm excitation wavelength are 1.00 and 0.54 respectively. This suggests that magnetic dipole transitions $^5D_0 \rightarrow ^7F_1$ become more prominent as compared to electric dipole transitions $^5D_0 \rightarrow ^7F_2$. It can occur only when Eu^{3+} locates at inversion symmetry site in the host [10]. The asymmetric ratio R (luminescence intensity ratio), for Eu^{3+} ions can be calculated from the expression $R = I\,(^5D_0 \rightarrow ^7F_2)/I\,(^5D_0 \rightarrow ^7F_1)$ [11]. From the integral intensities of the emission spectra, the asymmetric ratio is 0.5272 at 253 nm excitation wavelength. The main factors which affect the intensity of emission are surface roughness and porosity phosphor, scattering and reflection of light, UV transmittance. It is cleared that emission intensity varies directly with Eu^{3+} concentration till 1.5 m%, emission intensity decreases above 1.5m% because of concentration quenching effect. All these observations suggest that the prepared sample is a suitable for the application in solid state lighting. The correlation between the concentration of Eu^{3+} and emission intensity is shown in the inset of figure 4.

4. Conclusions

Europium (Eu^{3+}) doped Li_2SrSiO_4 was successfully synthesized by modified solid state reaction technique and studied for their XRD and PL spectroscopy. The SEM micrograph shows the Li_2SrSiO_4: Eu^{3+} having agglomerated particles with grain size varies in nanometer range. The PL-spectra of Li_2SrSiO_4: Eu^{3+} phosphor shows orange-red emission at 593 nm. The values of red to orange ratio decreased with the increase in the content of Eu^{3+} dopant which suggests that the tendency of Eu ions would be towards high symmetry sites. The prepared Eu^{3+} doped Li_2SrSiO_4 phosphor may be applicable in solid state lighting.

5. References

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