

Synthesis, Characterization and Photoluminescence properties of CaS: Eu³⁺ and SrS: Eu³⁺ phosphors for White LED

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Abstract : CaS: Eu³⁺ and SrS: Eu³⁺ phosphors were synthesized via solid state diffusion method. X-ray diffraction confirmed the cubic crystalline phase of Eu²⁺ ion doped CaS and SrS particles. The crystallite size of CaS: Eu³⁺ and SrS: Eu³⁺ particles were calculated using Debye-Scherrer formula was found to be 17nm and 66nm respectively conforms nano size. The morphological investigations of the particles were made using SEM and found to have an irregular aggregate morphology with an average size of 1.5µm and 3µm respectively. The PL excitation and emission characteristics of CaS and SrS phosphors, as a function of Eu³⁺ concentrations have been studied. FTIR spectra of phosphors determined the chemical bonds in the molecule. The characteristics of CaS: Eu³⁺ and SrS: Eu³⁺ phosphors make them suitable for use as wavelength tunable red emitting phosphors for three band white LEDs pumped by a blue LED (460nm). Fabricated a two band and three bands white LEDs by coating phosphors on to a blue LED chip and characterized its optical properties.

Keywords: Photoluminescence, Phosphor, LED, Solid state diffusion method, XRD, SEM, FTIR.

I. INTRODUCTION

Light-emitting diodes (LEDs) are excellent candidates for general lighting because of their rapidly improving efficiency, durability, and reliability, their usability in products of various sizes, and their environmentally friendly constituents. Effective lighting devices can be realized by combining one or more phosphor materials embedded on the chips. Although numerous phosphors have been proposed in the last decade, the range of phosphors that are suitable for LEDs are very much limited. Sulfide phosphors have attracted great attention recently because they are promising luminescent materials for phosphor-converted white light-emitting diodes (LEDs). White Light emitting diode (W-LEDs) is one of the most efficient solid state lighting sources. Currently, for the generation of white light using LEDs can be achieved by different techniques. One is combining blue, green, and red LEDs, second one is by coating the three colour phosphors on a nUV LED chip and the third one is coating the green and red phosphors on a blue LED chip [1-3]. A blue LED (460 nm) in

combination with Ce³⁺ doped yttrium aluminium garnet (YAG), a yellow emitting phosphor, is one of the best white light LED systems [4-7].

Alkali earth sulfide phosphors are good candidates for LED applications because all of them have strong absorption in the blue region that is suitable for blue LED pumping. During the last few decades many luminescence studies on alkaline earth sulphides doped with rare earth ions have been reported [8-11]. CaS, SrS, BaS and ZnS are wide-gap semiconductor materials and are commercially used as phosphors and also in thin film electroluminescent devices [12-16]. CaS, SrS have several applications when doped with Eu²⁺. They form highly efficient red and orange conversion material in LEDs due to their excitation and emission behavior, i.e. the emission spectrum of a blue LED perfectly overlaps with the excitation to the lowest 5d state and the emission is situated at longer wavelengths than YAG: Ce [17]. SrS and CaS have similar lattice symmetry, making them easier to adjust the positions of absorption and emission and to obtain better colour rendering for white LED applications [18-21].

The sulfide phosphors has the potential to be used in phosphor converted LED as a primary colour emitter in 3 band pc-LED or red spectrum enhancer in yellow phosphor converted white LED. Depending on the host lattice, the 4f-5d transitions in Eu³⁺ are spin and parity allowed and hence have high oscillator strength and so their luminescence intensities are high and the transitions are quite fast. However, synthesis of rare earth doped CaS and SrS particles using solid state method have received little attention. It was therefore decided to synthesis the phosphors using the solid state diffusion method.

In the present study, we investigated the optical and structural properties of Eu doped CaS and SrS phosphors, synthesized by solid state diffusion method, with focus on photo-luminescence (PL) characteristics of these phosphors with the various concentrations of Eu ion and the colour variations of phosphor converted coloured LEDs pumped by blue LEDs.

II. EXPERIMENTAL

2.1 Phosphors preparation: We have used solid state diffusion method for synthesizing CaS:Eu^{3+} and SrS:Eu^{3+} with varying concentrations of Eu^{3+} in the host lattice. CaCO_3 , SrCO_3 and Sulfur (S) were used as the starting materials for the host. Europium Oxide (Eu_2O_3) was used as the activator and added with a specified doping concentration for each phosphor is 0.004, 0.008, 0.02, 0.04 and 0.08 gm in CaS and in SrS. 0.1 gm of Ammonium Fluoride (NH_4F) was used as a flux to decrease the calcination time and to enhance the luminescence intensity. The calculated quantities of ingredients were taken and mixed thoroughly with the help of an agate mortar and pestle. The powder was placed in a clean alumina crucibles and a thin layer of carbon powder was spread over it. This crucible was covered with another similar crucible. The carbon layer over the powder created a reducing environment. This whole arrangement was placed in a muffle furnace and the phosphors were fired at 950°C for 2h.

2.2 Characterisation Techniques: The phosphors were characterized by X-ray powder diffraction (XRD) using a Scintag inc (USA) X-ray diffractometer -Advanced Diffraction System (ADS) using $\text{CuK}\alpha$ (1.54 \AA) source at a scanning step of 0.02 degree, continue time 20s, in the 2θ range from 10° to 60° . The shapes and sizes of the phosphor particles were recorded using scanning electron microscopy (SEM, Carl Zeiss - Leo 1530VP).

The photoluminescence excitation and emission spectra were measured at room temperature using a Spectrofluorophotometer (SHIMADZU, RF-5301 PC) with Xenon lamp as excitation source. The incident beam was perpendicular to the surface of the phosphor, and the observation angle was 45° relative to the excitation source. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm. The FTIR spectra were performed on FTIR spectrometer (Perkin Elmer-Spectrum-100) in the range from 500 to 4000cm^{-1} . To fabricate phosphor converted LEDs, a blue chip (460nm) was used simultaneously as a blue light source and an excitation source for the red-emitting phosphors at Kwaliti Photonics, Hyderabad.

III. RESULTS AND DISCUSSION

3.1. Physical properties: Fig.1 shows the photograph of the observed body colours of CaS:Eu^{3+} (red) and SrS:Eu^{2+} (orange) at room temperature under normal sun light after heating.

3.1. X-ray diffraction: The formation of the compound was confirmed by XRD. Fig.1 shows the XRD patterns of the phosphors. All the diffraction peaks were matched with standard International Centre for Diffraction Data (ICDD) database card. The XRD patterns of CaS and SrS matched perfectly with the ICDD card No. 77-2011 and 75-0895 respectively.

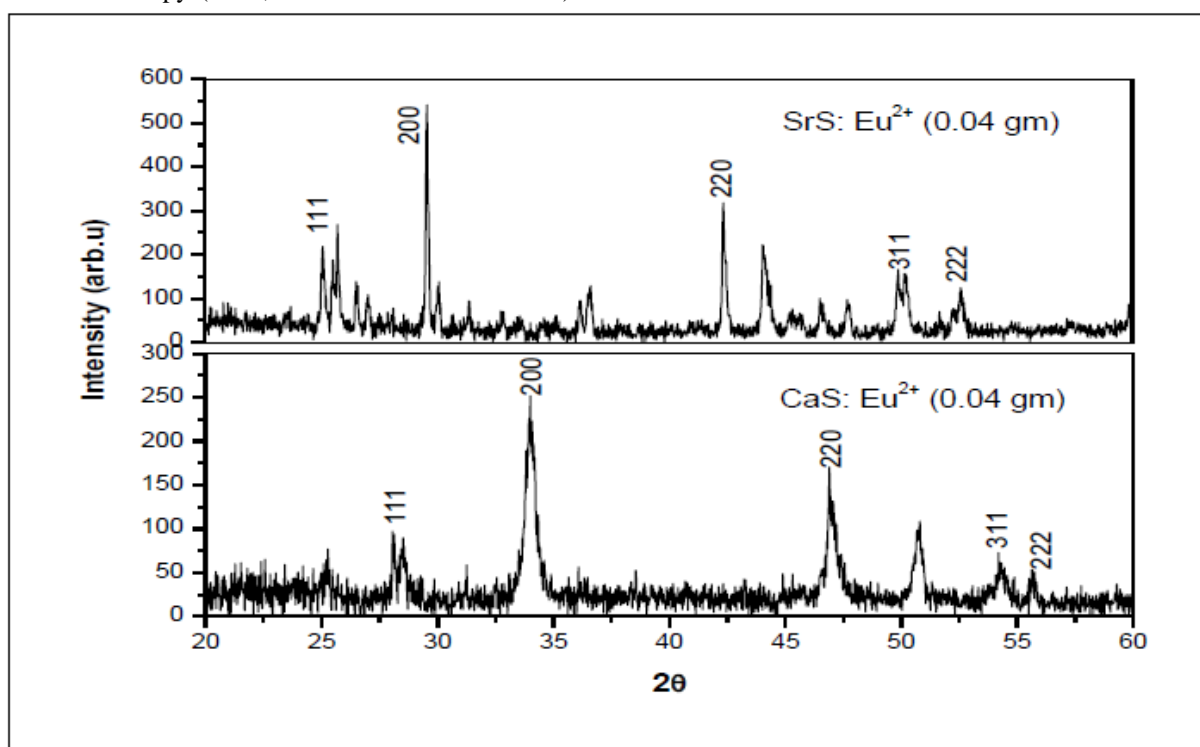


Figure 1 XRD patterns of SrS:Eu^{3+} (0.04gm) and CaS:Eu^{3+} (0.04gm) phosphors

The main peaks corresponds to diffraction at (111), (200), (220), (311) and (222) planes respectively. From the XRD patterns, in addition to the majority CaS and SrS phase, minor CaO and SrO phase are found may be

due to less heating duration. All the peaks can be indexed to the phase, indicating that the doping ions did not form any new phases in the synthesis process.

In the case of CaS:Eu^{3+} , the diffraction peaks are shifted to the higher angle side due to the decrease in lattice parameter. In the case of SrS:Eu^{3+} , the diffraction peaks are shifted to the lower angle side due to the slight increase in the lattice parameter. The broad peaks of (200) and (220) indicate that the nano crystalline behavior of the CaS:Eu^{3+} phosphor than SrS:Eu^{3+} phosphor which reflect in crystallite sizes.

The ionic radius of Sr^{3+} is 1.18 Å, Ca^{3+} is 1.05 Å and Eu^{3+} is 1.29 Å, respectively. Therefore, on the basis of effective ionic radius of cations, we predicted that Eu^{3+} would occupy the Sr^{3+} and Ca^{3+} sites in the host structure. The arrangement of anions about a cation as calculated from the ratio of the cation radius to the anion radius rC/rA , six anions can be arranged about a cation called octahedral. CaS has NaCl type structure, where Eu^{3+} sits in a six fold Ca^{3+} site surrounded by S^{2-} ions to make an O_h symmetry [22].

Fig.1 shows the variation in 2θ for the most intense peak and lattice constant of CaS:Eu^{3+} and SrS:Eu^{3+} . The crystallite size have been computed from the width of the (200) peak using Debye-Scherrer $D = k\lambda / \beta\cos\theta$ formula, where D is the crystallite size, k is the constant (0.9), λ is the wavelength of the X-ray source, β and $\cos\theta$ is the FWHM and angle corresponding to the big or broad peak. XRD results indicate that the CaS:Eu^{3+} and SrS:Eu^{3+} phosphors were well synthesized as a single phase. X-ray diffraction confirmed the cubic crystalline phase of Eu^{3+} ion doped CaS and SrS particles. The crystallite size of CaS:Eu^{3+} and SrS:Eu^{3+} calculated using Debye-Scherrer formula was found to be 17nm and 66nm.

3.2. Microstructures: SEM micrographs of CaS:Eu^{3+} (0.04 gm) and SrS:Eu^{3+} (0.04 gm) phosphors after annealing at 950°C are shown in fig.3. These images show that, the phosphors display an irregular aggregate morphology of CaS:Eu^{3+} (0.04 gm) with an average particle size of about 1.5 μm and of SrS:Eu^{3+} (0.04 gm) with an average particle size of about 3 μm .

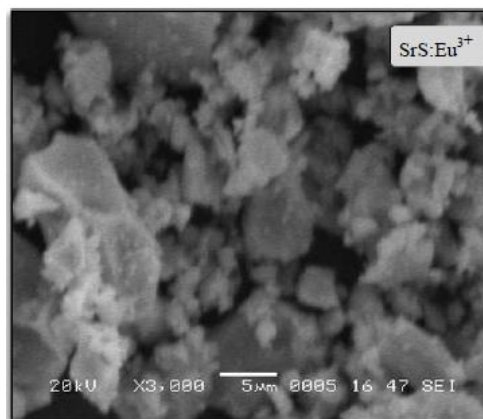
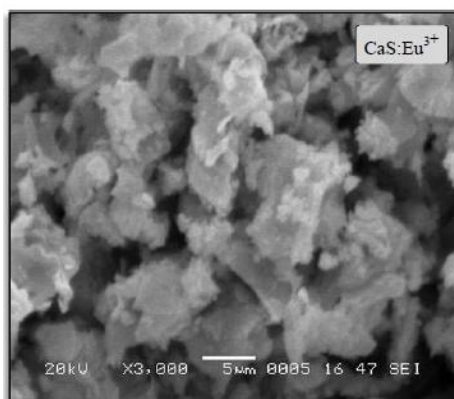


Figure 3 SEM photographs of CaS:Eu^{3+} and SrS:Eu^{3+} phosphors

3.3. Photoluminescence study

Fig 4(a) and (b) shows the PL excitation spectra of the CaS:Eu^{3+} and SrS:Eu^{3+} phosphors monitored under 650nm wavelength. From fig.4 (a) it was observed that the broad excitation bands of the 635nm emission are found at 265 and 585 nm. The bands at 265nm and 585nm can be attributed to the e_g and t_{2g} field splitting 5d bands of Eu^{2+} split into two levels located in UV and visible regions. From fig.4 (b) it was observed that the broad band excitation peaks of 600nm emission are found at 285 and 540nm. The broad band excitation peaks of 5d field splitting components e_g and t_{2g} are found to have a red shift to 285nm and a blue shift to 540nm. This indicates a weaker field splitting of the Eu^{3+} 5d state due to a weaker ligand field generated by a larger lattice. Band gap (4.679 eV) of CaS is more than that of the band gap (4.351 eV) of SrS. Lattice constant (6.0497Å) of SrS is more than that of lattice constant (5.2667Å) of CaS. The ligand field splitting of 5d level of Eu^{3+} results in red shifts for both emission and excitation peaks from CaS host to SrS host.

There is no charge transfer transition observed from Eu^{2+} ground state to the host conduction band, implying that the Eu^{3+} ground state is close to the host valence band [23], or lowest 5d band overlaps with the host conduction band [24, 25]. As the excitation intensity increased with the increase of the doped Eu^{3+} concentration, as seen in fig.4, a high portion of the emissions was slightly reabsorbed, and therefore the emissions at longer wavelengths acquired enough intensity to red-shift. That is, energy transfer would cause a red-shift of emission peak. The excitation spectra of the developed phosphors cover the wavelength range of commercially available blue LEDs. CaS and SrS have similar lattice symmetry, making them easier to have a solid solution in order to adjust the positions of absorption and emission and to obtain better color rendering for white LED applications.

Fig.5 shows the PL emission spectra of CaS:Eu^{3+} and SrS:Eu^{3+} phosphors at different concentrations (0.004, 0.008, 0.02, 0.04 and 0.08gm) under 460nm excitation. For the synthesized sulfide phosphors doped with rare

earth europium ion, PL arises due to electronic transitions in the rare earth ion. In Eu^{3+} , electronic transition ${}^4f_6 {}^5d_1 \leftrightarrow {}^4f_7$ is responsible for luminescence [26].

CaS:Eu^{3+} phosphors (fig.5 right side curves) have maximum emission intensity at 635nm with a FWHM of 50nm, corresponding to the ${}^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+} or 1.952eV energy [27, 28]. Emission intensities of phosphors under 460nm excitation wavelength are shown in table-2. The CIE coordinates of the CaS:Eu emission were (0.661, 0.338) indicating red emission. Smet et al [9] reported the broad emission maximum of CaS:Eu particle is at 653 nm at room temperature.

SrS:Eu^{3+} phosphor (fig.5 left side curves) have maximum emission intensity at 600nm with a FWHM of 62nm, corresponding to the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{2+} or 2.066eV energy. The CIE coordinates of the SrS:Eu emission were (0.567, 0.428) indicating orange emission. Dongdong Jia et al. [29] reported the broad emission maximum of SrS:Eu particle is at 607 nm.

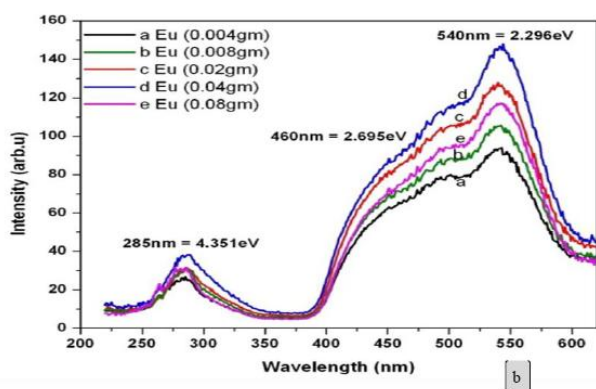


Figure.4 PL excitation spectra of (a) CaS:Eu^{3+} (b) SrS:Eu^{3+} phosphors, monitored under 650nm wavelength.

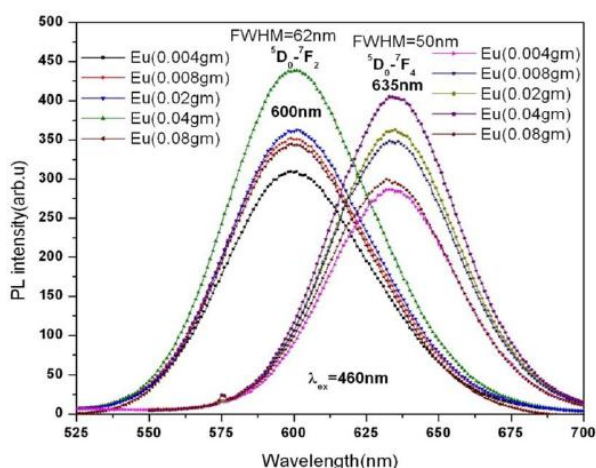


Figure 5 PL emission spectra of CaS:Eu^{3+} (635nm) and SrS:Eu^{3+} (600nm) phosphors under 460nm excitation

Table-2 Emission intensities under 460nm excitation wavelength

S. No	Concentration of Eu (gm)	Emission intensities (arb.u)	
		CaS:Eu^{3+} (635nm peak)	SrS:Eu^{3+} (600nm peak)
1	0.004	287	311
2	0.008	349	350
3	0.02	363	371
4	0.04	406	439
5	0.08	298	344

From the excitation and emission spectrums it was observed that Eu (0.04gm) doped phosphor shows highest intensity than other phosphors. Concentration quenching affect is observed in SrS and CaS phosphors. Beyond 0.04gm concentration, the excitation intensity was decreased due to the energy transferred back and forth between activators. It was found that the peak positions for all phosphors are same with different intensity clearly indicates that there is no change in the particle size.

The shift of the emission spectrum to shorter wavelengths when smaller Ca ions (1.05 Å) are replaced by bigger Sr ions (1.18 Å) is clearly observed. The shift of the emission spectrum of SrS:Eu to shorter wavelengths might be due to large crystallites (66nm) than that of CaS:Eu crystallites (17nm), might cause a change in the crystal field strength, resulting in a shift of the emission spectrum. It is also an evident from SEM study that the particle size of CaS:Eu^{3+} is smaller than the SrS:Eu^{3+} .

Comparison of these spectra indicates that a blue shift of the emission wavelength, with a color tuning range of about 35 nm. This blue shift can be interpreted in terms of the crystal strength. As the crystal field strength increases, the emission wavelength increases. Since CaS:Eu^{3+} and SrS:Eu^{2+} have cubic structures, each Eu^{2+} ion is surrounded by six S^{2-} ions. The excited state of the Eu^{2+} ion with a ${}^4f_6 {}^5d_1$ electronic configuration can be split into the lower t_{2g} state and the higher e_g state. Since the lattice parameter of SrS:Eu^{3+} (6.0497Å) is more than that of the lattice parameter of CaS:Eu^{3+} (5.2667 Å), the distance between the Eu^{2+} ion and S^{2-} ions in SrS:Eu^{3+} (3.0249Å) is longer than that in CaS:Eu^{3+} (2.6333Å). Increasing the distance between the Eu^{2+} ion and S^{2-} ions will decrease the crystal strength, which should lead to a decrease in the energy difference between t_{2g} and e_g states of the ${}^4f_6 {}^5d_1$ electronic configuration.

3.5. FT-IR Spectrum: The FTIR technique is to measure the absorption of various infrared radiations by the target material, to produces an IR spectrum that can be used to identify functional groups and molecular structure in the phosphor. FT-IR patterns of CaS:Eu^{3+} (0.04gm) and SrS:Eu^{3+} (0.04gm) phosphors was recorded using Perkin Elmer-Spectrum 100 FT-IR Spectrometer. The instrument wave number ranges from 4000–500 cm^{-1}

¹ with an accuracy of $\pm 0.01 \text{ cm}^{-1}$ and resolution of $\pm 1 \text{ cm}^{-1}$.

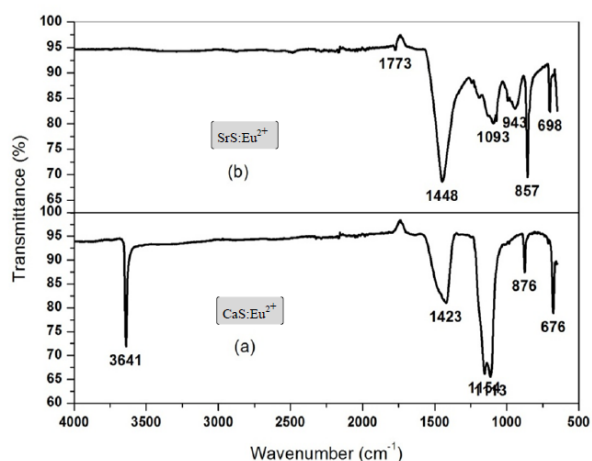


Figure 6 FT-IR patterns of (a) CaS:Eu³⁺ (0.04 gm) and (b) SrS:Eu³⁺ (0.04 gm) phosphors

Fig.6 shows the FTIR spectrum of CaS:Eu³⁺ (0.04gm) and SrS:Eu³⁺ (0.04gm) phosphors. CaS:Eu³⁺ shows sharp peak at 3641 cm⁻¹ was assigned to free OH stretching vibration may be due to absorption of moisture from the surroundings forming calcium hydroxide. The broad peaks at 1423, 1154, 1113cm⁻¹ were due to the characteristic frequency of inorganic ions. The sharp peaks at 876 and 676cm⁻¹ were assigned to the CaCO₃ band. Whereas SrS:Eu³⁺ shows almost similar broad peaks at 1448, 1093, 943 and sharp peaks at 857 and 698cm⁻¹ except at 3640 cm⁻¹. This clearly indicates that the absorption of moisture by the target material SrS:Eu³⁺ around 3650cm⁻¹ is not present. From the FTIR studies we observed that most of the bands from ligands and are Ca-S (Sr-S), Ca-O (Sr-O), Eu-S, and the O-H stretching vibrations. The variation of different absorption intensities are nothing but, the presence of ligands in different concentrations.

3.6. Making an LED device: In order to investigate the potential of the as-synthesized phosphor in LED application, a prototype LED was fabricated by pre-coating the optimized Eu³⁺ doped CaS and SrS phosphors onto a 460nm emitting InGaN chip. Eu³⁺ doped SrS and CaS phosphors were individually blended into transparent adhesives and dropped onto a blue chip to make a phosphor-coated LED. Fig.7 (a) shows 6 cups of SrS:Eu³⁺ (0.04 gm) coated on blue LED chip and fig.7(b) shows 6 cups of CaS:Eu³⁺ (0.04 gm) coated on blue LED chip. The luminous efficiency of the fabricated white LEDs were found as high as 23.6 and 35 lm/W under 20 mA driving current. The CIE co-ordinates of white LED were x = 0.3390, y = 0.2814 and x = 0.3395, y = 0.2434 with R_a values of 84.5 and 85, respectively.

An LED devices were made with 8 cups of CaS:Eu³⁺ and 4 cups of YAG:Ce³⁺ and as well as 8 cups of SrS:Eu³⁺ and 4 cups of YAG:Ce³⁺ by following the same procedure as mentioned in earlier. The prepared LEDs

show the warm white light as shown in the fig.8 (a) & (b).

The CIE co-ordinates of white LEDs are x=0.3395, y=0.3434 and x=0.3356, y=0.3032. The luminous efficiency of the fabricated white LED was found as 62 and 60 lm/W under 20 mA driving current with 3.29 forward voltage respectively. The Colour Rendering Index (CRI) value is 92 and 90 (R_a) respectively. The approach of Lumileds for a warm white light was to add a red emitter to the plain white of InGaN (blue) + YAG:Ce. They chose CaS:Eu²⁺ and achieved excellent CRI R_a > 90.

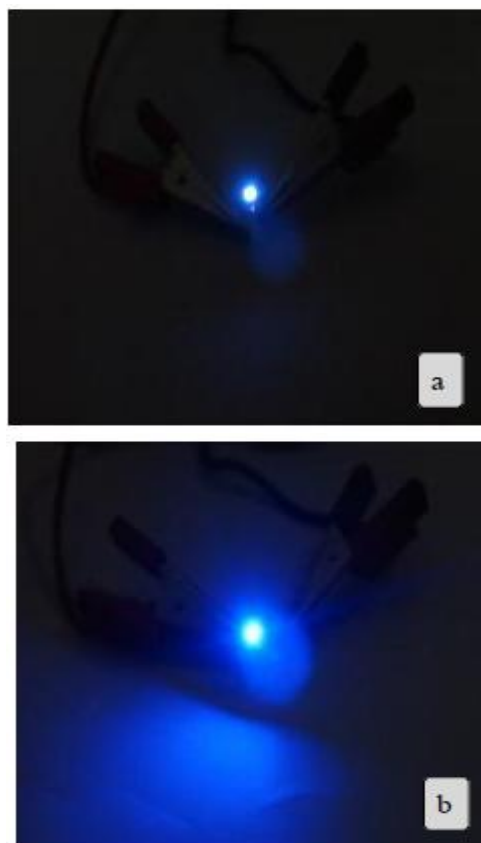
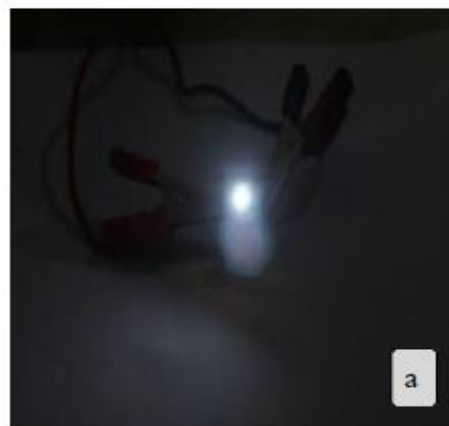


Figure 7 White light emission of (a) SrS:Eu³⁺ (0.04 gm) and (b) CaS:Eu³⁺ (0.04 gm) phosphors coated on 460nm blue LED chip



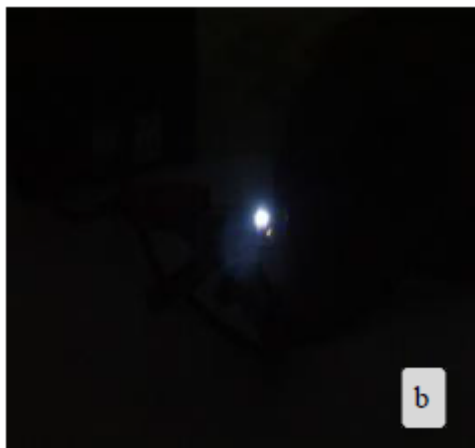


Figure 8 Warm white light emission from (a) CaS:Eu³⁺+YAG:Ce³⁺ (b) SrS:Eu³⁺+YAG:Ce³⁺ phosphors coated on 460nm InGaN blue LED chip

IV. CONCLUSIONS

CaS:Eu³⁺ and SrS:Eu³⁺ phosphors have been synthesized by solid state diffusion method successfully. Their crystal structure and optical properties were also investigated. XRD confirms the cubic crystalline phase of the CaS:Eu³⁺ and SrS:Eu³⁺ and the crystallite size was found to be 17nm and 66nm. The PL emission characteristics of CaS:Eu³⁺ and SrS:Eu³⁺ phosphors as a function europium concentrations have been investigated. Strong blue-green (450-580nm) absorption is observed in these phosphors. These phosphors can be used as wavelength tunable red emitting phosphors from 600nm to 635nm under blue excitation. The powder phosphors doped with Eu²⁺ ion at the optimized concentration of 0.04 gm (substitution at Ca²⁺ and Sr²⁺ site) was efficiently excited by blue light of wavelength 440-480 nm emit red at 635nm by CaS:Eu³⁺ phosphor and orange at 600nm by SrS:Eu³⁺ phosphor. The present results show that the white LEDs fabricated by coating the prepared phosphors on a blue LED chip have high luminescence and good colour properties. We also prepared and LEDs with our prepared CaS:Eu³⁺ along with YAG:Ce phosphor and obtained better output of white light with good Ra value.

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