

Synthesis and Photoluminescence Properties of White Emitting Alkaline Earth Chalcogenide Phosphors doped with Sn for Solid State Lighting

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Abstract: *Sn²⁺ doped white emitting alkaline-earth chalcogenide CaS and SrS phosphors were synthesized by carbo-thermal reduction method. In this method special requirement such as H₂S gas flow is not required as a source of sulphur and is comparatively easy method to prepare sulfides. The crystalline phase, morphology, and photoluminescence properties were characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), and fluorescence spectrophotometer, respectively. Phosphors exhibit broad band excitation which has excellent spread over nUV as well as blue region of visible light i.e. 440–480 nm. Emission is in the form of characteristic broad band of Sn²⁺ covering nUV and almost entire regions of visible spectrum i.e. 400–650 nm. The XRD pattern of prepared phosphor well matches with International Center for Diffraction Data. Synthesized phosphor particles are of different sizes, with smooth surfaces, from less than 1 micron to few microns. The chromaticity coordinates of synthesized phosphors have been calculated from its corresponding emission spectra monitored at their excitation wavelengths. They observed to falls in white region of CIE diagram. These points are close to standard white point D65, corresponding to daylight with correlated color temperature (CCT) 6500 °K, indicating better color purity of the synthesized phosphor and they are promising material for a color converter using blue LED as the primary light (pumping) source in phosphor converted white LED (pc wLED) for solid state lighting.*

Keywords: Solid State Lighting; carbo-thermal reduction; white phosphor; photoluminescence; chalcogenide

I. INTRODUCTION

In the past few decades energy-efficient solid-state lighting and less power consuming white light emitting diodes (w-LEDs), which are regarded as the source of light in coming generation, used in display lighting sources and illuminating systems for domestic as well industrial applications. In present situation, white light-emitting diodes (w-LEDs), as the next generation of solid-state lighting, have attracted much attention due to their special advantages, such as high efficiency, long lifetimes, weak environmental impact, absence of mercury, short response times, applicability in final products of various sizes, and so on [1, 2]. In the case of the phosphor converted white light LEDs (pc wLED), the phosphor materials play an important role. For example, the most common and simple wLED source is combined of a blue-emitting InGaN chip and a Ce³⁺ doped yttrium aluminium garnets (YAG:Ce³⁺) yellow phosphor [3], which is very stable and exhibits high luminescence efficiency. However, in some respects YAG:Ce³⁺ based dichromatic systems often suffer from reduced thermal stability and exhibit a poor color-rendering index (CRI) caused by the color deficiency in the red and blue-green of the phosphor. In principle, using a single white phosphor instead of phosphor blends could help to reduce some of this variability, which relies critically on the phosphor properties. In recent years, numerous efforts have been made to develop single-phase white-light-emitting phosphors for near-ultraviolet or blue

excitation to solve the above challenges with certain achievements. We obtained white light emission in a single-phase alkaline-earth chalcogenide CaS and SrS as host phosphors with single Sn²⁺ dopant. These materials are indirect band gap semiconductors at ambient conditions [4]

II. EXPERIMENTAL

2.1. Material and Method

Polycrystalline samples of Sn²⁺ doped CaS and SrS phosphors for different dopant concentrations were prepared by two step synthesis technique of carbo-thermal reduction method starting from high purity AR grade nitrate precursors. In first step extremely fine sized snow white sulphates were produced [5, 6]. In second step this sulphates are reduced by carbo-thermal reduction method at 750 °C for 3 h in reducing atmosphere produced by activated charcoal and then allowed to cool slowly to room temperature [7]. The fine sized soft powders of dull white body color chalcogenide phosphors were obtained. Corresponding balanced reactions with molar ratios of precursors are given in the Table 1.

Table 1: Balanced chemical reactions with molar ratios of ingredients for synthesis of Sn²⁺ doped alkaline earth chalcogenide phosphors

Sr.No.	Products	Reactions
1	Ca _(1-x) S:Sn ²⁺ _x , (X= 0.001, 0.003, 0.005, 0.01, 0.02)	1. (1-x)Ca(NO ₃) ₂ .4H ₂ O + xSn(NO ₃) ₂ .6H ₂ O + H ₂ SO ₄ → Ca _(1-x) SO ₄ : Sn ²⁺ _x ↓ + 5 H ₂ O + 2NO ₂ ↑ + O ₂ ↑ 2. Ca _(1-x) SO ₄ :Sn ²⁺ _x → Ca _(1-x) S:Sn ²⁺ _x + 2O ₂ ↑
2	Sr _(1-x) S:Sn ²⁺ _x , (X= 0.001, 0.003, 0.005, 0.01, 0.02)	1. (1-x)Sr(NO ₃) ₂ .4H ₂ O + xSn(NO ₃) ₂ .6H ₂ O + H ₂ SO ₄ → Sr _(1-x) SO ₄ : Sn ²⁺ _x ↓ + 5 H ₂ O + 2NO ₂ ↑ + O ₂ ↑ 2. Sr _(1-x) SO ₄ :Sn ²⁺ _x → Sr _(1-x) S:Sn ²⁺ _x + 2O ₂ ↑

2.2. Characterization

The prepared materials were characterized by powder XRD. Powder X-ray diffraction measurements were taken on Rigaku Miniflex II X-ray Diffractometer and compared with the ICDD file. The Surface morphology of the annealed particles was performed on Hitachi Field Emission Scanning Electron Microscope model S-4800. It is equipped with energy-dispersive X-ray spectroscopy (EDS) system that enables sample elemental analysis. The photoluminescence (PL) and PL excitation (PLE) spectra were measured on Hitachi F-7000 fluorescence spectrophotometer at room temperature. The parameters such as spectral resolution, width of the monochromatic slits (1.0 nm), photomultiplier tube (PMT) detector voltage and scan speed were kept constant throughout the analysis of samples. The color chromaticity coordinates were obtained according to Commission International de l'Eclairage (CIE).

III. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction Patterns (XRD)

The XRD pattern of the as synthesized phosphors CaS:Sn²⁺ shows good agreement with standard ICDD Files No. 03-065-2926 of host matrix shown in **Figure 1(a)** whereas XRD patterns of the as prepared SrS:Sn²⁺ phosphors powder matches well with standard ICDD Files No. 01-075-0259 of host matrix as shown in **Figure 1(b)**. For different concentrations of Sn²⁺ XRD patterns remains unchanged indicating no other phase is formed and there no residue of precursor is present. When the concentration of Sn²⁺ ions were varied from 0.001 to 0.02 mole there was no change found in the XRD peaks pattern. This indicates that the sites of Ca²⁺ and Sr²⁺ ions have been successfully replaced by Sn²⁺ ions in the phosphors without affecting the crystal structure of the host lattices as expected from the corresponding ionic radii of Ca²⁺, Sr²⁺ and Sn²⁺ ions [8].

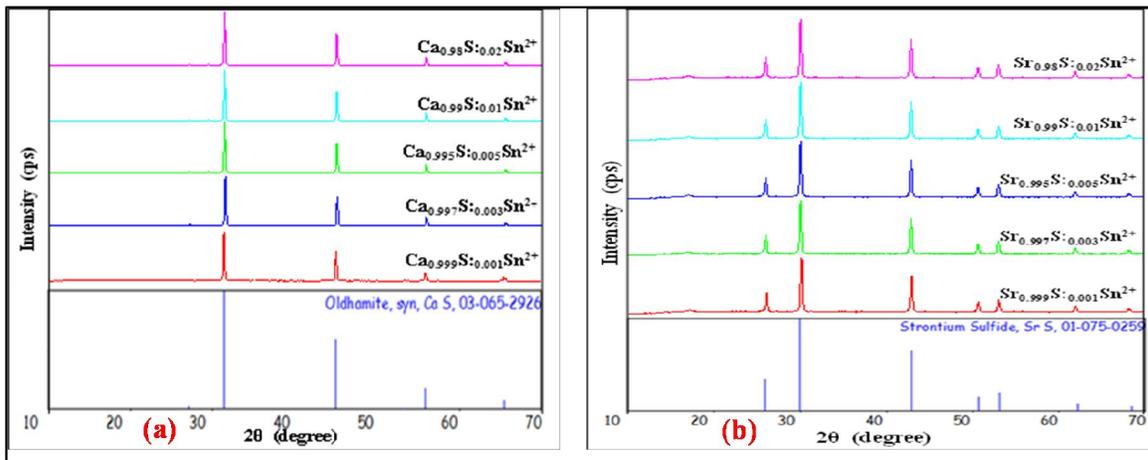


Figure 1: X-ray diffraction patterns with different Sn^{2+} concentrations of as synthesized (a) $\text{CaS}:\text{Sn}^{2+}$ and (b) $\text{SrS}:\text{Sn}^{2+}$ phosphors

Both the phosphors have cubic crystal structure with space group $\text{Fm}\bar{3}\text{m}$ (225), for host lattice, with $\alpha = \beta = \gamma = 90^\circ$ and $Z = 4$ for both the phosphors. For CaS phosphor the lattice parameters are $a = b = c = 5.6940 \text{ \AA}$ and volume = 184.609 \AA^3 **Figure 2(a)** whereas for SrS the lattice parameters are $a = b = c = 6.0079 \text{ \AA}$ with volume = 216.854 \AA^3 **Figure 2(b)**.

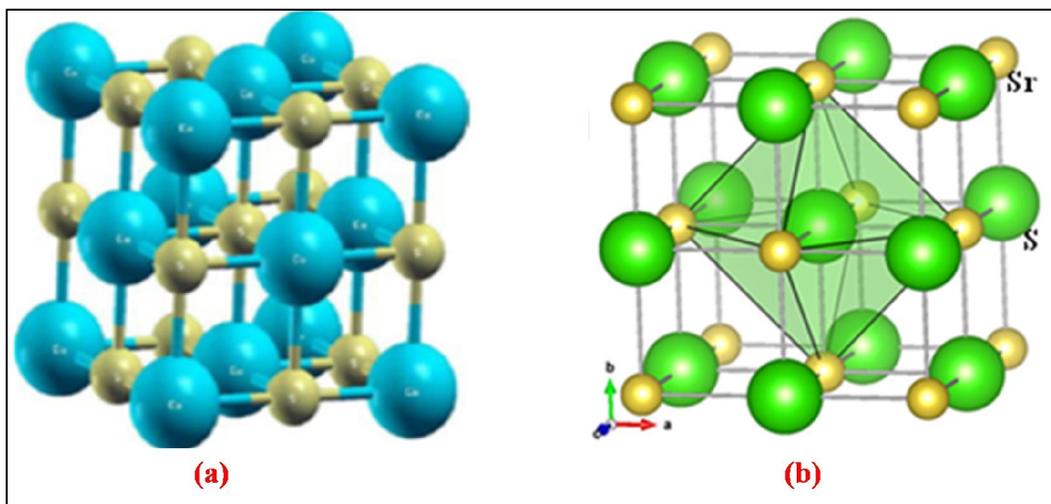


Figure 2: Schematic crystal structure diagrams of CaS and SrS host lattices in Sn^{2+} doped phosphors

3.2. EDS Patterns

The corresponding EDS spectrum $\text{CaS}:\text{Sn}^{2+}$ is shown in **Figure 3 (a)** mainly composed of Ca and S atoms in appropriate proportion of elemental composition whereas the EDS spectrum $\text{SrS}:\text{Sn}^{2+}$ is shown in **Figure 3 (b)** mainly composed of Sr and S atoms in appropriate proportion of elemental composition in prepared phosphors. No other impurity was detected except small amount of Sn indicating that Sn element is successfully doped in the prepared phosphors. In addition to these small peaks corresponding to Pt arises as a result of platinum used during sample preparation for scanning electron microscopy (SEM).

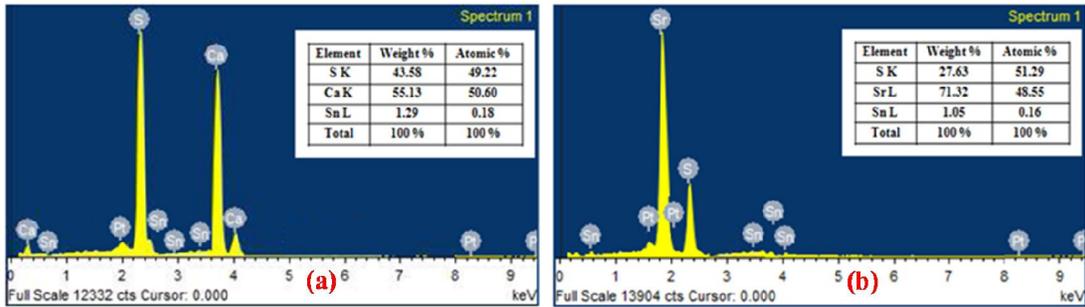


Figure 3: EDS spectrum of as synthesized (a) CaS:Sn²⁺ and (b) SrS:Sn²⁺ phosphors

3.3. Morphology Study (SEM)

SEM images of synthesized CaS:Sn²⁺ and SrS:Sn²⁺ phosphor, are shown in Figure 3 (a) and (b) respectively, shows that particles are of different sizes with smooth surfaces. The image also shows aggregated non homogeneous particles that consist of elongated and spherical shape with sizes from less than 1 micron to few microns which is a suitable size for fabrication of SSL devices [9]. In addition, an aggregation of irregular lumps that consisted of irregular particles was also observed.

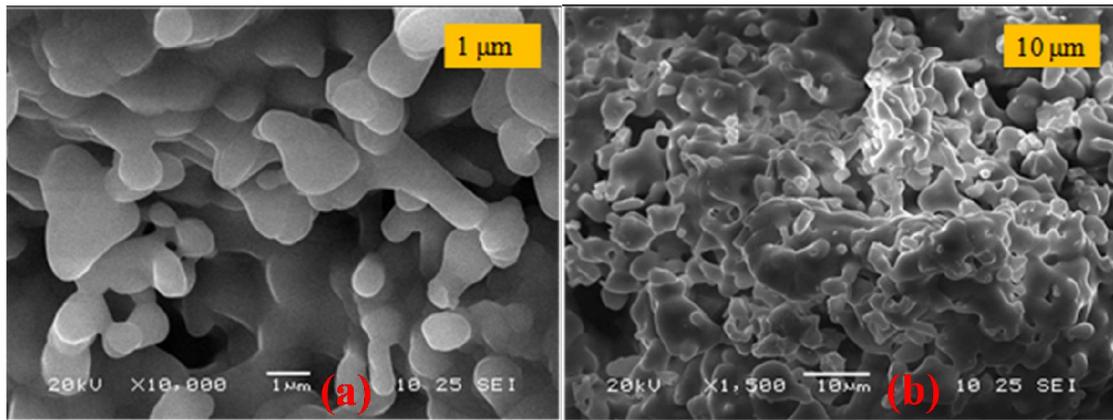


Figure 4: SEM images of as synthesized (a) CaS:Sn²⁺ and (b) SrS:Sn²⁺ phosphors

3.4. Photoluminescence Study

3.4.1. Energy Level Diagrams for Sn²⁺ Doped Alkaline earth Chalcogenide Phosphors

Schematic energy level diagrams for Sn²⁺ doped CaS and SrS phosphors are shown in Figure 5.

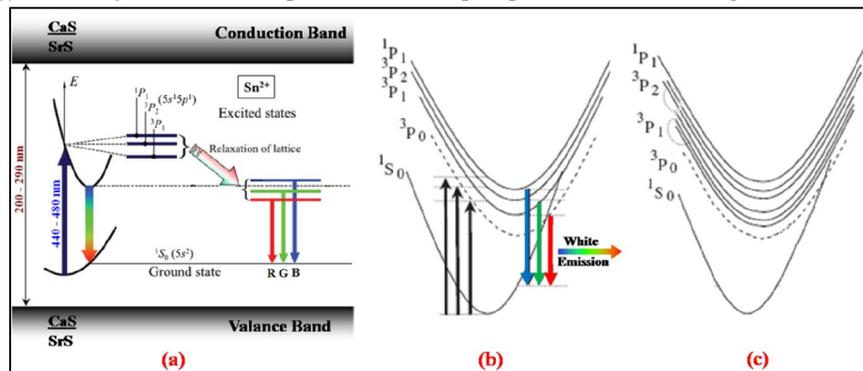


Figure 5: Schematic energy level diagrams for Sn²⁺ ions in CaS and SrS host lattice

An s^2 ion, such as Sb^{3+} , Pb^{2+} , Bi^{3+} or Sn^{2+} , has 1S_0 ground state and spexcited states (3P_0 , 3P_1 , 3P_2 , 1P_1) **Figure 5 (a)**. The triplet states 3P_0 , 3P_1 , and 3P_2 can be split owing to the spin-orbit interaction **Figure 5 (c)**. The energies of these absorption peaks are usually dependent on the metal and are typically modified by the host matrix material. The $^1S_0 \rightarrow ^3P_0$ transition is forbidden and is therefore usually not observed in any optical spectra **Figure 5 (b)**[10].

3.4.2. Combined Excitation and Emission Spectra of Sn^{2+} Doped Alkaline Earth Chalcogenide Phosphors

Combined excitation and emission spectrum of prepared phosphor is shown in **Figure 6 (a)** and **(b)**. Photoluminescence properties $CaS:Sn^{2+}$ can be explain in the view of **Figure 4**. The fundamental excitation band in CaS occurs at 200–290 nm was characterized as host excitation centered at 260 nm **Figure 5 (a)**. Along with this band other bands due to $^1S^0 \rightarrow ^3P_1$, $^1S_0 \rightarrow ^3P_2$ and $^1S_0 \rightarrow ^1P_1$ transitions of Sn^{2+} centers are present, in the order of increasing photon energy, with maximum intensity band centered at 469 nm [11] **Figure 5 (a) and (b)**. The excited states in these transitions have triplet (3P_1), doublet (3P_2), and singlet (1P_1) structures respectively **Figure 5 (c)**. The high energy low intensity narrow excitation band due to singlet is in the range of 290 nm to 312 nm centered at 300 nm, moderate energy medium intensity band due to doublet structure has multiple peaks in the range of 312 nm to 423 nm with maximum intensity peak at 370 nm followed by low energy high intensity band due to triplet structure again has multiple peaks from 423 nm onwards with highest intensity peak centered at 469 nm. The PL spectrum in of $CaS:Sn^{2+}$ consists of moderate intensity multiple peak Blue and Green broad emission bands with high intensity single peak broad band centered at 568 nm in green-yellow region of visible spectrum followed by very low intensity Red band located at 636 nm. These emission bands are traditionally assigned to energy levels arising from the Jahn–Teller effect on the triplet state of s^2 ions in alkaline earth chalcogenides [11].

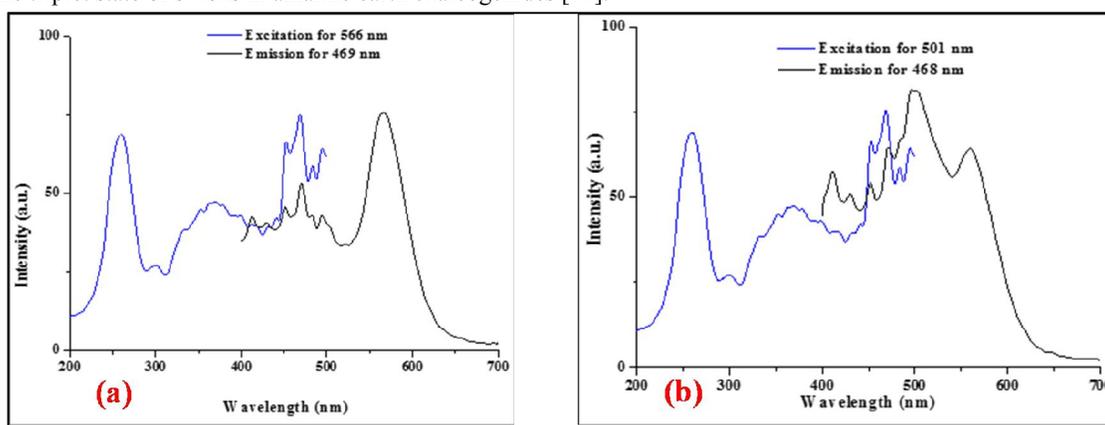


Figure 6: Combined excitation and emission spectra of (a) $CaS:Sn^{2+}$ and (b) $SrS:Sn^{2+}$ phosphors

Photoluminescence properties $SrS:Sn^{2+}$ can be explain in the view of **Figure 5**. PLE spectrum is similar to that of $CaS:Sn^{2+}$ except variation in intensities. The PL spectrum in $SrS:Sn^{2+}$ is slightly different from of $CaS:Sn^{2+}$. It consists of moderate intensity multiple peak broad Blue band with high intensity peak centered at 469 nm and high intensity multiple peak broad Green bands with highest intensity peak centered at 501 nm, the emission intensity of peak in yellow region is found to decrease drastically in SrS as compared to CaS , followed by very low intensity Red band located at 644 nm. The experimental data in **Figure 6 (a)** and **(b)** clearly indicate that the observed luminescence in CaS and SrS are due to the Sn^{2+} center [**Figure 5**].

3.4.3. Effect of Sn^{2+} concentrations on emission intensity of Sn^{2+} doped alkaline earth chalcogenide phosphors

For different concentrations of Sn^{2+} there is no change in shape and position of emission band in $CaS:Sn^{2+}$ and $SrS:Sn^{2+}$ phosphors except emission intensity. Optimum concentration is in case of CaS phosphor is 0.005 mole of Sn^{2+} and the ratio (G/Y) of luminous intensities of green (494 nm) and greenish-yellow (567 nm) emission bands for different Sn^{2+} concentration is constant (0.57). The inset shows relative luminescence intensity at 494 nm and 567 nm as a function of Sn^{2+} concentrations **Figure 7 (a)**. Whereas optimum concentration is in case of SrS phosphor is 0.01

mole of Sn^{2+} and the ratio (G/Y) of luminous intensities of green (496 nm) and greenish-yellow (559 nm) emission bands for different Sn^{2+} concentration is also constant (1.27). The inset shows relative luminescence intensity at 496 nm and 559 nm as a function of Sn^{2+} concentrations **Figure 7 (b)**.

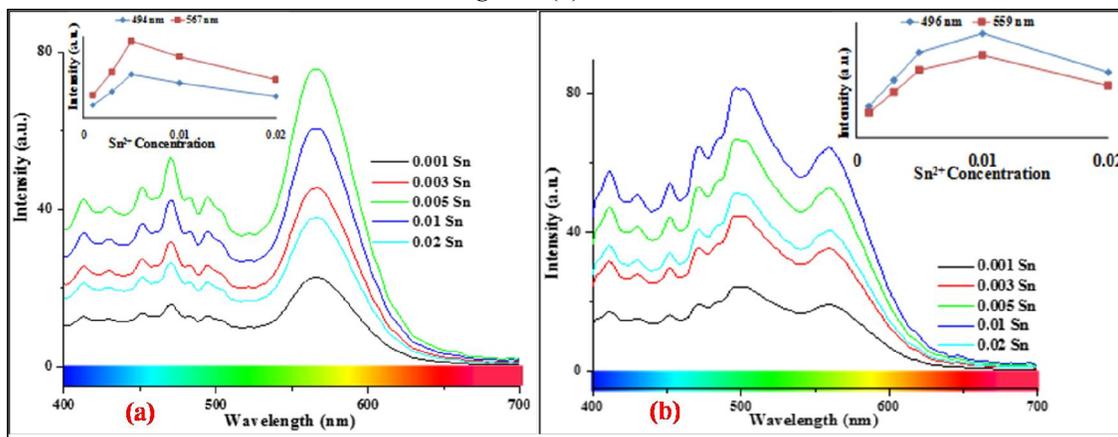


Figure 7: Effect of dopant concentrations on emission of as synthesized (a) $\text{CaS}:\text{Sn}^{2+}$ and (b) $\text{SrS}:\text{Sn}^{2+}$ phosphors, the inset shows relative luminescence intensity at green and yellow peaks for different Sn^{2+} concentration

3.5. Study of Color Chromaticity of Sn^{2+} Doped Alkaline Earth Chalcogenide Phosphors

The chromaticity coordinates of $\text{CaS}:\text{Sn}^{2+}$ and $\text{SrS}:\text{Sn}^{2+}$ phosphors have been calculated from their corresponding emission spectra monitored at their respective excitation wavelengths. They are (0.304, 0.361) and (0.298, 0.357) falls in white region of CIE diagram. These points are in close proximity to standard white points D65 as shown in **Figure 8 (a)** and **(b)**, corresponding to daylight and equal energy having correlated color temperature (CCT) 6500°K and 5400°K respectively, indicating better color purity of the synthesized phosphor.

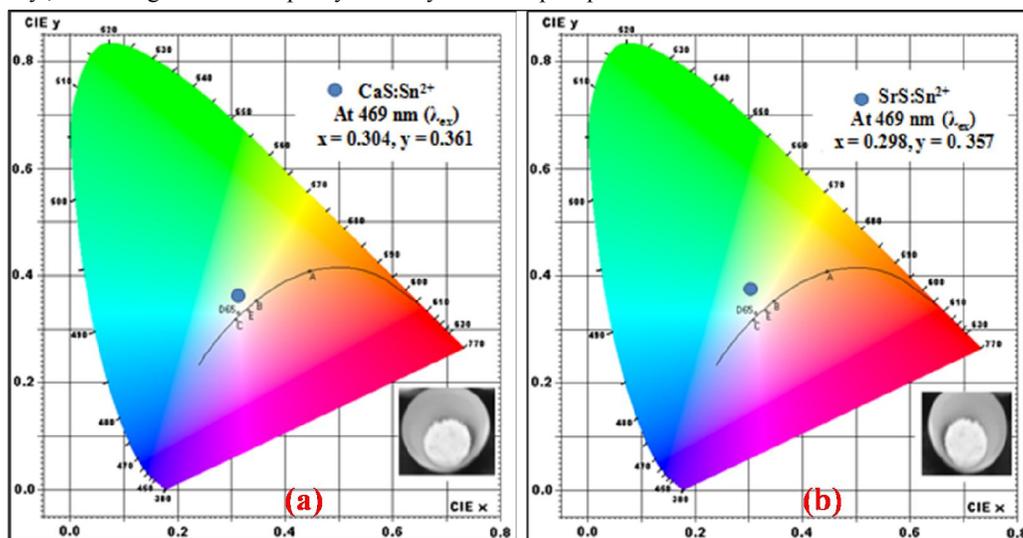


Figure 8: CIE diagram with the inset images of as synthesized (a) $\text{CaS}:\text{Sn}^{2+}$ and (b) $\text{SrS}:\text{Sn}^{2+}$ phosphors

VI. CONCLUSION

The white emitting alkaline earth chalcogenide phosphors $\text{CaS}:\text{Sn}^{2+}$ and $\text{SrS}:\text{Sn}^{2+}$ covering almost entire region except prominent red of visible spectrum with highest intensity emission bands centered in green and yellow region respectively of visible spectrum are successfully synthesized by carbo-thermal reduction method. The CIE coordinates

of as prepared phosphors are (0.304, 0.361) and (0.298, 0.357) respectively. The prominent excitation peak of phosphors is located at 469 nm (blue light i.e. 440–480 nm), which indicates that the phosphors are very suitable for a color converter using blue LED as the primary light source in pc wLED. When these phosphor will be excited using blue LED broad emission bands can be accomplished due to characteristic emissions of Sn²⁺ ion in the phosphor along with blue LED emission, which when used as a pumping source. This will occur because the absorption wavelength of Sn²⁺ ion in this phosphor will match with that of the LED blue emission. Therefore upon illumination with the LED blue light, the part of blue light is absorbed by the phosphor and rest will be emitted along with the other color light emitted from the phosphors to realize better spectral properties. The obtained spectrum in the present form will not result in good CRI due to lack of red component. This can be achieved either by blending these phosphors with that emits in red region or co-doping them with appropriate red emitting activator along with Sn²⁺. Thus phosphors are promising phosphors to be used along with red emitting phosphors to obtain white light in pc wLED for solid state lighting.

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