

## Synthesis and Photoluminescence Properties of White Emitting CaS Phosphor doped with Sn for Solid State Lighting

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### ABSTRACT

We have synthesized Sn<sup>2+</sup> doped CaS white emitting phosphors by carbo-thermal reduction method. In this method special requirement such as H<sub>2</sub>S gas flow is not required as a source of sulphur and is comparatively easy method to prepare sulfides. The phase purity and surface morphology of prepared material was investigated by using X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). Phosphor exhibit broad band excitation which has excellent spread over nUV as well as Blue region. Emission is in the form of characteristic broad band of Sn<sup>2+</sup> covering entire regions of visible spectrum with HWFM of 60 nm. The XRD pattern of prepared phosphor well matches with ICDD (International center for diffraction data) file. Synthesized phosphor particles are of different sizes, with smooth surfaces, from less than 1 micron to few microns. CIE coordinates are (0.304, 0.361) under the excitation at 469 nm. The prominent excitation peaks located at 370 nm (nUV) and 469 nm (blue light i.e. 440–480 nm), which indicates that the phosphors 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 Method, White Phosphor, Photoluminescence

### 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 Ce<sup>3+</sup>

doped yttrium aluminium garnets (YAG:Ce<sup>3+</sup>) yellow phosphor [3], which is very stable and exhibits high luminescence efficiency. However, in some respects YAG:Ce<sup>3+</sup> 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.

## II. EXPERIMENTAL

### 2.1. Material and method

Polycrystalline samples of Sn<sup>2+</sup> doped CaS 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 CaSO<sub>4</sub>:Sn<sup>2+</sup> were produced [4, 5]. In second step this sulphate is 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 [6]. The fine sized soft powders of dull white body color CaS:Sn<sup>2+</sup> phosphor were obtained.

### 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 element 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:Sn<sup>2+</sup> shows good agreement with standard ICDD Files No. 03-065-2926 of host matrix. Figure 1(a) shows that for different concentrations of Sn<sup>2+</sup> XRD pattern remains unchanged indicating no other phase is formed and there no residue of precursor is present.

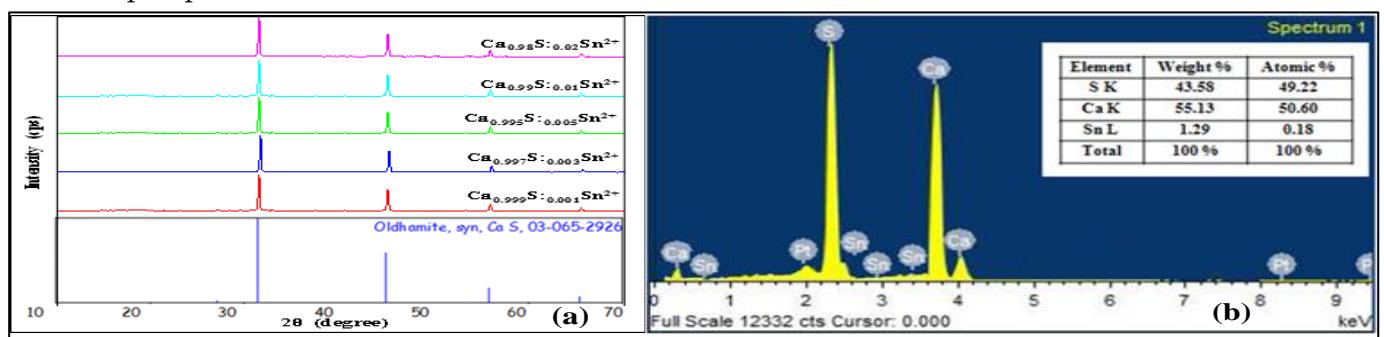


Figure 1: X-ray diffraction patterns with different Sn<sup>2+</sup> concentrations (a) and EDS pattern (b) of as synthesized CaS:Sn<sup>2+</sup> phosphor

### 3.2. EDS Patterns

The corresponding EDS spectrum as shown in Figure 1 (b) mainly composed of Ca 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 platinum was used during sample preparation for scanning electron microscopy

### 3.3. Morphology study (SEM)

SEM images in Figure 4 (a) shows synthesized phosphor particles are of different sizes with smooth surfaces. Shape of particles is elongated and spherical with sizes from less than 1 micron to few microns which is a suitable size for fabrication of SSL devices [7].

### 3.4. Photoluminescence study

#### 3.4.1. Energy level diagrams for Sn<sup>2+</sup> doped alkaline earth sulfide phosphors

Schematic energy level diagrams for Sn<sup>2+</sup> doped CaS are shown in Figure 2. An s<sup>2</sup> ion, such as Sb<sup>3+</sup>, Pb<sup>2+</sup>, Bi<sup>3+</sup> or Sn<sup>2+</sup>, has 1S<sub>0</sub> ground state and sp excited states (3P<sub>0</sub>, 3P<sub>1</sub>, 3P<sub>2</sub>, 1P<sub>1</sub>) Figure 2 (a). The triplet states 3P<sub>0</sub>, 3P<sub>1</sub>, and 3P<sub>2</sub> can be split owing to the spin-orbit interaction Figure 2 (c). The energies of these absorption peaks are usually dependent on the metal and are typically modified by the host matrix material. The 1S<sub>0</sub>→3P<sub>0</sub> transition is forbidden and is therefore usually not observed in any optical spectra Figure 2 (b) [8].

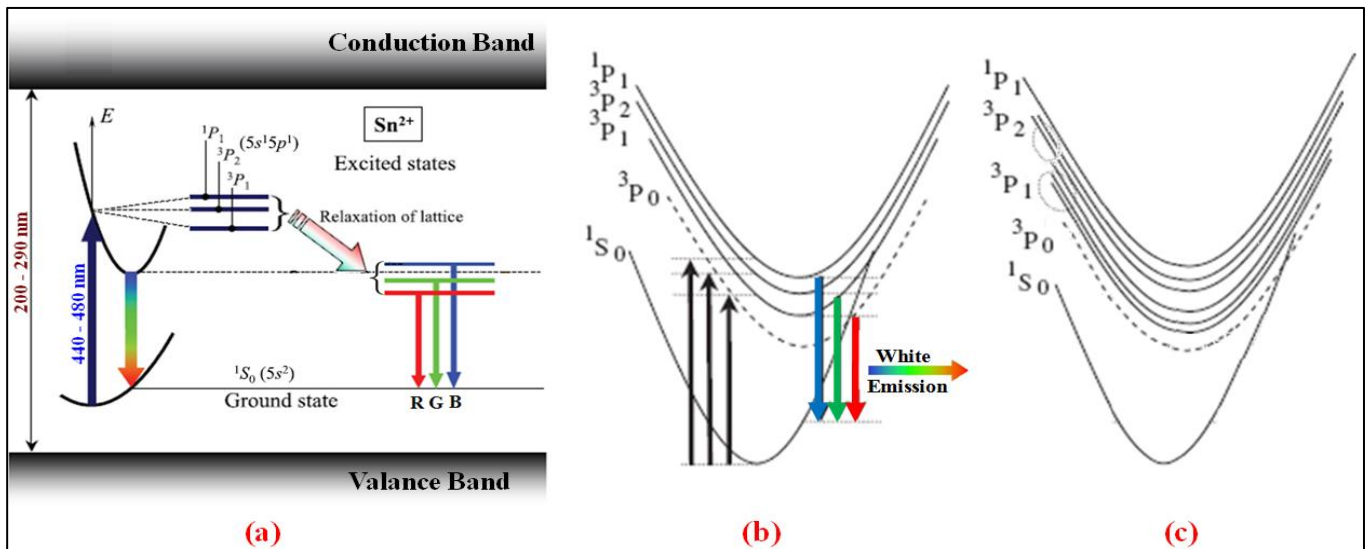


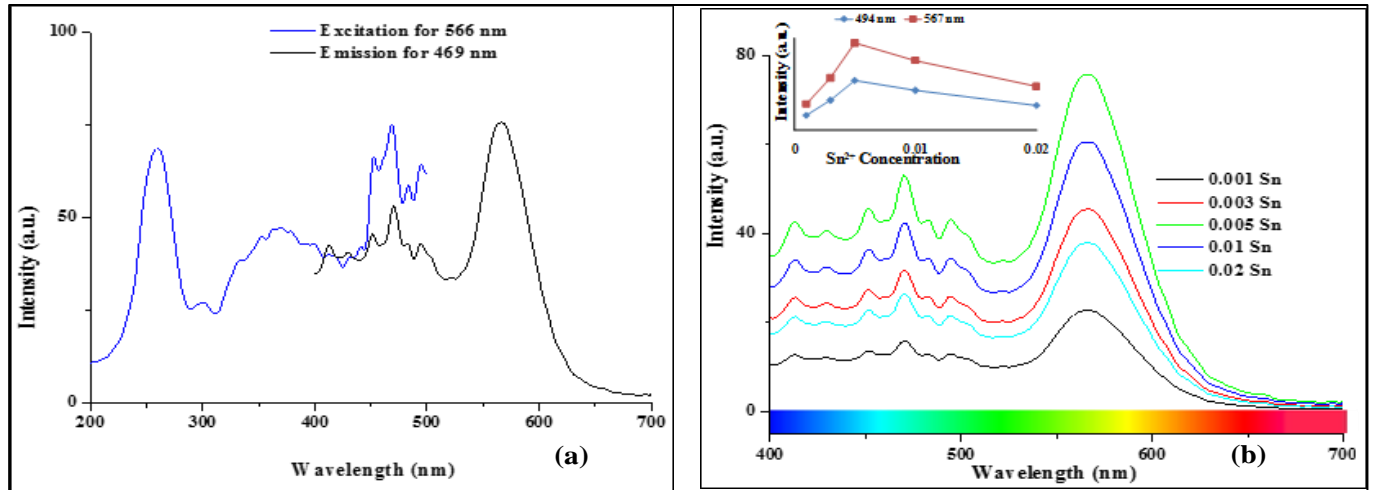
Figure 2: Schematic energy level diagrams for Sn<sup>2+</sup> ions in CaS host

#### 3.4.2. Combined Excitation and Emission spectra of CaS:Sn<sup>2+</sup> phosphor

Combined excitation and emission spectrum of prepared phosphor is shown in Figure 3 (a). Photoluminescence properties CaS:Sn<sup>2+</sup> can be explain in the view of Figure 2. The fundamental excitation band in CaS occurs at 200–290 nm was characterized as host excitation centered at 260 nm Figure 2 (a). Along with this band other bands due to 1S<sub>0</sub> → 3P<sub>1</sub>, 1S<sub>0</sub> → 3P<sub>2</sub> and 1S<sub>0</sub> → 1P<sub>1</sub> transitions of Sn<sup>2+</sup> centers are

present, in the order of increasing photon energy, with maximum intensity band centered at 469 nm [9] Figure 2 (a) and (b). The excited states in these transitions have triplet (3P<sub>1</sub>), doublet (3P<sub>2</sub>), and singlet (1P<sub>1</sub>) structures respectively Figure 2 (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<sup>2+</sup> 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



**Figure 3: (a) The excitation and emission spectra and (b) effect of Sn<sup>2+</sup> concentrations on emission of as synthesized CaS:Sn<sup>2+</sup> phosphor, the inset shows relative luminescence intensity at 494 nm and 567 nm for different Sn<sup>2+</sup> concentration**

### 3.4.3. Effect of Sn<sup>2+</sup> concentrations on emission intensity of CaS:Sn<sup>2+</sup>

For different concentrations of Sn<sup>2+</sup> there is no change in shape and position of emission band except emission intensity [Figure 3 (b)]. Optimum concentration is 0.005 mole of Sn<sup>2+</sup>. The ratio (G/Y) of luminous intensities of green (494 nm) and greenish-yellow (567 nm) emission bands for different Sn<sup>2+</sup> concentration is constant (0.57). The inset shows relative luminescence intensity at 494 nm and 567 nm as a function of Sn<sup>2+</sup> concentrations.

### 3.5. Study of colour chromaticity of CaS:Sn<sup>2+</sup>

The chromaticity coordinates of CaS:Sn<sup>2+</sup> phosphor have been calculated from its corresponding emission spectra monitored at 469 nm. They are (0.304, 0.361) falls in white region of CIE diagram. This point is in close proximity to standard white points D65 and E as shown in Figure 4 (b), corresponding to daylight and equal energy having correlated colour temperature

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<sub>2</sub> ions in alkaline earth sulfides [9]. The experimental data in Figure 3 (a) clearly indicate that the observed luminescence in CaS is due to the Sn<sup>2+</sup> center [Figure 2].

(CCT) 6500°K and 5400°K respectively , indicating better colour purity of the synthesized phosphor.

## IV. CONCLUSION

The white emitting sulfide phosphors CaS:Sn<sup>2+</sup> covering almost entire region except prominent red of visible spectrum with highest intensity emission bands centered at 567 nm and 496 nm respectively are successfully synthesized by carbo-thermal reduction method. The CIE coordinates of as prepared phosphors are (0.304, 0.361). The prominent excitation peak of phosphor 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 the phosphor will be excited using blue LED broad emission bands can be accomplished due to characteristic emissions of Sn<sup>2+</sup> ion in the phosphor along with blue LED emission,

which when used as a pumping source. This will occur because the absorption wavelength of  $\text{Sn}^{2+}$  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 colour 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  $\text{Sn}^{2+}$ . Thus phosphor is promising to be used along with red emitting phosphors to obtain white light in pc wLED for solid state lighting.

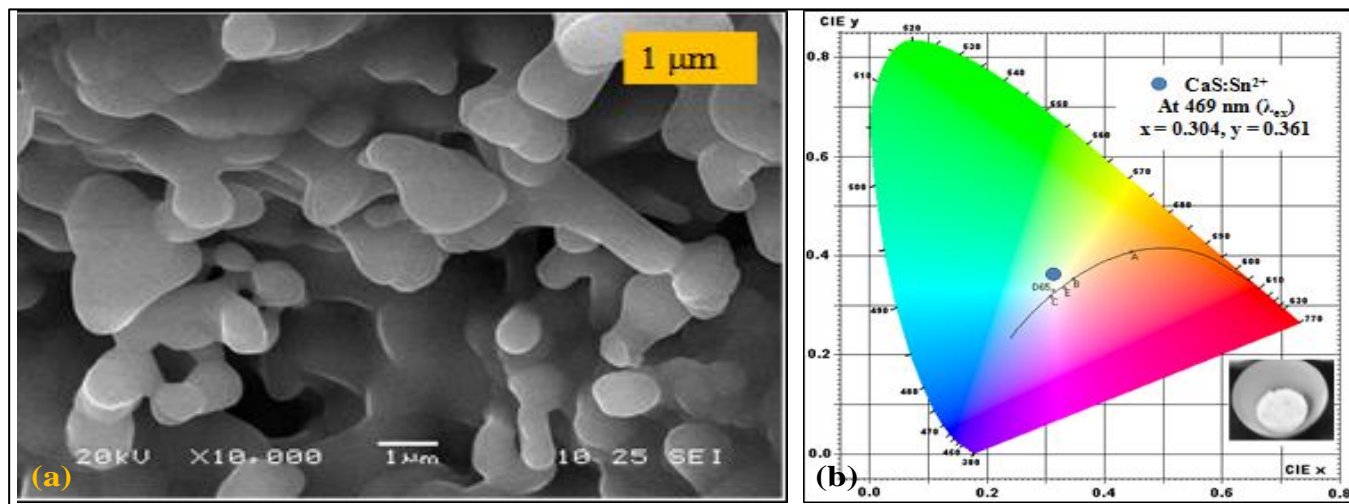


Figure 4: (a) SEM image and (b) CIE diagram of with image of as synthesized  $\text{CaS}:\text{Sn}^{2+}$  phosphor

## V. ACKNOWLEDGMENTS

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