Materials Discovery xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Materials Discovery

journal homepage: www.elsevier.com/locate/md

# Converted white light emitting diodes from $Ce^{3+}$ doping of alkali earth sulfide phosphors

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ARTICLE INFO

*Article history:*
Received 29 May 2016
Received in revised form
24 September 2016
Accepted 26 September 2016
Available online xxx

*Keywords:*
Sulfide
$Ce^{3+}$- doped
Solid state lighting
Carbo-thermal reduction
wLED

ABSTRACT

Polycrystalline $CaS:Ce^{3+}$ and $SrS:Ce^{3+}$ phosphors were successfully synthesized via the carbo-thermal reduction method. The XRD patterns of prepared phosphors were well matched with ICDD files and surface morphology of prepared phosphors were found to be in sub micron range. Photoluminescence emission spectra of $CaS:Ce^{3+}$ and $SrS:Ce^{3+}$ exhibits green and blue broad band emissions centered at 504 nm and 477 nm respectively. The concentration quenching phenomena was observed for prepared phosphors. CIE coordinates of $Ce^{3+}$ doped CaS and SrS phosphors were calculated. The critical transfer distance (Rc) is calculated by equation proposed by Blasse. Thus prepared phosphors are suitable for pc-WLED.

## 1. Introduction

In the past to three decades, energy-efficient solid-state lighting and low power consuming white light emitting diodes (wLED), have become a potential next generation light source as they have comparable a visible spectrum to sunlight, attracting attention for use in display lighting sources and illuminating systems [1–6]. Currently wLED can be achieved by combining blue, green, and red LED or by coating the three color (tricolor) phosphors to an UV LED or green and red phosphors to a blue LED [7–9]. These simple coating methods are commonly used because of the lower cost. Coating on a blue LED is more popular because of their higher energy conversion efficiency. Therefore, green and red phosphors with strong blue absorption are needed. In the case of the phosphor converted white-light LED (pc wLED), phosphor materials play an important role. In all cases efficiency of the devices is largely dependent on the efficiency of the phosphors. Color rendering of the phosphors is also critical to obtain a spectrum close to sunlight. Therefore, highly efficient blue, green and red emitting phosphors are important components for wLED [10].

Most of the phosphors used in LED applications are from the traditional lamp phosphors with absorption at the LED emissions. For example, a blue LED emitting at 460 nm in combination with $Ce^{3+}$ doped yttrium aluminum garnet ($YAG:Ce^{3+}$), a yellow emitting phosphor, is one of the best white light LED systems [11,12]. Alkali earth sulfide phosphors such $CaS:Eu^{2+}$ (red), $CaS:Ce^{3+}$ (green), $SrS:Ce^{3+}$ (blue) and $SrS:Eu^{2+}$ (orange) are also good candidates for LED applications because all of them have strong absorption in the blue region that is suitable to blue LED excitation. The $SrS:Ce^{3+}$ phosphor is an efficient blue emitter both in thin film and powder form. Very limited information is available on the precise nature of the local environment of the $Ce^{3+}$ in the host lattice and the way it influences the blue emission and excitation characteristics of the spectrum.

Sulfide phosphors have been ignored for a long time because of the problem of their chemical stability. Similarly when sulfides are exposed to moisture they decompose to carbonates or sulfates affecting their original luminescence to a great extent [13]. Sulfide phosphors may also degrade when exposed to high energy UV or bombarded with an electron beam [14]. However, sulfide phosphors are fit for LED applications using blue excitation when sealed with adhesive (epoxy resin).

From the viewpoint of chemical and thermal stability, ecological responsiveness, suitable synthesis conditions and cost effectiveness, it becomes urgent to search for new phosphors with high

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http://dx.doi.org/10.1016/j.md.2016.09.002
2352-9245/

Please cite this article in press as: D.N. Game, et al., Converted white light emitting diodes from $Ce^{3+}$ doping of alkali earth sulfide phosphors, Mater. Discov. (2016), http://dx.doi.org/10.1016/j.md.2016.09.002

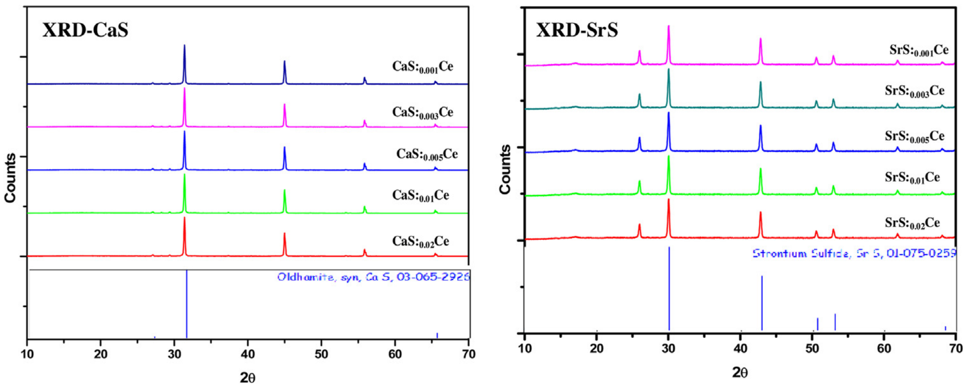

**Fig. 1.** XRD patterns of CaS and SrS phosphor doped with different concentration of $Ce^{3+}$ ions matching with ICDD files (shown as bottom spectra). The lack of response with $Ce^{3+}$ addition demonstrates the substitution of Ca and Sr sites.

chemical stability. Therefore, in order to develop new phosphors for the potential applications of wLED, we have examined the luminescence and color chromaticity properties as well as the particle nature of $Ce^{3+}$ activated CaS and SrS phosphors in the present work. For the first time we have synthesis Ce activated CaS and SrS phosphor by carbo-thermal reduction method. Our study shows that doped $Ce^{3+}$ ions occupy $Ca^{2+}$ and $Sr^{2+}$ sites in the structure of the host lattices, which results in submicron range particle size phosphors- and emission of- green and blue light, respectively, with high color saturation, particularly in the case- of CaS.

## 2. Experimental

### 2.1. Materials and method

For development of $Ce^{3+}$ doped polycrystalline samples of CaS phosphor, $CaSO_4$:$Ce^{3+}$ phosphor was first synthesized by the co-precipitation method [15,16] in an aqueous medium from high purity AR grade starting materials. Precursor $Ce(NO_3)_3$ was obtained by reacting $Ce_2O_3$ with dilute $HNO_3$ and evaporating to get dry $Ce(NO_3)_3$. The solution of this freshly prepared cerium nitrate and calcium nitrate in stoichiometric amounts was precipitated by concentrated sulfuric acid. This precipitate was repeatedly washed by double distilled water and oven dried at 40 °C. Extremely fine sized, snow white $CaSO_4$:$Ce^{3+}$ was produced. This product was then heated in close assembly at 950 °C for 3 h a in reducing atmosphere in the presence of charcoal and then allowed to cool slowly to room temperature. The dull white body color, fine sized soft powder of $Ce^{3+}$ doped CaS phosphor was thus obtained. Similarly, $Ce^{3+}$ doped SrS phosphor was obtained by using $Sr(NO_3)_2$ in place of $Ca(NO_3)_2$.

### 2.2. Instruments and characterizations

The prepared materials were characterized by powder XRD technique. XRD measurements were taken on Rigaku Miniflex II X-ray Diffractometer and compared with the ICDD file. The structural and morphological characteristics were confirmed by using JEOL's Scanning Electron Microscope model JSM-6360A fitted with an EDS facility. The photoluminescence (PL) and PL excitation (PLE) spectra were measured on a 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 I'Eclairage (CIE).

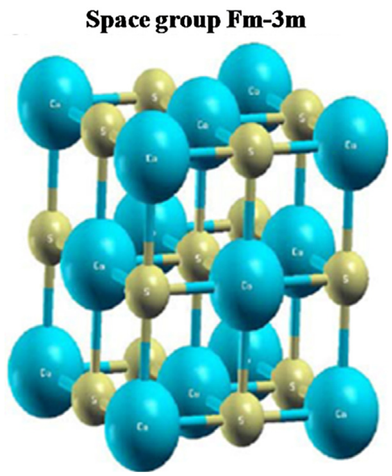

**Fig. 2.** Unit Cell of host lattice CaS with cubic crystal structure and Fm-3 m space group.

## 3. Result and discussion

### 3.1. XRD analysis

The XRD technique was used to identify the phase composition, structure and their crystalline nature. Fig. 1 shows the XRD patterns of $Ce^{3+}$ doped CaS and SrS phosphors with ICDD (International Center for Diffraction Data) files. The XRD pattern of the as prepared phosphors powder shows good agreement with standard ICDD Files with Card No. CaS: 03-065-2926 and SrS: 01-075-0259. Both the phosphors have cubic crystal structure with space group Fm−3 m (225), as shown in Fig. 2 for host lattice CaS [17], 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 Å and volume = 184.609 $Å^3$ whereas for SrS the lattice parameters are a = b = c = 6.0079 Å with volume = 216.854 $Å^3$.

When the concentration of Ce ions were varied from 0.001 to 0.02 mol there was no change found in the XRD pattern. This indicates that the sites of Ca and Sr have been successfully replaced by $Ce^{3+}$ ions in the phosphors without affecting the crystal structure of the host materials.

It is apparent that the trivalent $Ce^{3+}$ does not fit the lattice neutrality of a divalent cation site. Therefore the substitution of $Ce^{3+}$ for $Ca^{2+}$ in CaS or $Sr^{2+}$ in SrS phosphors is seems to be non-equivalent as far as charge compensation is concerned. Therefore, charge compensators appear to be essential for the incorporated trivalent ion in the divalent site to have charge neutrality and improved luminescence efficiency. But lattice defects created during crystal formation

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