

## Spectral and kinetic characterization of CaS:Pr<sup>3+</sup> phosphor synthesized through chemical co-precipitation route and post annealing process

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### ABSTRACT

Synthesis of Pr<sup>3+</sup> doped CaS phosphor has been reported through chemical co-precipitation route and post annealing in the presence of NaCl, KCl and NH<sub>4</sub>Cl flux. Good crystallinity and cubic CaS phase is achieved after post-precipitation calcinations of powder at 900 °C for 1 h duration. Pseudo-spherical morphostructural features of micron-size particles are observed for phosphor prepared via chemical route. Phosphor samples are also prepared via solid-state carbothermal reduction technique for comparative studies and exhibit dendrite like structures. Prominent excitation bands at 276, 320 nm are observed for the present phosphor samples. The emission spectra show a duo-band feature at 495 and 580 nm where a spectral overlap of host lattice emission due to intrinsic defects and characteristic spectral features of Pr ion due to <sup>3</sup>P<sub>0</sub>–<sup>1</sup>H<sub>4</sub>, <sup>3</sup>P<sub>1</sub>–<sup>1</sup>H<sub>5</sub>, <sup>1</sup>D<sub>2</sub>–<sup>3</sup>H<sub>4</sub> and <sup>3</sup>P<sub>0</sub>–<sup>3</sup>F<sub>2</sub> transitions can be observed. The carbothermal route synthesized CaS:Pr shows spectral features of Pr ion due to <sup>3</sup>P<sub>0</sub>–<sup>1</sup>H<sub>4</sub> and <sup>3</sup>P<sub>0</sub>–<sup>3</sup>F<sub>j</sub> transitions. Electron spin resonance investigations reveal the presence of unintentional Mn<sup>2+</sup> through a sextet signature. F<sup>+</sup> electron trapping center is detected having *g* = 2.0034. Thermoluminescence glow curves possess a broad duo-band feature between room temperature –100 °C and >125 °C under host UV irradiation. Kinetic characterization using glow curve deconvolution reveals quasicontinuous distribution of traps having energy between 0.56 and 1.15 eV and frequency factors between 10<sup>7</sup> and 10<sup>11</sup>/sec.

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### 1. Introduction

Calcium sulfide (CaS) is a technologically important optical material with widest possible application in the areas of luminescent devices. It is an excellent host material for efficient Cathode Ray Tube (CRT) phosphor when activated with rare earth (RE), radiation dosimetry, fast high resolution OSL imaging and IR sensitive devices [1–3]. On the other hand, the trivalent praseodymium ion (Pr<sup>3+</sup>) in solids presents an intricate energy level scheme, with energy gaps of various magnitudes, and several metastable levels emitting multi-colored light [4]. The complex spectral output of Pr<sup>3+</sup> doped alkaline earth sulfide has given this system its opening recognition as a potential white light emitting thin film electroluminescence device [5]. It is a good candidate offering various site symmetries and possibilities of laser site-selective excitations [6] and lasing <sup>3</sup>P<sub>1</sub>–<sup>3</sup>F<sub>3</sub>; <sup>3</sup>P<sub>0</sub>–<sup>3</sup>F<sub>2</sub> fluorescent levels bearing potential for a solid-state laser [7]. Energetically favorable defect structure within the photophysical environment of host lattice has captivated the materials engineering community and, as a result recently, the research on Pr doped CaS has gained a fresh impetus due to its possible afterglow features when co-doped with Eu

and Ce impurities [8,9]. The wide band-gap of this phosphor has been effectively utilized by Kojima et al., to perturb the space charge neutrality conditions by invasion of new ions leading to an increase in the persistent behavior with near-UV and visible photon irradiability as an added advantage [8–10]. Drifting away from the traditional methods of alkaline earth sulfide (AES) phosphor preparation and as an extension of our previous work based on the fabrication of SrS:Pr microcrystals [11], in the present work, we propose a chemical synthesis route and post annealing procedures that overcomes problems related to conventional synthetic routes to fabricate technologically viable CaS:Pr luminescent materials. We present our results via spectral and kinetic characteristics of Pr in CaS host under the presence of various mineralizing agents. Also, the luminescence of post treated products has been compared to those prepared with conventional carbothermal reduction technique.

### 2. Experimental

#### 2.1. Synthesis

In the present synthesis, calcium chloride tetrahydrate (CaCl<sub>2</sub>·4H<sub>2</sub>O) (E-Merck India Ltd.), hydrazine monohydrate (99%) (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) (Ranbaxy India), elemental sulfur (Ranbaxy), ammonium

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carbonate  $(\text{NH}_4)_2\text{CO}_3$  (Ranbaxy India) were used as starting materials. First hydrazine/sulfur solutions were prepared by dissolving 670 mg sulfur powder into 5 mL hydrazine hydrate. An exothermic reaction occurred with an evolution of nitrogen gas and a dark orange colored solution was obtained. Next, 3.7092 g of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.45 mol.% of  $\text{PrCl}_3 \cdot x\text{H}_2\text{O}$  (Aldrich–Sigma) were dissolved in 25 mL N, N dimethylformamide (Ranbaxy India) (DMF) solution in a round bottom flask and stirred using a magnetic stirrer for 30 min. The solution of sulfur in hydrazine hydrate, prepared previously, was filtered under gravity and the filtrate was added drop wise to the metal chloride solution while stirring. The color of this solution turned yellow. After 2 h of continuous stirring, precipitation was achieved by adding drop wise 10 mL of 0.9 M ammonium bicarbonate solution. The yellow-orange suspension thus obtained was filtered and washed several times with ethanol to remove remnants. The synthesis was carried under ambient atmosphere at room temperature. The precipitates were dried in a vacuum oven at 80 °C overnight. The dry precipitates were mixed with three different fluxing agents viz. NaCl, KCl and  $\text{NH}_4\text{Cl}$  (5% by mass) using slurry mixing technique, packed into graphite crucibles (fitted with a lid) and fired for 1 h. at different temperatures under reducing CO atmosphere and finally quenched to room temperature. Phosphor samples with same activator concentrations were also prepared by chemically reducing calcium sulfate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) with carbon particles (solid-state carbothermal reduction method [12]) in the presence of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), which act as the flux for better crystallization of the product, for comparative studies.

## 2.2. Characterization

The phase of the obtained powders is identified at room temperature in a wide range of Bragg angle ( $10^\circ \leq 2\theta \leq 90^\circ$ ) using an X-ray diffractometer Rigaku Miniflex II with Cu- $\text{K}_\alpha$  target, a curved graphite monochromator, a flat plate sample holder in a Bragg-Brentano para-focussing optics configuration. The X-ray generator is operated at 15 kV and 30 mA with the scan speed fixed at 2 deg/min in a continuous scanning mode with a fixed divergence

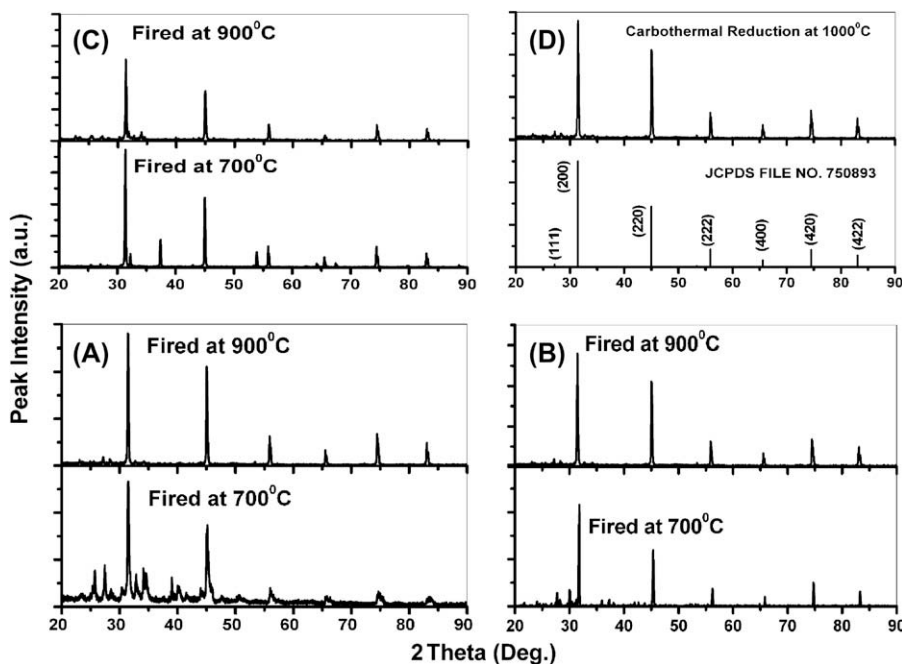
slit of 1.25 deg. Morphological investigation was carried out using JEOL scanning electron microscope (SEM) Model 6360. The photoluminescence excitation and emission spectra and fluorescence decay measurements were carried out on Edinburgh Instruments FLSP 920 using a microsecond pulsed xenon flash lamp.

Nucleonix Integrated Thermoluminescence Reader, TLD10091, supplied by M/s Nucleonix Systems Pvt. Ltd., Hyderabad, India is used to perform the TL experiments. Philips (Holland) 8 W tube is used as a UV-irradiation source. The entire glow curves were recorded by heating the sample at a linear heating rate of 2 °C/s. The samples were annealed at 300 °C for a period of 30 min, prior to subsequent irradiation during each experiment, to erase any residual information. During the thermally stimulated luminescence (TSL) experiments, the sample was readout two times to check the consistency of the results. EPR measurements were made on a Varian E-line century series E-112 X-band EPR spectrometer which utilizes 100 kHz field modulation. Tetracyanoethylene TCNE ( $g = 2.00277$ ) was used as a standard for  $g$ -factor measurements.

## 3. Results and discussion

### 3.1. Phase verification of phosphor after post-precipitation annealing and carbothermal reduction and morphology

X-ray diffraction pattern of CaS:Pr (0.45 mol.%) powder samples prepared via chemical co-precipitation route and annealed at temperatures 700 and 900 °C utilizing different fluxing agents and the one synthesized via a carbothermal route are shown in Fig. 1A–D alongwith reflections from standard JCPDS File No. 750893. At 900 °C, together with the prominent peaks of cubic CaS lattice, minor peaks at  $2\theta = 27.9^\circ$ ,  $27.5^\circ$ ,  $82.39^\circ$ ,  $44.83^\circ$  and  $73.98^\circ$  belonging to cubic praseodymium sulfide (JCPDS File No. 650312) with corresponding (hkl) values as (013), (112), (422), (220), (420), respectively, were detected. Also minor peaks at  $2\theta = 32.32^\circ$  and  $53.93^\circ$  belonging to (111) and (220) (hkl) planes of CaO lattice (JCPDS No. 780649) were found to be present in the diffractogram of powders annealed at 900 °C.



**Fig. 1.** XRD patterns of CaS:Pr (0.45 mol.%). (A) prepared via chemical route and annealed using NaCl as flux, (B) using  $\text{NH}_4\text{Cl}$  as flux (C) using KCl flux and (D) phosphor prepared via solid-state carbothermal reduction at 1000 °C. The vertical strokes in (D) indicate (hkl) reflections from diffraction pattern of JCPDS file 750893. The chemically co-precipitated powders annealed at different temperatures below 700 °C were a mixture of unwanted phases and hence are not shown here.

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