



PLANT MEDIATED COMBUSTION SYNTHESIS OF Tb³⁺ DOPED STRONTIUM ALUMINATE NANOPHOSPHOR FOR DISPLAY DEVICE APPLICATIONS.

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ABSTRACT For the first time pure and Tb³⁺ (1-7 mol%) doped SrAl₂O₄ nanophosphors were synthesized via solution combustion method by using the *Calotropis gigantea* plant milk as fuel. The prepared samples were calcined at 800 °C for 3 hours, the final product was well characterized. The powder X-ray diffraction (PXRD) profiles of nanophosphors showed crystalline monoclinic phase. The effect of concentration of bio-fuel play a vital role in tuning the morphologies of SrAl₂O₄. The samples show the pores and voids on the surface that formed by the escaping gases during the combustion method. The morphology of the powders reflects the inherent nature of the combustion process. The images show non uniform and irregular shapes of the particles. The particle sizes were further confirmed by Transmission electron microscope (TEM) and were found to be in the range of 17-29 nm. The energy band gaps for the prepared samples estimated using DRS were found to be in the range 5.81-6.11 eV. Fourier transform infrared spectral studies were also carried out to evaluate the stretching and vibrational bands in the product. Photoluminescence (PL) studies were carried out for SrAl₂O₄: Tb³⁺ (1-7 mol %) nanophosphors under 376 nm excitation wavelength. The strongest emission peak is located 516 nm and was attributed to ⁵D₄-⁷F₃ transition, while the other peaks at ~486 nm, ~541 nm corresponds to the transitions ⁵D₄-⁷F₆, ⁵D₄-⁷F₅ respectively. Further CIE and CCT were estimated and found that the color co-ordinates fall in the green color region. The overall results together indicate that the prepared nanophosphors were highly useful in display device applications.

KEYWORDS : Photoluminescence; Diffuse Reflectance; Energy Band Gap; Green Emission.

1. Introduction

An important class of fluorescent lamp and plasma display phosphors are based on compounds in the alkaline-earth-rare-earth-aluminate systems. These materials can absorb the visible light, store the energy and gradually release the energy as visible light [1]. SrAl₂O₄, a binary alkaline earth aluminate [2,3] is one of the typical matrices for luminescent materials, which are doped with Eu, Ce, Tb, etc. and is an efficient host lattice with a wide band gap which can generate a broad band emission [4]. As compared with other synthesis methods, the combustion method is very simple, saving energy and it takes only few minutes without requiring subsequent intermediary calcinations stages [5, 6]. Tb³⁺ is one of the most widely used Rare-Earth ions activator for green luminescent materials and has been used widely in tricolor energy saving fluorescent lamp and its emission mainly originate from ⁵D₄ to ⁷F_j (j=0-6) transition [7, 8]. The SrAl₂O₄ host belongs to the tridymite-like structure. The structure is formed by three dimensional corner-sharing AlO₄ tetrahedron frame-work. The divalent Sr²⁺ cation balance the charge and occupies an interstitial site within the tetrahedral frame-work [9, 10].

This paper is concerned with the systematic study of crystal structure for Tb³⁺-activated binary alkaline earth aluminates and with aspects such as plant mediated synthesis of these refractory compounds. To find the potential applicability of the synthesized SrAl₂O₄ nanophosphors, the photometric properties (PL, CIE, CCT and color purity) were evaluated.

2. Materials and Methods:

Tb³⁺ (1-7 mol%) doped SrAl₂O₄ powders were prepared by green combustion synthesis using Strontium nitrate [Sr(NO₃)₂ (99.9%, Aldrich)], aluminium nona hydrate Al(NO₃)₃·9H₂O, Terbium nitrate [Tb (NO₃)₃·6H₂O (99.9%, Aldrich)] and milk of *Calotropis gigantea* plant. Initially the metal nitrates were taken stoichiometrically and were dissolved in a minimum amount of de-ionized water taken in pyrex dish and stirred for few minutes to get a homogeneous solution. Subsequently, the appropriate amount (15 ml) of C.G milk was added to this solution and the mixture was continuously stirred with magnetic stirrer for ~ 5 min. Finally a milky precipitate was obtained and placed in a furnace preheated at 500 °C for ~ 20 min. In about five minutes the solution boiled and underwent dehydration followed by decomposition with escaping large amount of gases (oxides of nitrogen and ammonia) resulting in a fine powder product. The obtained product was grinded well to fine powder and annealed at 800 °C for 3hr. The as prepared powders were dark brown in colour. The colours of the prepared samples changed from brownish yellow to light yellow after they were calcined to 800 °C in a reduced atmosphere.

3. Characterizations

Phase purity and crystallinity of nanostructures were measured using a powder X-ray diffractometer (PXRD, Shimadzu 7000). Scanning electron microscopy (SEM) measurements were performed on a Hitachi table top microscope (TM 3000). Hitachi H-8100 transmission electron microscope (TEM) was used to estimate the crystallite size. The Diffuse reflectance spectroscopy of the samples was recorded on spectrometer Perkin Elmer (Lambda-35). The FT-IR studies were performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. The Jobin Yvon Spectrofluorimeter Fluorolog-3 operational with 450W Xenon lamp as an excitation source was used for photoluminescence (PL) measurement.

4. Results and Discussions:

4.1. PXRD analysis

The PXRD patterns of pure and Tb³⁺ (1-7 mol %) doped SAL calcined to 800 °C were shown in Fig.1 (a). The results confirmed the monoclinic phase of SAL:Tb³⁺ with JCPDS card no.(74-0794).

The average crystallite size was estimated by using Debye – Scherrer's equation; $D = \frac{0.9\lambda}{\beta \cos \theta}$

Where; β ; full width at half maximum (FWHM in radian) caused by the crystallites, λ ; wavelength of the X-ray (1.542 Å), θ ; Bragg angle. The crystallite size was estimated by using Debye Scherrer's relation and found to be in the range of 17–23 nm for doped annealed samples and 28 nm for calcined pure sample. The Williamson Hall (W-H) plots were used to estimate crystallite

size and strain present within the sample and was given by equation;

$$\beta \cos \theta = \varepsilon (4 \sin \theta) + \frac{\lambda}{D}$$

Where; β ; FWHM of peaks in radians, ε ; the strain in the sample, D ; the crystalline size and θ ; Bragg's angle shown in Fig. 1(b). The estimated crystallite size, strain and energy gap values are tabulated in Table 1.

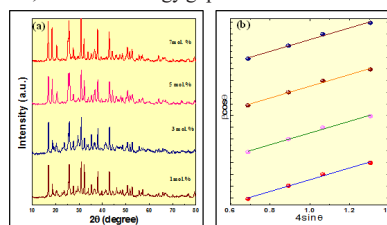


Figure 1(a) PXR patterns and (b) W-H plot of Tb³⁺ (1-7 mol %) doped SrAl₂O₄.

Table.1 Estimated crystallite size, strain & E_g values of Pure & Tb³⁺ (1-7 mol %) doped SrAl₂O₄:Tb³⁺ nano structures.

Tb ³⁺ (mol %)	Crystallite size (nm)		Strain ε x (10 ⁻³)	Energy gap (E _g) in eV
	Scherrer's	W-H		
undoped	28	39	1.23	5.75
1	23	29	1.30	6.11
3	20	25	1.32	5.92
5	17	22	1.15	5.86
7	24	27	1.33	5.82

Fig.2 shows the SEM micrographs of 1,3,5 & 7 mol % Tb³⁺ doped SrAl₂O₄ nanostructures at concentration of C.G (15 ml). The images indicate that the C.G concentration greatly impacts on the morphology of the products. Fig.3 shows the TEM image of Tb³⁺ (7mol %) doped SAL nanophosphors. The crystallite size was found to be in the range of 25-30 nm which was in good agreement with PXR results.

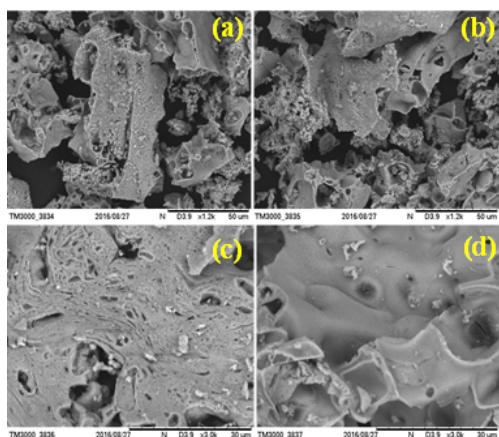


Fig.2 SEM micrographs of a) 1mol% b) 3mol% c) 5mol% and d)7mol% Tb³⁺ doped SrAl₂O₄

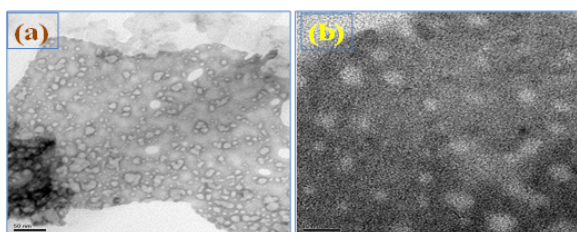


Fig.3 (a) & (b) TEM images of SrAl₂O₄: Tb³⁺ (7mol %).

Fig.4 shows the FTIR spectra of 5 mol% Tb³⁺ doped SAL in the region of 400-4000 cm⁻¹. The broad band near 3456 cm⁻¹ due to the OH⁻ stretching vibrations of free and hydrogen-bonded hydroxyl groups. However a weak absorption bands at 1772 cm⁻¹ and 2480 cm⁻¹ appears from deformation vibrations of water molecules [11]. The metal-oxygen stretching frequencies in the range 400-1000 cm⁻¹ are associated with the vibrations of Al-O, Sr-O and Sr-O-Al bonds [12]. The sample showed a strong peak at 858.37 cm⁻¹ assigned to the formation of SrAl₂O₄ [13]. The absorption at 1453.26 cm⁻¹ due to SAL appeared, indicating a well-defined crystallization of SAL.

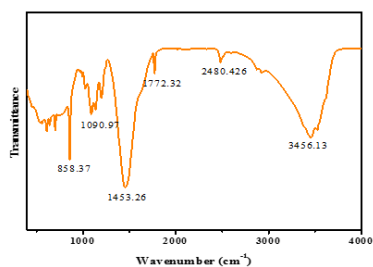


Figure 4. FTIR spectrum of 5 mol% Tb³⁺ doped SrAl₂O₄. The diffuse reflectance spectra and energy band gap plots were shown

in Fig.5 (a & b). The DRS was recorded at room temperature in the range of 200-1100 nm. The spectra exhibited major peaks at 320 nm, 382 nm, 400 nm, 500 nm, 580 nm, 980 nm & 1000 nm due to the transitions of the 4f electrons of Tb³⁺ from the ground-state. The band gap values were observed to be decreased as the Tb concentration was increased. This clearly showed there was a blue shift in the absorption bands of the phosphors. Band gap values were calculated by using Kubelka-Munk functions and they were found to be in the range of 5.75-6.11 eV [14].

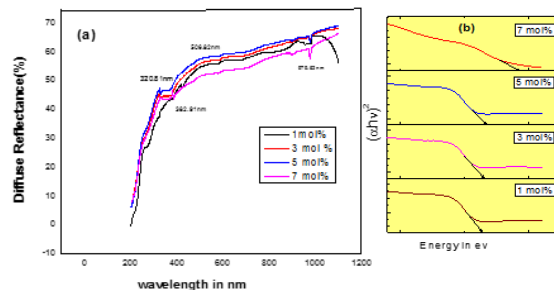


Figure 5 a) Diffuse reflectance spectra & b) Energy band gap

4.2 Photoluminescence studies:

Fig.6 (a) shows the PL excitation spectrum of 5 mol% Tb³⁺ doped SAL monitored at 376 nm emission wavelength. The excitation spectrum shows the sharp peak at 376 nm corresponding to f-f transition. Fig.6(c) shows the emission spectra recorded in the range of 450-675 nm at 376 nm excitation wavelength. The strongest emission peak is located at 516 nm and was attributed to self-trapped excitonluminescence, while the other peaks at 486 nm, 541 nm corresponds to the transitions ⁵D₄-⁷F₆, ⁵D₄-⁷F₅ respectively. The Commission International de l'Éclairage (CIE) 1931 X-Y chromaticity diagram of SAL:Tb³⁺ (1-7 mol%) were presented in Fig.6(b) excited under 376 nm. As shown in the inset of Fig.6 (b) the CIE chromaticity coordinates were located in the green region. To identify technical applicability of this Green emission, correlated color temperature (CCT) was determined from CIE coordinates [15]. Fig.6(d) shows the CCT diagram of SAL:Tb³⁺ (1-7 mol%) excited under 376 nm [16]. The quality of green light in terms of color correlated temperature (CCT) was given by Mc Camy empirical formula.

$CCT = -437 n^3 + 3601 n^2 - 6861 n + 5514 .31$ (theoretical) where $n = (x-x_c)/(y-y_c)$ the inverse slope line and chromaticity epicenter was at $x_c = 0.17$ and $y_c = 0.19$. Generally, a CCT value greater than 5000 K indicates the Green light used for commercial lighting purposes. In the present study, the CCT of SAL: Tb³⁺ (1-7 mol %) were found to be ~5989 K which was well within the range of vertical daylight. Thus it can be useful for artificial production of green light in illumination devices.

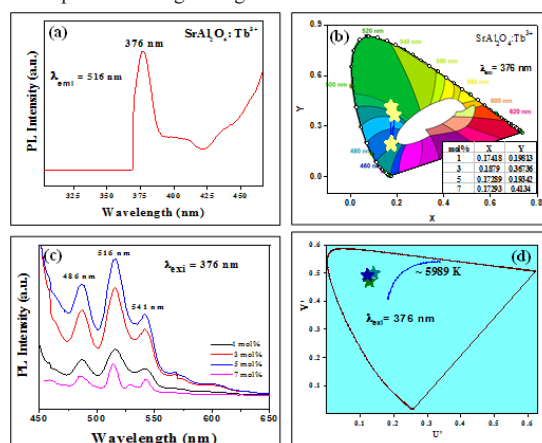


Fig.6(a) PL excitation (c) Emission spectra (b) CIE & (d) CCT diagram of SrAl₂O₄: Tb³⁺ (1-7 mol %)

5. Conclusions

Herein SAL:Tb³⁺ (1-7 mol%) nanophosphors were successfully synthesized via green combustion route using milk of C.G as fuel. Various shaped particles were observed from SEM studies. TEM

micrographs indicates that the crystallite size was in the range 25-30 nm which are well comparable to the results obtained from PXRD patterns. The excellent dark Green emission properties and the estimated CIE chromaticity co-ordinates (x, y) were very close to NTSC standard value and CCT was found to be 5989 K. Hence the optimized SAL: Tb³⁺ (5 mol %) nanophosphors were potentially used as light Green emitting components in LEDs.

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