

Luminescence and surface properties of Tb³⁺ doped Sr₃(VO₄)₂ nanophosphorsAK Bedyal^a, Vinay Kumar^{a,c,d}, Vishal Sharma^b, O.M. Ntwaeaborwa^c and H.C. Swart^c^aSchool of Physics, Shri Mata Vaishno Devi University, Katra-182320 (J&K) India^bInstitute of Forensic Science and Criminology, Panjab University, Chandigarh 160014, India^cDepartment of Physics, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa.

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ABSTRACT

In this paper, we present a detailed investigation of the luminescence and surface properties of Tb³⁺ doped Sr₃(VO₄)₂ nanocrystalline phosphors, synthesized by the combustion method. X-ray diffraction (XRD) peaks in the patterns corresponding to the reflection of rhombohedral pure phase of Sr₃(VO₄)₂. The average particle sizes have been found in the range of 30-34 nm. Scanning electron microscopy (SEM) indicated that an agglomerated peanut like morphology was obtained. Photoluminescence (PL) spectroscopy has been utilized to investigate the spectral properties of the phosphor. Under 237 nm excitation, it shows several bands centered at 487, 544, 588 and 624 nm, which result from ⁵D₄ → ⁷F_J (J = 6, 5, 4 and 3) transitions of Tb³⁺, and the green emission band (⁵D₄ → ⁷F₅) located at 544 nm is dominant. The chemical states and bonding characteristics in the host were analyzed with X-ray photoelectron spectroscopy (XPS).

Keywords: Photoluminescence, orthovanadate, nanophosphors, XPS, Combustion Synthesis

Introduction

Recently, there is large work going on to develop inorganic luminescent materials owing to their widespread applications for solid state lasers, scintillation detectors, biological technologies, CR tubes, and LED's, TV screens, X-ray imaging etc.¹⁻⁶. Among them alkaline earth metal orthovanadates with general formula A₃(VO₄)₂, captured the attention of various researchers because of their broad and deep charge transfer (CT) absorption bands in the near-UV, therefore they are capable of capturing the emission over a broad range of wavelength and consider as a fine host material for rare earth activator ions. The band associated with charge transfer from oxygen to metal ion is very deep and the energy is transferred to the luminescent centre by a non-radiative

mechanism^{7, 8}. Also few reports available on doped Ca₃(VO₄)₂ and Ba₃(VO₄)₂ suggesting that the solid solutions of doped Ca₃(VO₄)₂ and Ba₃(VO₄)₂ have luminescence intensity approaching that of the YVO₄:Eu³⁺ showing their huge importance in solid state lighting⁹.

Also, from last few years, studies on phosphors for white light-emitting diodes (WLED) paying attention of researchers, owing of its admirable advantages over the halogen lamp and conventional incandescent lamp such as high durability, low energy consumption, extremely long life, mercury free, environmental friendly etc.¹⁰⁻¹². The strategies involved in developing white light are (i) the combination of blue LED with a yellow phosphor; (ii) the combination of UV-LED with blue, green and red phosphors; and (iii) the combination of blue, green and red LEDs. Among the above strategies the use of RGB LEDs promises high efficiencies and flexible, user controlled colour. So, in this study efforts had been made to develop, Sr₃(VO₄)₂:Tb³⁺ green emitting nanophosphors by combustion method, also their surface and spectral properties have been investigated to explore its application.

Experimental

Combustion method was employed for the synthesis of Sr₃(VO₄)₂:Tb³⁺. Strontium nitrate (Sr(NO₃)₂), vanadium pentoxide (V₂O₅), terbium nitrate (Tb(NO₃)₃) and Urea (H₂NCONH₂) of analytical reagent grade purchased from Merck Chemicals were used as the starting materials. The stoichiometric composition of the metal nitrate (oxidizer) and urea (fuel) was calculated taking O/F = 1, in order to have the

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energy released as a maximum for complete combustion. The calculated amount of starting materials and urea were dissolved into the smallest possible amount of distilled water and thoroughly mixed in a mortar to obtain a paste. The paste was then transferred to an alumina crucible and inserted into a pre-heated muffle furnace maintained at 600 °C. The paste was then self-ignited with a white flame and yields highly porous foamy solid product. After the reaction was completed, the foamy product was cooled to room temperature and finally ground into a fine powder. The fine powder was then calcined at 900°C four hours to get complete crystallinity.

For phase identification and purity examination, X-ray diffractogram of the prepared phosphor were recorded in the range of (25° 2θ to 50°) using Bruker Advance D8 X-ray diffractometer with Cu Kα irradiation ($\lambda \approx 1.5406\text{\AA}$). Shimadzu SSX Superscan scanning electron microscopy was used to examine the composition and morphology of the product. The emission and excitation spectra (PL) were recorded by using Cary-Eclipse Spectrofluorometer. CL measurements were done by using a vacuum chamber from PREVAC ready with an ES40C electron gun power supply unit and USB2000+ spectrometer under different accelerating voltages and emission currents in a base pressure of $\sim 2 \times 10^{-8}$ torr. To study the chemical states and the surface of the nanophosphors, XPS studies were carried out, using a PHI 5000 versa probe spectrometer with same measurement details as in ref¹³.

Results and discussions

Structural studies

Fig.1 shows the XRD pattern for $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$

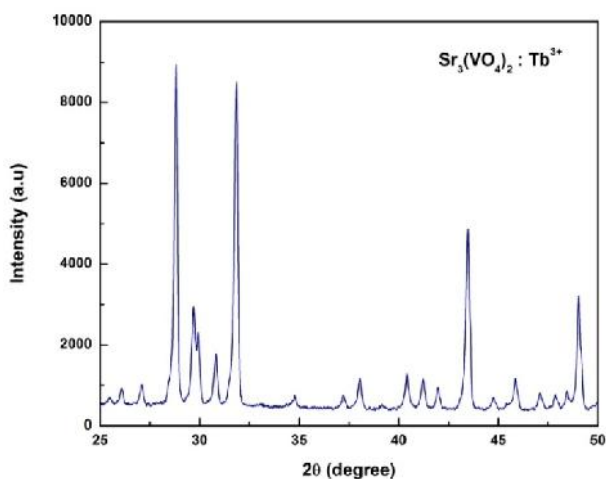


Figure 1: XRD pattern of the $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ nanoparticles Calcined at 900 °C.

nanophosphor annealed at 900°C. All diffracted peak positions are matched well with the standard pattern reported in literature¹⁴. Also no extra peak was found in the pattern corresponding to metal ions or activator ion, which confirms

that there is no other phase present in the material. The structure of the host material has rhombohedral phase with R3m space group. The broadening in the diffraction peaks indicates very small crystalline size of the particles, which was calculated by using well known Scherrer's

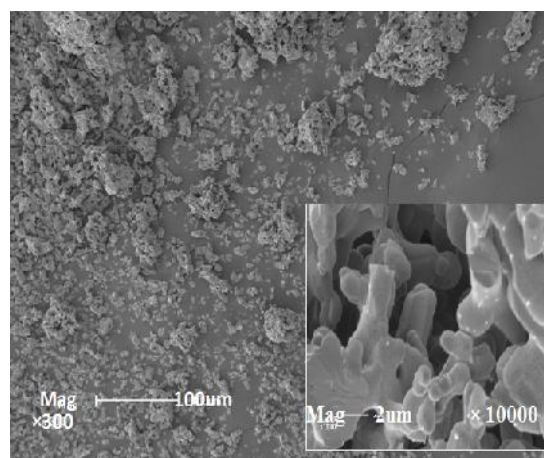


Figure 2: SEM images of annealed $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ phosphor at different magnification.

formulae¹⁵ and found to be in the range of 30-34nm. In order to study the morphology of the phosphor Scanning Electron Microscopy (SEM) has been carried out. Fig 2 shows the SEM image of the $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ nanophosphors, indicates that an agglomerated peanut like morphology was obtained.

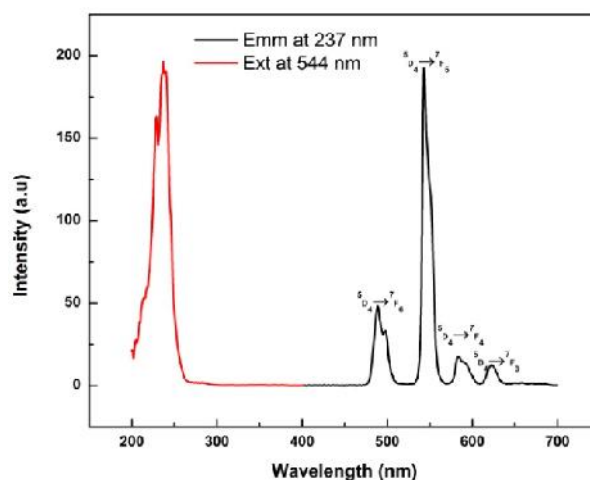


Figure 3: PL excitation and emission spectra of the $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ nanoparticles.

The excitation (at $\lambda_{\text{em}}=544\text{nm}$) and emission (at $\lambda_{\text{ext}}=237\text{nm}$) spectra of $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ phosphors is shown in Fig 3. The excitation spectra consist of intense excitation band from 200 - 260 nm with maximum intensity at 237 nm, attributed due to $^4\text{F}_8 \rightarrow ^4\text{F}_7, ^5\text{D}_1$ transition¹⁶.

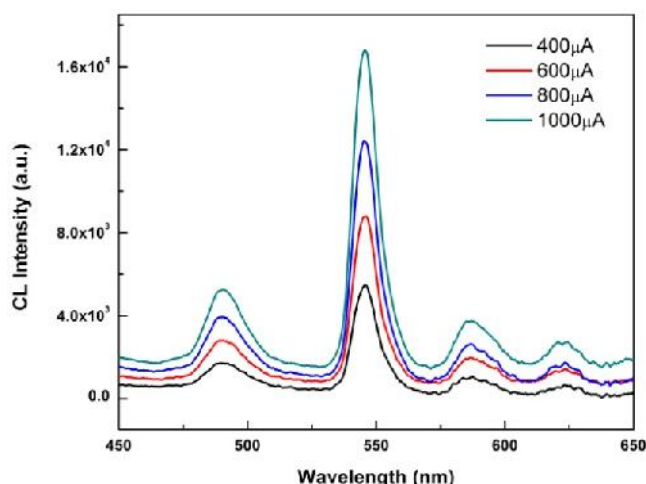


Figure 4: CL spectra of the $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ at an accelerating potential of 4 keV with different emission current.

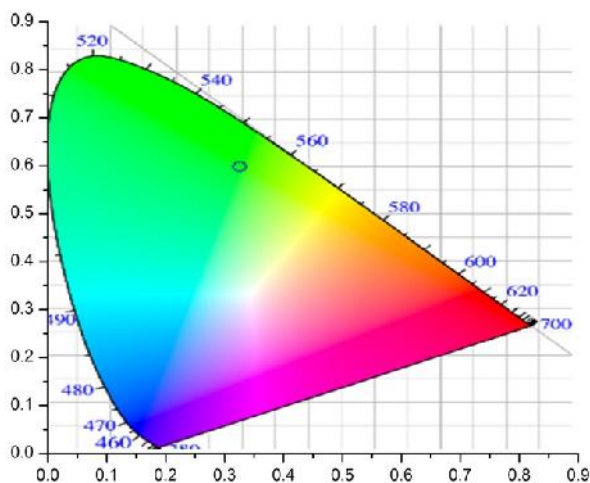


Figure 5: The CIE 1931 chromaticity diagram for $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ phosphor under 237 nm excitation.

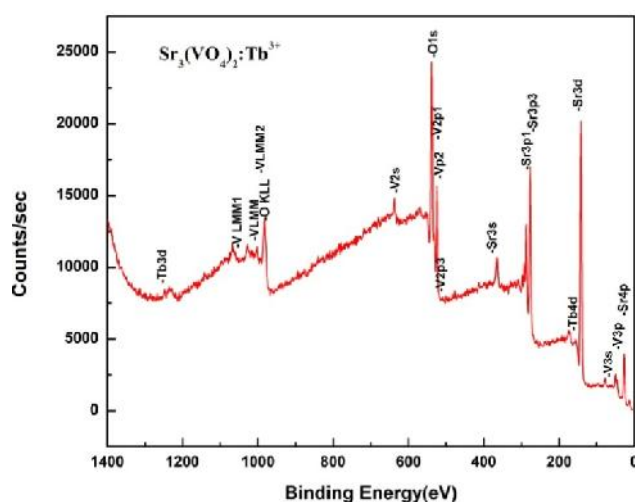


Figure 6: XPS wide scan spectrum of the $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ nanophosphors.

The emission spectra recorded at excitation wavelength 237 nm contains emission peaks at 487 nm, 544 nm, 588 and 624 nm due to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions, respectively¹⁷.

Also the peak located at 544 nm corresponds to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition is dominant one. Fig.5 represents the CIE 1931 chromaticity diagram for the

$\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ nanophosphor under 237nm excitation. It can be seen from the Fig 5 that the CIE coordinates (x, y) of (0.327872, 0.597455) correspond to the shade of green emission of Tb^{3+} .

Fig 4 presents the CL emission spectra of $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ phosphor recorded at constant 4 KeV beam voltage and different emission current from 400 to 1000 μA . The CL intensity increase with an increase in emission current, this may be due to larger electron beam current density and deeper penetration of electrons into the phosphor.¹⁸

XPS Studies

The X-ray photoelectron spectroscopy was employed to examine the oxidation state and the bonding characteristics on the surface of the synthesized nanophosphors. Fig.6 shows the XPS wide scan spectrum of the $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ nanophosphors. It shows that all the constituents i.e Sr, V, O, and Tb of $\text{Sr}_3(\text{VO}_4)_2:\text{Tb}^{3+}$ are present corresponding to their binding energies and there is no other impurity present on the surface of the sample.

Conclusions:

In summary, $\text{Sr}_3(\text{VO}_4)_2$ terbium activated nanophosphors has been successfully synthesized by combustion method. Under the excitation wavelength of 237 nm, the phosphor shows strong characteristic emission peaks of terbium ion $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$ and 3) and the emission peak centered at 544 nm corresponds to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition is dominant one. The phosphor shows the same emission peaks when excited with electron beam. XPS studies were done for surface characterization, which shows that all the elemental components of the phosphor are present on the surface of the sample.

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