

The Luminescence in Self Activated and Sm³⁺ Rich Garnet Phosphor Sr₂NaZn₂V₃O₁₂ Prepared by Solid-State Reaction

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Abstract

A new self-activated vanadate garnet phosphor Sr₂NaZn₂V₃O₁₂ and doped with Sm³⁺ vanadate garnet phosphor Sr₂NaZn₂V₃O₁₂ were produced by a simple conventional solid-state reaction that calcined for six hours at 950 degrees Celsius and then left to cool to room temperature. Vanadate garnet phosphor is utilized for high-performance tasks because of its excellent strength and hardness. The single-phase garnet structures in the prepared materials have been verified by X-ray diffraction (XRD) and Rietveld polishing. The behaviours of rare earth-doped luminescence and self-activated luminescence have been thoroughly examined. The prepared Sr₂NaZn₂V₃O₁₂ compound was observed a wide-band at wavelength of 485 in visible region of greenish emission that originates due to VO₄³⁻ emission. With lifetime measurement and photoluminescence (PL), In Sr₂NaZn₂V₃O₁₂: Sm³⁺ garnet-type phosphors, the energy transfer characteristics from VO₄³⁻ (vanadate) to Sm³⁺ (samarium trivalent) ions have been shown. While excitation was reported at 485 nm for vanadate garnet phosphor and 601 nm for samarium-rich garnet phosphor, the produced materials were excited by 338 nm for vanadate and 405 nm for Sm³⁺ rich phosphor. Scanning electron microscopy was used to study the topography and morphology. The findings suggest that Sm³⁺ doped Sr₂NaZn₂V₃O₁₂ garnet phosphors and self-activated Sr₂NaZn₂V₃O₁₂ exhibit significant promise for use in near-UV stimulated white LEDs.

Keywords: Luminescence, Sr₂NaZn₂V₃O₁₂:Sm³⁺, garnet phosphor, vanadate garnet phosphor.

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Introduction

There are numerous technological uses for inorganic phosphors in materials science. There is currently a high demand for the design and development of multifunctional phosphors. In addition to temperature sensing and solid-state lighting, inorganic phosphors have a wide range of applications in bio-sensing, anti-counterfeiting, and latent fingerprint detection [1]. The non-contact thermometry is related for utilizing thermographic phosphors with optical thermometry. To use the traditional approach, the thermometer has to come into direct touch with the bodies of interest. [2].

The classes of multi-sublattice oxides that are found as natural minerals all over the world are called garnets. Ca₃Al₂Si₃O₁₂ (Grossular), Mg₃Al₂Si₃O₁₂ (Pyrope),

Mg₃Fe₂Si₃O₁₂ (Andrade), Fe₃Al₂Si₃O₁₂ (Almandite), Mn₃Al₂Si₃O₁₂ (Spessartine), Mg₃Cr₂Si₃O₁₂ (Knorringite), Ca₃Cr₂Si₃O₁₂ (Uvarovite), and others are the most well-known. After the invention of the LASER and MASER in the 20th century, significant attempts were made for creating an extensive array of synthesized garnet-type crystals with different optical properties [3]. The most commonly utilized garnet-type phosphor material for a variety of lighting device applications is garnet (YAG): Y₃Al₅O₁₂. Among the several simple garnet compounds that are now generated utilizing various crystal growth and sintering techniques [4]. The heavy Sm³⁺ doped Sr₂NaZn₂V₃O₁₂ (SNZVG) based garnets are of particular interest these days for use in white LEDs. Additionally, Sr₂NaZn₂V₃O₁₂ garnet doped with Sm³⁺ has recently been established as an effective pro-convention medium for white LEDs [5].

The choice of the host material is crucial in this situation. The host material must effectively facilitate energy transfer among the luminescence centers and possess a substantial bandgap and low phonon energy, among other

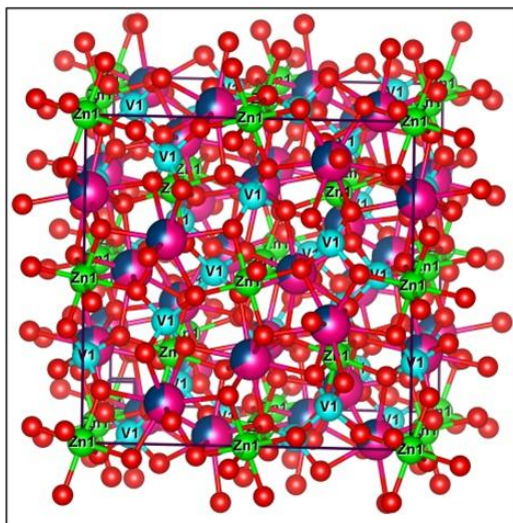


Figure 1(a): The Ball and Stick representation of $\text{Sr}_2\text{NaZn}_2\text{V}_3\text{O}_{12}$.

characteristics. Because of the ${}^3\text{T}_{1,2} - {}^1\text{A}_1$ transitions, vanadate-rich hosts are well known for their significant absorption and luminescent that activates on its own [6-7]. The samarium trivalent ions rich vanadate host configuration facilitates the passage of phonon energy from VO_4^{3-} to Sm^{3+} . Phonon-assisted energy transfer from VO_4^{3-} to Sm^{3+} is facilitated by the Sm-activated vanadate host structure. It is possible to design a phosphor with improved optical sensitivity by adjusting the emission characteristics of the structure. Currently, garnet-structured hosts are recognized for their ability to tune the photo-physical response through polyhedral substitution and the ensuing correlation of structure properties [8]. Garnet-type hosts have the usual chemical formula $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$, where A, B, and C represent dodecahedral sites, octahedral sites, and tetrahedral sites, respectively, and cubic crystallize structure with Ia-3d space group. Figure 1(a, b) show the Ball-Stick representation and Polyhedral representation of $\text{Sr}_2\text{NaZn}_2\text{V}_3\text{O}_{12}$ respectively.

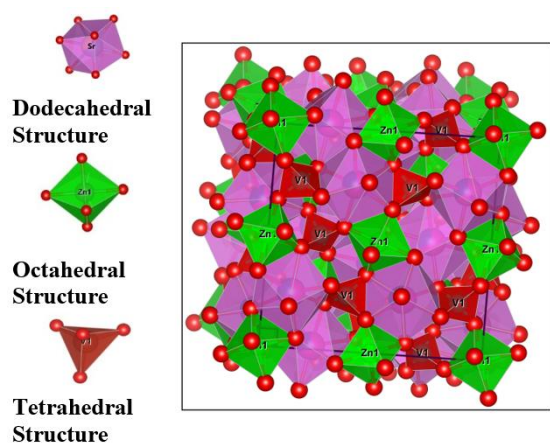


Figure 1(b): The Polyhedral representation of $\text{Sr}_2\text{NaZn}_2\text{V}_3\text{O}_{12}$.

Materials with garnet structures are renowned for their distinctive compositional diversity and structural framework, which satisfy the needs of a range of lighting and sensing applications [9]. As a result, Sm^{3+} -activated vanadate garnet-based phosphors are a great option for both w-LEDs and orange-red LEDs. In general, vanadate garnet has low phonon energy, which is necessary for improved luminescence characteristics. Our team has recently conducted a thorough investigation into the photoluminescence of the Sm^{3+} -activated $\text{Sr}_2\text{NaZn}_2\text{V}_3\text{O}_{12}$ system [10]. Because of its superior luminescence characteristics, $\text{Sr}_2\text{NaZn}_2\text{V}_3\text{O}_{12}$ (SNZVG) is chosen as the host material in order to fill this knowledge gap regarding the potentiality of vanadate garnets [11]. Sm^{3+} is another prominent orange-red emitter ion among RE ions. The electronic transitions from ${}^4\text{G}_{5/2}$ to ${}^6\text{H}_{5/2}$, ${}^4\text{G}_{5/2}$ to ${}^6\text{H}_{7/2}$ and ${}^4\text{G}_{5/2}$ to ${}^6\text{H}_{9/2}$ are represented by the orange-red emission. White light emitting diodes (w-LEDs) have overtaken conventional lighting sources in recent years because of their many advantages, which include increased efficiency, lower energy and power consumption, longevity, environmental friendliness, and superior thermal and chemical stability. These beneficial characteristics of w-LEDs have facilitated their use in communication, display devices, and solid-state lighting [12].

Experimental Procedures

(1) Chemicals and Synthesis:

Using a solid-state reaction method, the polycrystalline phosphors $\text{Sr}_2\text{NaZn}_2\text{V}_3\text{O}_{12}:\text{Sm}^{3+}$ were prepared. The chosen reagents, SrCO_3 , Na_2CO_3 , ZnO , and NH_4VO_3 and Sm_2O_3 (>99%, ACS MERCK), were combined using an agate mortar and pestle after being weighed in a stoichiometric ratio. All mixture of powder form was then calcined for six hours at 950 degrees Celsius. The powders were homogenized and sent for further characterizations after calcination.

(2) Characterization Techniques:

The X-ray powder diffraction method (Rigaku Miniflex 600, 40 kV and 30 mA, Cu $\text{K}\alpha$ wavelength 0.154059 nm) was used to identify the phase. Using a step size of 0.04 degree and a continuous scanning rate of 2θ between 10 and 80 degrees, phase formation was determined at a rate of $4^\circ/\text{min}$ using Rietveld analysis. Data from powder diffraction were acquired by means of the FullProf_Suite computer program. Using a photomultiplier tube running at a 135 W Xe lamp as the excitation lamp, the photoluminescence spectra were recorded at atmospheric temperature using a fluorescence spectrophotometer (F-7000 FL, 1914-024, Version-5J14000 03). Colour chromaticity data were used to compute the lifetimes and colour coordinates. FE-SEM JEOL, JSM-6500F with an 80

W Xeon light source and a 25 kV high tension voltage between the anode and cathode electron accelerating voltage was used to optimize the topographical and compositional characterizations.

Results and Discussion

Phase Identification by XRD Pattern

The crystalline structure and phase homogeneity of vanadate garnet and Sm³⁺ doped Sr₂NaZn₂V₃O₁₂ (SNZVG) materials are examined using XRD patterns. The XRD patterns of SNZVG are displayed in Figure 2(a).

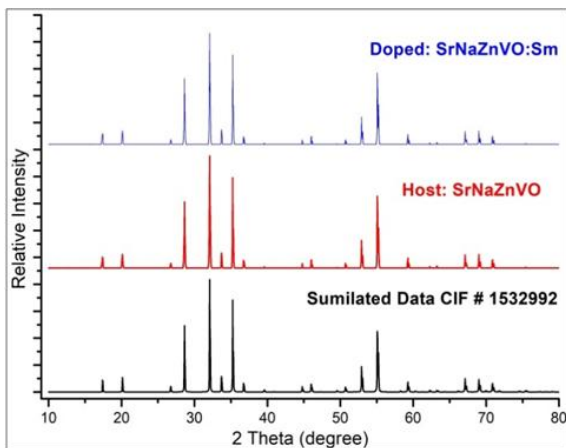


Figure 2(a): XRD patterns of the self-activated vanadate garnet Sr₂NaZn₂V₃O₁₂, 8% Sm³⁺ doped garnet Sr₂NaZn₂V₃O₁₂:Sm³⁺ and simulated CIF # 1532992 is also given for comparison.

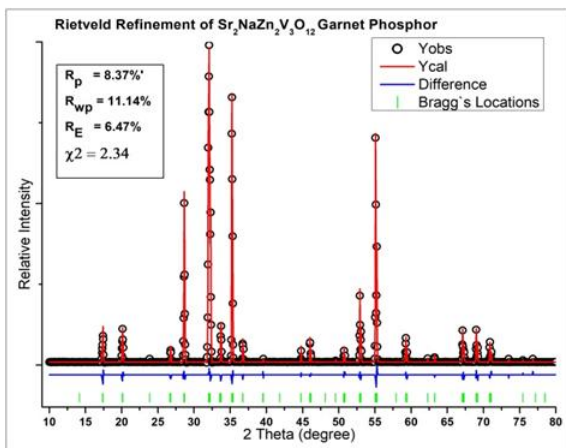


Figure 2(b): The Rietveld Refinement of vanadate garnet phosphor Sr₂NaZn₂V₃O₁₂: observed intensities (black circles), red lines are calculated patterns and difference between observed, calculated intensity is indicated by blue line and tick-greenish lines are Bragg's locations.

The Rietveld polishing (refinement) pattern of SNZVG and SNZV: 8% Sm³⁺ indexed to the cubic structure having space group as Ia-3d (230, Oh¹⁰) are shown in Figure 2(b). Sr₂NaZn₂V₃O₁₂ is used in all single-phase, isostructural compositions (simulated CIF # 1532992). It has been established that adding Sm³⁺ to the dodecahedral site has no effect on the samples' crystallinity. In contrast to the general

stoichiometry, Sr²⁺ and Na⁺ form Sr/NaO8 dodecahedra and the dodecahedral site (24c) is occupied with 2/3 and 1/3. Zn²⁺ ions are completely occupied in the octahedral site (16a), V⁵⁺ ions are completely occupied in the tetrahedral site (24d), and O²⁻ ions are completely occupied in the general sites (96h). The dodecahedral site is substituted with the lanthanide ions Sm³⁺. Table 1 list the crystallographic information and refined unit cell parameters for the Sr₂NaZn₂V₃O₁₂:Sm³⁺ phosphor. The Sm³⁺ occupancy in the dodecahedral site is confirmed by the reliability parameters that were obtained. The lattice parameter of the Sr_{1.84}Sm_{0.08}Na_{1.08}Zn₂V₃O₁₂ system is 1.22317 nm. Furthermore, micro-strain ($\epsilon = 0.0003841$) determined that lattice contraction occurs because the larger Sr²⁺ ion is replaced by the smaller ionic radii of Sm³⁺.

Excitation and Emission of Photoluminescence

Figure 3(a) depicts the excitation spectrum of Sr₂NaZn₂V₃O₁₂: Sm³⁺. The material was excited at 338 nm for vanadate garnet phosphor and at 403 nm for samarium doped garnet phosphor. The excitation spectrum was recorded at 485 nm for VO₄³⁻ in transitions from ¹A₁ - ¹T₂ and ¹A₁ - ¹T₁ and at 601 nm for Sm³⁺ in transition from ⁶H_{5/2} to ⁴K_{1/2} as shown in Figure 6(b).

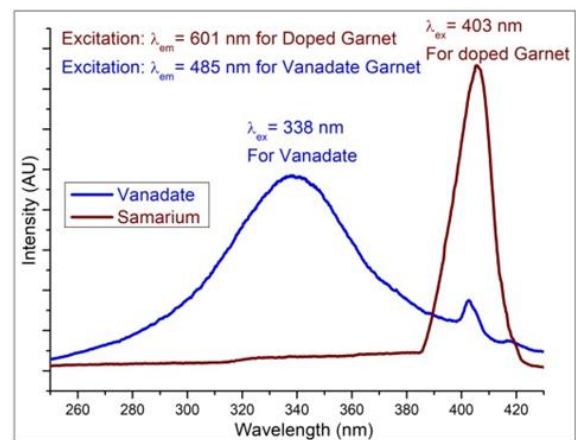


Figure 3(a): Excitation spectrum of both doped and un-doped vanadate phosphor.

Figure 3(b) displays the photoluminescence emission (PL) spectra of vanadate garnet phosphor and the emission wavelength was observed at 485 nm in transition ³T_{1,2} to ¹A₁. This transfers the energy to samarium doped garnet phosphor. Figure 3(c) displays the emission spectrum of Sr₂NaZn₂V₃O₁₂: Sm³⁺ at emission wavelengths 564 nm in electronic transitions from ⁶G_{5/2} to ⁶H_{5/2}, 601 nm in electronic transitions from ⁶G_{5/2} to ⁶H_{7/2} and 648 nm in electronic transitions from ⁶G_{5/2} to ⁶H_{9/2} but more intense peak was found at 601 nm in transition ⁶H_{7/2}.

It is observed that VO₄³⁻ emission decreases with Sm³⁺ concentration. Nonetheless, the Sm³⁺ band's intensity rises with concentration; at 0.08 Sm³⁺, the maximum intensity is

achieved. The variation of intensity vs Sm^{3+} concentration is shown in Figure 3(d).

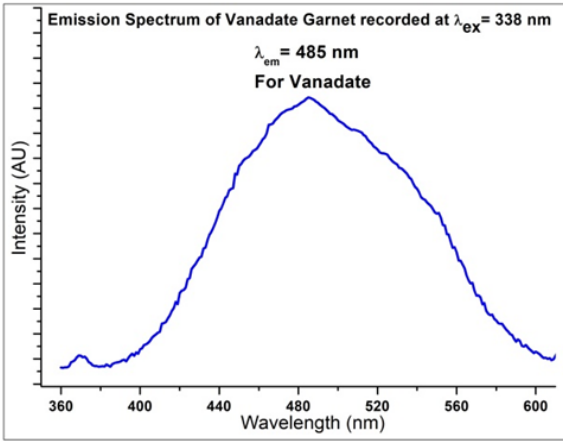


Figure 3(b): Emission spectrum of vanadate garnet phosphor

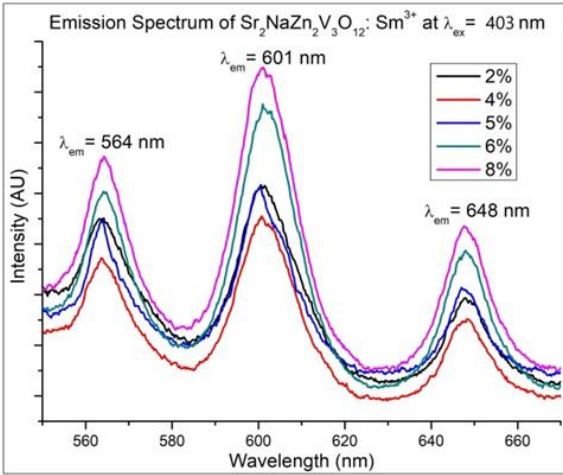


Figure 3(c): Emission spectrum of garnet phosphor $Sr_2NaZn_2V_3O_{12}: xSm^{3+}$ ($x = 2\%, 4\%, 5\%, 6\%$ and 8%)

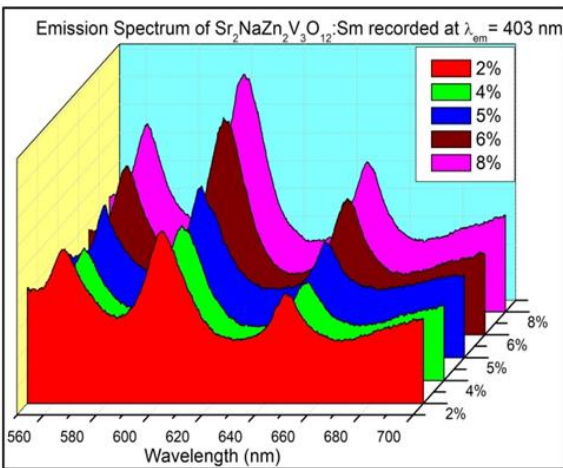


Figure 3(d): Variation of intensities due to Sm^{3+} concentration and 3D view of the $Sr_2NaZn_2V_3O_{12}: Sm^{3+}$

Topographical and Compositional characterizations

Table 1: The crystal structural parameters and refined data parameters of vanadate garnet phosphor of $Sr_2NaZn_2V_3O_{12}$.

Crystal Structure Parameters	$Sr_2NaZn_2V_3O_{12}$ Garnet	Refinement Parameters	$Sr_2NaZn_2V_3O_{12}$ Garnet (refined)			
Crystal lattices	Cubic	Chi ²	2.34			
Space group	Ia-3d (230)	Factors R _p (%)	8.37			
(hkl)	(311) at 2θ = 32.08°	Factors R _{wp} (%)	11.14			
lattice parameters	1.22317 nm	Expected R _w (%)	6.47			
Error in a	1.8 % (compare with CIF # 1532992)	Wyckoff Positions				
Volume of unit cell	1.774.505 nm ³	Sr ²⁺ (2/3) + Na ⁺ (1/3)	24c			
Z	8	Zn ²⁺	16a			
Average Crystalline Size D _{obs}	43.43547 nm	V ⁵⁺	24d			
Average Crystalline Size D _{cal}	45.13333 nm	O ²⁻ (for Ia-3d)	96h			
% error in Crystalline size D	3.90 %	Atomic Locations				
β (FWHM) at dominate peak (β _{max})	0.002094393 rad (0.12 degree)	Ions	x	y	z	Occp
		Sr ²⁺	0.125	0	0.25	0.667
Microstrain (ε)	0.0003841	Na ⁺	0.125	0	0.25	0.333
		Zn ²⁺	0	0	0	1
Dislocation Density (δ)	2.10379x10 ⁻⁴ per nm ²	V ⁵⁺	0.375	0	0.25	1
		O ²⁻	-	0.0526	0.1565	1

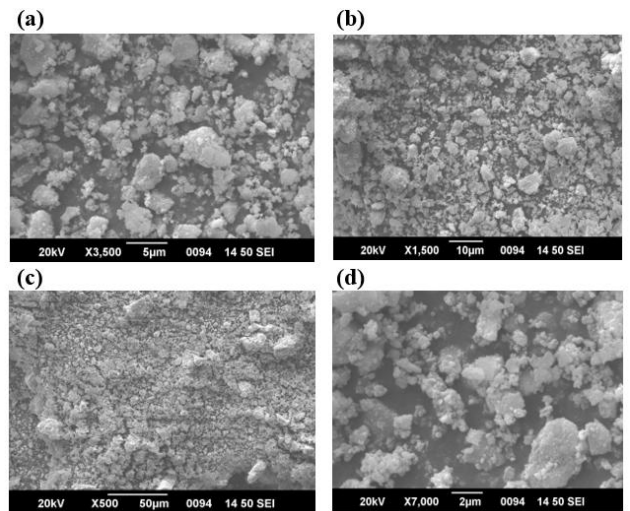


Figure 4(a-d): SEM photographs of $Sr_2NaZn_2V_3O_{12}: Sm^{3+}$ garnet phosphor at different magnifications.

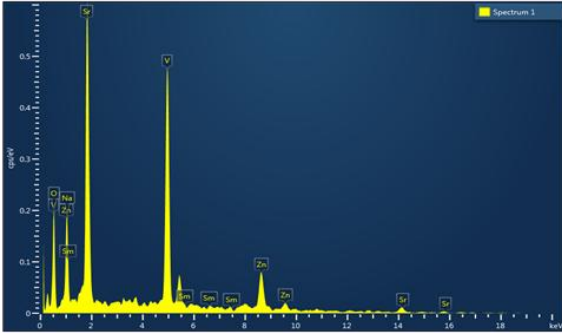


Figure 5: EDS of Sr₂NaZn₂V₃O₁₂:Sm³⁺ for chemical composition

SEM pictures of the synthesized Sr₂NaZn₂V₃O₁₂:Sm³⁺ garnet phosphors are shown in Figure 4(a-d) to analyse its morphology. It is discovered that the Sr₂NaZn₂V₃O₁₂:Sm³⁺ particle size and morphology are comparable, which is consistent with the average size of the crystallite of these materials. However, the morphology of every sample under study is a distinctive feature of garnet phosphor that was first documented [13]. Together with the theoretical composition, the measured chemical composition of Sr₂NaZn₂V₃O₁₂:Sm³⁺ garnet phosphoric is listed in Table 2. Considering the potential measurement error (< ±1%), it can be said that all samples exhibit good conformance to the theoretical and determined composition.

Table 2: The chemical composition of the prepared Sr₂NaZn₂V₃O₁₂:Sm³⁺ were determined by EDS and calculated.

Elements	O (%)	Sr (%)	V (%)	Zn (%)	Na (%)	Sm (%)	Total Wt %
EDS Data	22.8	27.7	28.0	16.3	3.9	1.0	100
Calculated Data	23.0	27.5	28.0	16.3	4.0	1.0	100

Colour Calculation by CIE Chromaticity Diagram

Figure 6(a) displays CIE coordinate of the vanadate garnet phosphor observed at (0.246, 0.317) and CCT was 11659.2 K. The CIE coordinators of Sm³⁺-activated garnet phosphor for different concentrations are listed in Table 3. The colour purity was calculated 85.13% at dominant peak. The colour purity of the Sm³⁺ doped sample was increasing with concentration. The CCT (K), Colour Purity (%) and lifetime (ns) were calculated by equations (1), (2) and (3) respectively [13].

$$CCT (K) = -437r^3 + 3601r^2 - 6861n + 5514.31 - (1)$$

Where, $r = \frac{(x-x_e)}{(y-y_e)}$ and $x_e = 0.3320$ & $y_e = 0.1858$ are chromaticity epicenters.

$$Colour Purity (CP) = \sqrt{\frac{(x-x_s)^2 + (y-y_s)^2}{(x_d-x_s)^2 + (y_d-y_s)^2}} \times 100 - (2)$$

Where, (x, y) are CIE coordinates of sample (entire wavelengths range), (x_s, y_s) are Coordinates of UV Sours lamp for illuminant the sample (356 nm, 6W), (x_d, y_d) are dominant coordinates of sample (at peak wavelength).

$$Average Life Time (\tau) = \frac{\int t \times i(t) dt}{\int i(t) dt} - (3)$$

Where, i(t) is intensity count of the function of time t.

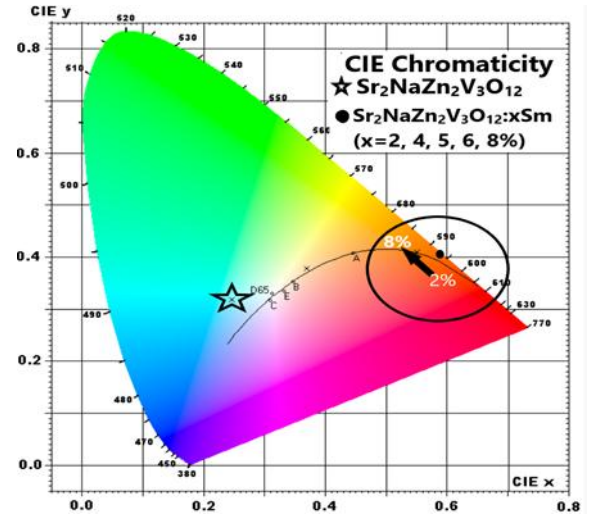


Figure 6(a): CIE digital photographic diagram of Sr₂NaZn₂V₃O₁₂:Sm³⁺ garnet phosphors.

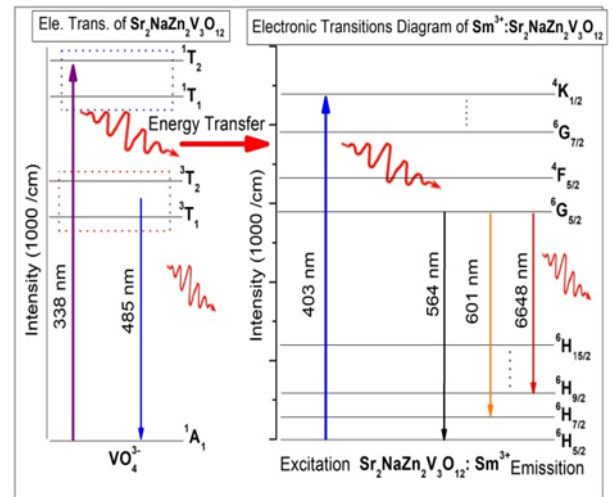


Figure 6(b): Vanadate (VO₄³⁻) and Sm³⁺: excitation and emission transitions with the energy transfer process between the respective energy levels.

Table 3: Colour coordinators of Sr₂NaZn₂V₃O₁₂:Sm³⁺ from CIE chromaticity.

Dopes: Sm	(x, y)	(x _d , y _d)	CCT (K)	CP (%)	Lifetime (ns)
0%	(0.246, 0.317)	(0.073, 0.185)	11659.2	73.65	516.4994
25	(0.551, 0.448)	(0.632, 0.368)	2040.42	84.23	616.3309
4%	(0.554, 0.445)	(0.632, 0.368)	2003.73	84.60	617.2414

5%	(0.556, 0.443)	(0.632, 0.368)	1983.75	84.86	618.2637
6%	(0.558, 0.441)	(0.632, 0.368)	1963.95	85.13	616.0152
8%	(0.558, 0.441)	(0.632, 0.368)	1964.21	87.71	616.6067

Conclusion

We have successfully prepared the vanadate (self-activated) and Sm³⁺ doped Sr₂NaZn₂V₃O₁₂ garnet phosphors using the solid-state procedure. The results of the XRD analysis show the prepared materials have a single-phase compound with a garnet structure. By examining at the luminescent features, we may conclude that energy transfer takes place from the vanadate (VO₄³⁻) to the trivalent Sm³⁺ ions. With a maximum emission at 485 nm, Sr₂NaZn₂V₃O₁₂ (vanadate garnet) has a wide emission band encompassing 400–700 nm. The emission spectra for the Sm³⁺ doped Sr₂NaZn₂V₃O₁₂ phosphors consist of the wide-band emission at wavelength 485 nm (in visible region of greenish colour) and its emission as reflected to the f–f shifts due to Sm³⁺. Because of the amount of energy transmission between VO₄³⁻ and the Sm³⁺ ions, the CIE parameters of Sr₂NaZn₂V₃O₁₂: Sm³⁺ garnet luminescence materials may be adjusted by varying the percentage of rare earth Sm³⁺ ions. According to the investigation and results, there is a great deal of promise for using the produced phosphor in near-UV stimulated white LEDs.

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