

Influence of Pva, Pvp on Crystal and Optical Properties of Europium Doped Strontium Aluminate Nanoparticles.

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ABSTRACT: The Photoluminescence properties of Polymer passivized Europium doped Strontium Aluminate powder with Polyvinyl Alcohol, Polyvinylpyrrolidone, as dispersing agent by direct chemical-combustion process was reported in this research work. XRD results confirmed the formation of SrAl₂O₄ Orthorhombic phase, yielding crystal sizes of 39.00nm –42.00nm, for the samples. The calculated band gap and the Optical linear absorption coefficient were in the ranges of, 4.69eV –4.97eV, and 5.81m⁻¹- 6.10m⁻¹ respectively. Photoluminescence analysis excited at 365nm wavelength, gave concise Eu³⁺ transition between ⁵D₂ →⁷F₁ to ⁵D₀→⁷F₄ of the colour wavelengths. Higher broadband was observed majorly within the Bluish -Green colour wavelengths with Polyvinylpyrrolidone sample having the highest photoluminescence intensity and unpassivized sample having the lowest photoluminescence intensity. The results from this research suggest that significant Photoluminescence enhancement could be achieved for SrAl₂O₄:Eu³⁺ using polymer passivation without significant changes in the crystal size of the powder; hence can possibly be applied as the newly developed blue-green efficient phosphor in the field of lighting and display.

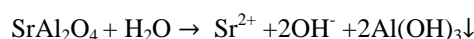
Keywords: Photoluminescence, PVA, PVP, Strontium Aluminate, XRD.

I. INTRODUCTION

Nanostructured functional material in recent time has drawn much research interest due to their distinguished size, shape, and surface morphology which play important role in controlling the physical, chemical, optical and electronic properties of these nanoscale materials [1, 2]. Strontium aluminate when activated with a suitable dopant like europium acts as a photoluminescent phosphor with long persistence of phosphorescence [3]. The excitation wavelengths range from 200 to 450nm. The wavelength for its green formulation is 520nm, its blue-green version emits at 505nm, and the blue one emits at 490nm.

In the present work, we aimed to study the influence of polyvinyl alcohol (PVA) and Polyvinylpyrrolidone(PVP) on SrAl₂O₄:Eu³⁺ preparation by chemical-combustion method at higher temperature. Polyvinyl alcohol (PVA) [C₂H₄O] and Polyvinylpyrrolidone(PVP) [C₆H₉NO] has a relatively simple chemical structure with a pendant hydroxyl group. The hydrolysis reaction does not go to completion resulting in polymer with certain degree of hydrolysis reaction that depends on the extent of reaction. The degree of hydrolysis or the content of acetate groups in the polymer has overall effect on its chemical properties, solubility and the crystallites.

The degree of hydrolysis and polymerization affect the solubility of PVA or PVP in water [4-5]. These polymers, (high physical-chemical stability, high degree of transparency, high melting and transition temperatures, lack of toxicity) grades with high degrees of hydrolysis have low solubility in water, that is, the higher the solubility (%), the lower the degree of hydrolysis (%). Good dispersing agents on the host materials. Weak water resistance is still a well-known drawback for this type of phosphors. Hydrolysis occurs if they are into water as indicated by the equation below [6]:



Invariably, the pH value of the suspension will increase spontaneously. This will deteriorate badly the luminescence of the phosphor. Guo *et al* 2007 analysed the rate of hydrolysis that is observed in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ intensively as quoted by Zhu *et al* [7]. Recently, the polymer was used as template to prepare a number of oxide nanoparticles where polymer skeleton eventually limits the growth in a specific shape of the lattice [8-11]. A metal ion-polymer complex forms via a kind of ligand reaction with active OH groups of surfaced PVA molecules.

Metal oxide semiconductor nanoparticles (SNPs) have strong absorption as well as emission behaviour than that of organic dyes and phosphors. Various chemical and physical techniques are employed overtime to investigate the optical properties of nanocrystal SrAl_2O_4 [12]. This has to do with organic layers and inorganic layer. Organic layers cover phosphors by precipitation, which entails elaborate equipment. It's worth noting that neither the organic nor inorganic layer phosphors are water repellent. Inorganic layers are inclined to crack, while organic layer are subject to water infiltration. Aluminate phosphor capped with organic or inorganic layer undergoes luminescence degradation [13-14].

II. MATERIALS AND METHODS

2.1 Materials

The following materials were used in the synthesis, characterization of $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ passivized with PVA and PVP at 1000°C for 2 hours. Strontium Nitrate [$\text{Sr}(\text{NO}_3)_2$], Europium (III) Chloride [$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$], Aluminium Nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], Boric Acid [H_3BO_3], ThioUrea [$\text{CH}_4\text{N}_2\text{S}$] (all the chemicals used are of analytical grade, no further purification was carried out) and Deionized water.

2.2 Method of Preparation of the Nanoparticles

For the synthesis of $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$, 0.98g of $\text{Sr}(\text{NO}_3)_2$, 0.02g of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 2g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 3.90g of $\text{CH}_4\text{N}_2\text{S}$ as the starting material was dissolved in 10ml of deionised water and stirred well for 20 minutes at a temperature of 80°C on a magnetic stirrer until a clear solution was formed. The precursor was introduced into a vacuum oven for drying at 80°C for 20hrs. Initially, the solution boiled and gave room for dehydration and decomposition with evolution of large gases such as oxides of carbon, ammonia, and nitrogen. Spontaneous ignition occurred at which smouldering combustion with swelling of the sample with white foamy and voluminous SrAl_2O_4 . The dried sample was further annealed at 300°C for 30 minutes to remove remaining moisture content. The white powder obtained was crushed and 0.30g of Boric acid was added as a reflux [15]. These were subsequently annealed at 1000°C for 2hrs in a muffle furnace, producing $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ phosphor nanoparticles labelled SAE.

The above procedure was repeated with addition of 0.326g of PVA or 0.326g of PVP into the solution as a passivation agent respectively to the starting material before drying in an oven for 20hrs; forming PVP-SAE and PVA-SAE phosphor nanoparticles.

The samples were characterized using the following: An X-Ray Diffractometer (X'pert Pro, PANalytical) made in Netherland with Cu K α radiation at 40kv, 40mA and a scan rate of $0.02^\circ/\text{s}$ in the 2 θ range from 10° to 70° for the verification of the crystal structure and the average size of the particles at Sheda Science and Technology Complex Abuja-Nigeria. The morphology of the powders were obtained using SEM model PhenomproX desktop. The elemental chemical composition was obtained using XRF model OXFORD Instrument Benchtop XRF Analyser-X-Supreme 8000 (+carousel). Jenway 6405 UV/vis spectrophotometer analyser was used to obtain the various absorption values of the nanomaterial at Chemical Engineering and Multi-purpose Research Centre, A.B.U Zaria-Nigeria; Photoluminescence Spectrometer, Perkin-Elmer LS-55 Fluorescence spectrometer at CSIR Pretoria South Africa.

III. RESULTS AND DISCUSSION

3.1 Structural Analysis

Fig. 1(a,b,c) illustrates the XRD patterns of $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ (SAE), PVP-SAE, and PVA-SAE nanoparticles respectively. Four strong characteristics XRD peaks of spinel strontium aluminate at (27.135° , 30.150° , 32.830° & 44.354°), (27.068° , 30.016° , 32.763° & 44.287°) and (27.001° , 30.016° , 32.696° & 44.072°) 2θ were considered respectively from the curves. These were indexed to spinel (021), (211), (121), (311) for SAE, PVP-SAE and PVA-SAE crystal planes. Both samples showed orthorhombic structure which is in agreement with the standard ICDDs card values of 089-0954.

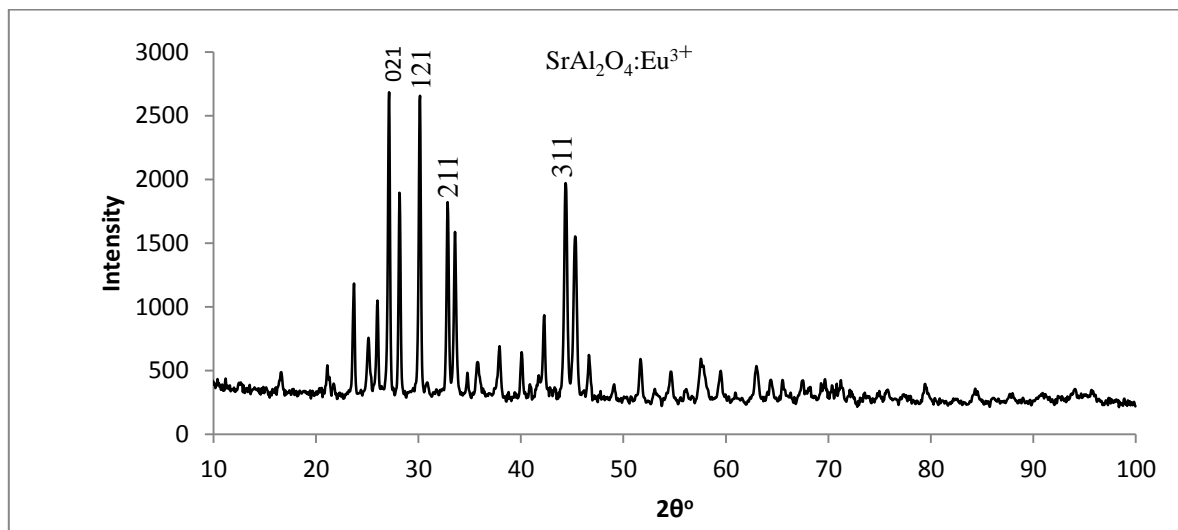


Fig.1a XRD patterns of sae

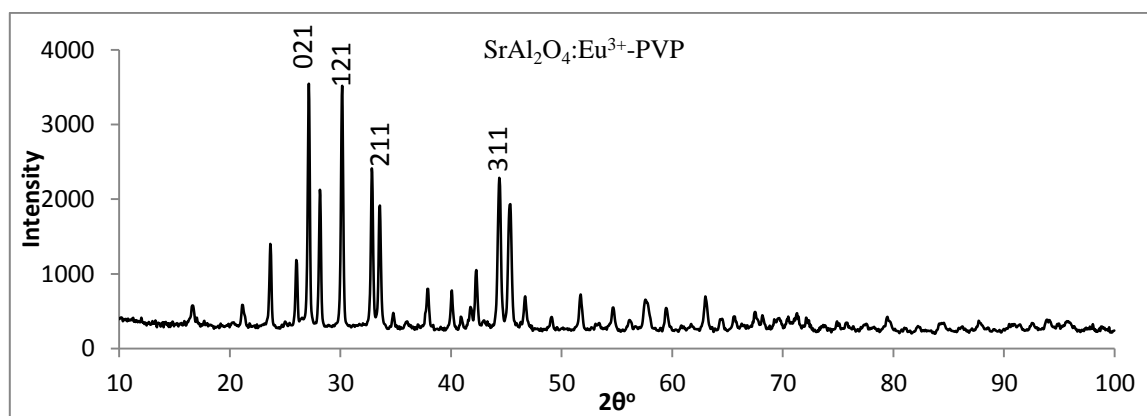


Fig.1b XRD patterns of SAE-PVP

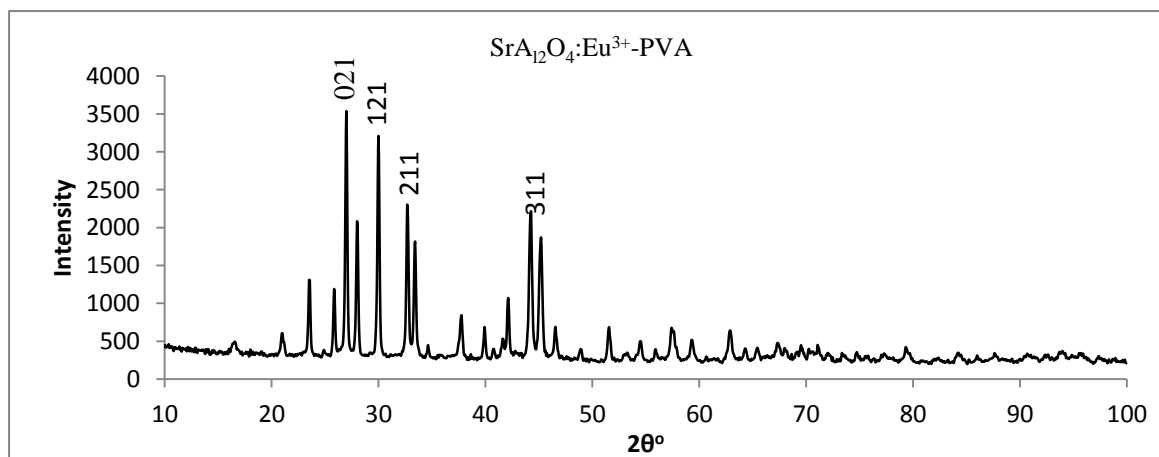


Fig.1c XRD patterns of SAE-PVA

The obtained diffraction patterns was found to be consistent with data reported in ICDD [16], indicating that a pure SrAl_2O_4 phase was successfully prepared at a temperature of 1000°C . In the conventional solid-state process, the required temperature for synthesizing SrAl_2O_4 is around 1400°C - 1600°C [17]. It clearly indicates that chemical-combustion process can significantly lower the heating temperature for preparing SrAl_2O_4 phase. As can be seen, pure monoclinic phase diffraction peaks of SrAl_2O_4 are predominant in the XRD patterns, which is similar with that obtained by Peng [18].

The broadening of the diffraction peaks indicates nanocrystalline nature of the samples. Debye-Scherrer's formula $D = \frac{k\lambda}{\beta \cos\theta}$ was used to estimate the average particle size, where D is the particle size, k is the geometric factor 0.89, λ is the X-Ray wavelength 1.54056\AA , β is the FWHM of diffraction peak, and θ is the diffraction angle.

The crystal size of the unpassivized SAE; PVA-SAE and PVP-SAE particle calculated from the highest peaks are 39.35nm, 40.81nm, and 41.54nm respectively as the inter-planar distance. These sizes of nanocrystals of the powder are in strong charge conferment regime.

3.2 Optical Analysis

In determining the true value of the optical band gap, the fundamental absorption which corresponds to electron excitation from the valence band to conduction band helps. The band gap was evaluated from the absorbance A versus wavelength λ_{nm} curve. The band gap is therefore, obtained from the relation (Song *et al.*, 2010) $E_n = \frac{hc}{\lambda_c}$; where E_n is the band gap, h Planck's constant, c speed of electromagnetic wave and λ_c wavelength of the absorption edge. The calculated band gap energies are 4.69eV, 4.78eV and 4.94eV respectively.

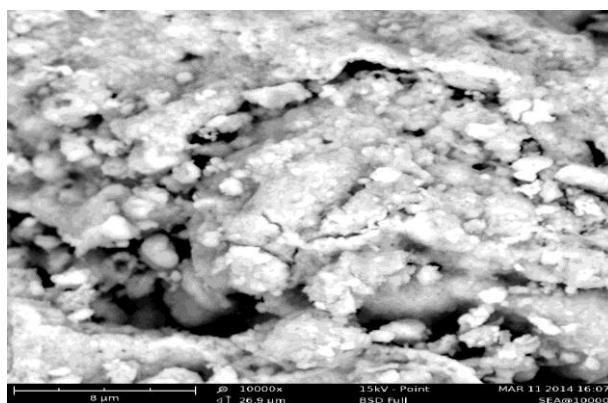
3.3 Optical Linear Absorption Coefficient

This is obtained using Beer Lamber's relation $\alpha = \frac{2.303A}{l}$

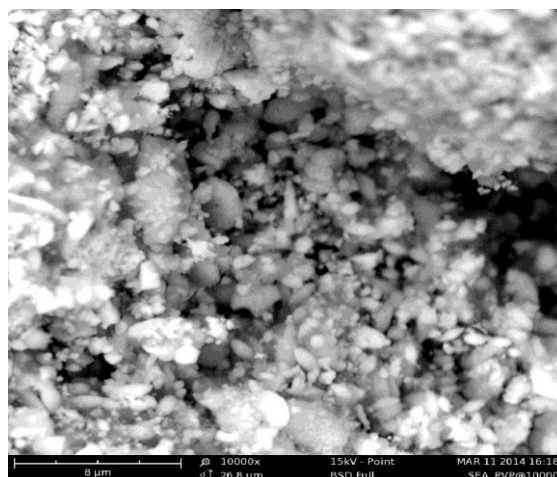
where A is the absorbance wavelength from the UV results above and l is the optical path length (1cm). The various optical linear absorption coefficients for SAE, SAE-PVA and SAE-PVP are 5.81m^{-1} , 5.98m^{-1} and 6.10m^{-1} respectively.

3.4 Surface Morphology Analysis

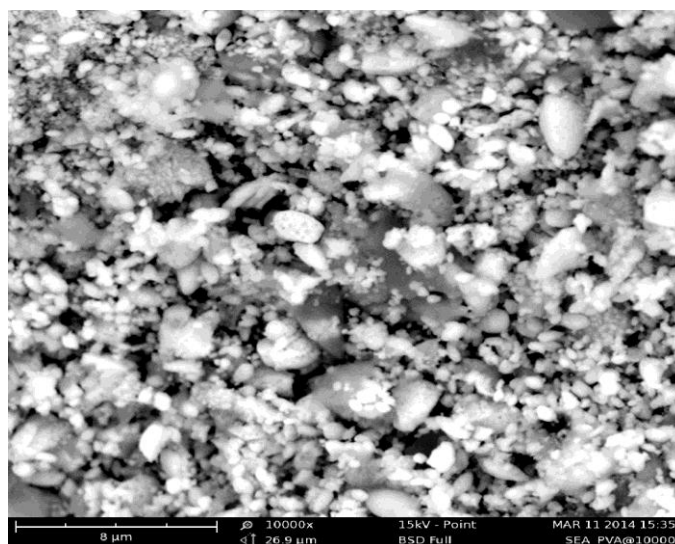
Fig.3 shows the SEM images of (a) SAE (b) PVP-SAE and (c) PVA-SAE nanoparticles. Sr and Al elements are the main chemical element compositions of the samples as indicated by the EDX analysis.



(a)



(b)



(c)

Fig.2 The SEM micrograph analysis results of sample (a) unpassivized sae (b) PVP-SAE (c) PVA-SAE nanoparticles.

3.4 Chemical Analysis

The XRF chemical analysis of sample of SAE unpassivized, PVP-passivized SAE and PVA-passivized SAE searched in the current research is present in Table 1. H_3BO_3 and Europium levels of the phosphors could not be determined by XRF [21].

Table 1. The XRF chemical analysis results of sample SAE, SAE-PVP and SAE-PVA

Element	SAE-Weight %	SAE-PVP Weight %	SAE-PVA Weight %
Al_2O_3	16.886	20.940	21.885
SiO_2	23.102	22.223	26.533
SO_3	16.512	17.819	19.974
SrO	43.136	37.497	29.987
P_2O_5	0.329	0.470	0.506
Mn_2O_3	0.035	0.489	0.338
Na_2O	-	0.562	0.777

3.5 Photoluminescence analysis

Fig.3. shows the PL emission spectrum of the samples as indicated. In comparing PL properties of these samples, the PVP passivized $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ is having more PL intensity followed by PVA due to controlled and homogeneous growth of the nanoparticles in the solution prepared.

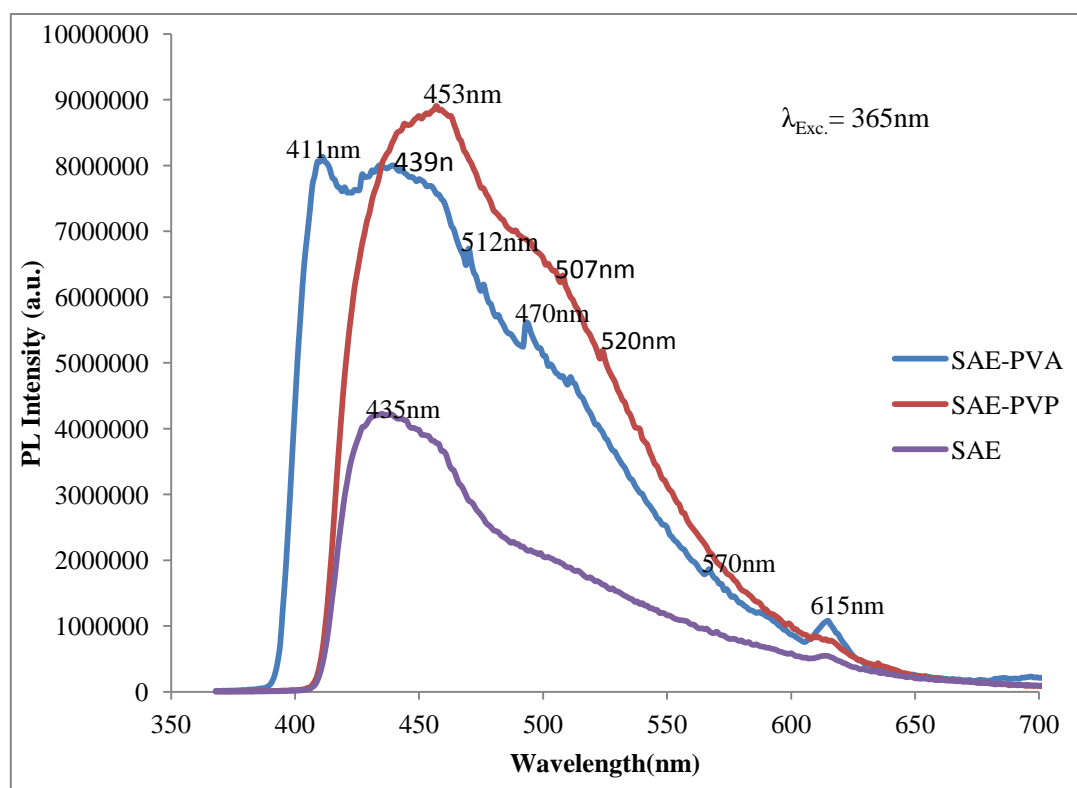


Fig. 3: photoluminescence emission spectral of the samples

Inhibition of diffusion is the limiting procedure for the crystal growth in this research, since coiled structures of the polymer chains will alter the diffusion-driven mechanism within the network. There's possibility that polymer chains may be blocked by connecting to the same nanoparticles and so many of such bridged chains crystals could lead to particle clustering [19]. At temperature below 400°C , higher ionic content in PVA, PVP has effected a more efficient clustering of the ionic groups into domains of small size [2]. Crystalline nature of PVA or PVP results from the strong intermolecular interaction between PVA, PVP chains through the intermolecular hydrogen bonding. This may be the reason that the interaction between their chain and $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ particles led to increase of intermolecular interaction, resulting in increasing the crystalline degree of PVP, PVA and enhanced PL intensity for both emission above the host nanoparticles when annealed at higher temperature.

Table 2: Summary of work results table

Samples	XRD Intensity (a.u.)	Crystal size (nm)	Band Gap energy (eV)	Optical Linear Coefficient (m^{-1})	PL Intensity (a.u)
PVP-SAE	3543.7	41.54	4.69	6.10	8797200
PVA-SAE	3539.1	40.81	4.78	5.98	8135300
SAE	2685.5	39.35	4.94	5.81	4228100

IV. Conclusion

Passivation $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ nanoparticles via chemical precipitation and combustion method with different polymers as capping agents were successfully carried out. The passivated samples and the unpassivated Strontium Aluminate nanoparticles were researched in with respect to the effect of passivation on the structural, morphological, optical and PL intensity properties of SrAl_2O_4 nanoparticles.

Observed increase in crystal sizes from XRD analysis depicts the influence of passivation materials on the SrAl₂O₄ nanoparticles was not in line to those obtained for PVA, polymers capped ZnO and ZnS nanoparticle at room temperature [20,2], indicating that high temperature give rise to higher crystal size. The analytical result has shown that the nanomaterials phosphor have pure orthorhombic SrAl₂O₄ phase at 1000°C with the increase crystal size in the range of 39nm-42nm. Optical properties of SrAl₂O₄ nanoparticles decrease revealed in the band gap energy with decrease in absorption edge are green shifted due to decrease in particle sizes emanating from passivation agent due to confinement effects.

From SEM micrographs, it is observed that passivation on SrAl₂O₄ nanoparticles enhances the optical properties of the nano-materials. The SEM with EDX analysis carried out shows the passivation effects on the particle surface by passivizing agent with micrographs of smooth surface of pure SrAl₂O₄ nanoparticles.

At the photoluminescence excitation of 365nm, SrAl₂O₄:Eu³⁺ with the three samples phosphor emits in the bluish-green between 411-650 nm which agrees with the emission characteristics of Eu³⁺. The maximum emission intensity was obtained for sample with PVP-SAE (⁵D₂ → ⁷F₁). The emission bands can be attributed to the Eu³⁺ transition of ⁵D₂ → ⁷F₁ state to the ⁵D₀ → ⁷F₄ as shown in Fig.3 above.

In all ramifications, the result shows that the higher the crystal size of the nanomaterial, the better its PL, XRD intensity spectra and its UV-optical linear absorption coefficient; but it inversely proportional to the energy band gap depicted in Table 2. The results from this research suggest that significant Photoluminescence enhancement could be achieved for SrAl₂O₄:Eu³⁺ using polymer passivation without significant changes in the crystal size of the powder; hence can possibly be applied as the newly developed blue-green efficient phosphor in the field of lighting and display.

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