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Luminescence Characteristics of Polymer Passivized Strontium Aluminate Phosphor

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Authors' contributions

This work was carried out in collaboration between all authors. Author AAN designed the experiment, synthesize samples, perform the characterization from his thesis research work and wrote the first draft of the manuscripts. Author JPR provided basics on the polymers and author AAR supported in carrying out experimental work. All authors read and approved the final manuscripts.

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Original Research Article

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ABSTRACT

Trivalent Europium ions doped strontium aluminate as the host and passivized by Polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and carboxyl methyl cellulose (CMC) shows luminescence arising from various 5D_2 and ${}^5D_0 \rightarrow {}^7F_4$ transition of Eu³⁺ ion upon excitation at 285 nm. The influence of the varied polymers concentration on crystal structures and optical properties was studied by means of X-ray diffraction (XRD) and photoluminescence (PL) spectrometer. XRD pattern revealed a dominant phase characteristics of orthorhombic strontium aluminate compound at 1000°C with an average crystal sizes of the phosphors calculated to be ~39 nm - 42 nm. Photoluminescence emission spectral showed a broad peak at 648 nm with PVP sample having the highest luminescence intensity. These materials are likely to have high efficiency of conversion in the LED and display industries without a significance changes in the crystal sizes within the various phosphor samples.

Keywords: CMC; phosphors; optical properties; PL; PVA; PVP; strontium aluminate.

1. INTRODUCTION

Photoluminescent material with long afterglow is a kind of energy storage material that can absorbs both ultraviolet (UV) and visible lights from sunlight, and gradually releases the energy in the dark at a certain wavelength. These sorts of materials have great potential for various device applications and have been widely studied by many researchers [1].

Phosphorescence, called afterglow, refers to a luminescence with delayed radiative return that is caused by the trapping of photo-generated electrons and/or holes at intrinsic or extrinsic defect sites of the material [2,3]; hence, when freed by thermal energy, these trapped charge carriers recombine at the ionized luminescent centers. Phosphorescence in other words, is a thermoluminescence mechanism with detrapping at room temperature [4].

Strontium aluminate in recent years has attracted numerous researches globally due to their excellent properties like high quantum, efficiency, chemical and thermal stability and long persistence of phosphorescence [5].

Strontium Aluminate phosphors doped with rare earth metal ions have emerged as materials with great potential especially europium ion [6]. The mechanism of photoluminescence properties appears to depend mainly on the doping elements [7]. The rare earth metal europium has a strong red emission when doped in different matrices [8,9,10] the prominent is 612 nm arising from electric dipole moment allowed transition [11].

The intensity and duration of the phosphoresce of $SrAl_2O_4$ (especially Eu^{2+} , Dy^{3+} doped) makes it possible to envisage a continuous light emission; the materials with larger size are prepared using solid-state reaction techniques [2,12].

To obtain much smaller particles, larger phosphor particles need to be further grinded, but this can introduce additional defects easily, hence luminescence efficiency reduction [3]. Different synthetic routes are employed to achieve high purity, homogenous single phase, thermally stable and radiation resistant fine particle powders [13]. The light output is affected by particle size distribution as well as the particle shape [14].

Since nanoparticles have extremely high tendency of adhesion and high level of

aggregation, it is of great importance to develop relevant techniques to control the dispersive/ aggregation phenomena of nanoparticle to apply them into materials that are functional; Hence the choice of suitable passivizing agents (PVP, PVA and CMC) which has been capped with ZnS and ZnO majorly but less attention of it function was given to capping it with SrAl₂O₄:Eu³⁺ phosphor.

Newer technologies developed to solve this challenge include, reverse micro emulsion [6], combustion technique [15], sol-gel and coprecipitation were employed to prepare $SrAl_2O_4$ phosphors. The importance of these research findings involving different polymers as passivizing agents on $SrAl_2O_4$:Eu³⁺ phosphor was to verify their influence on the crystals sizes and luminescence emission characteristics at the excitation of 285 nm.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of SrAl₂O₄:Eu³⁺-(PVP; CMC; PVA) Phosphors

SrAl₂O₄:Eu³⁺ passivized by PVP, CMC and PVA were synthesized by direct combustion technique grade of using analytical $Sr(NO_3)_2$ Al(NO₃)₃.9H₂O, EuCl₂.6H₂O and CH₄N₂O as a starting materials. Stoichiometric amount of starting materials was dissolved in 5 mL of deionised water, stirred continuously for 20 mins until clear solution was obtained. The doping concentration of Eu³⁺ ions was 0.2 mol %. This solution was kept aside and labeled Sol A. In another section, 0.3 M of PVP or CMC or PVA was dissolved in 5 mL of de-ionised water and rigorously stirred until clear solution was formed, this solution was also kept aside and labeled Sol B. Sol A and Sol B were added together, mixed, stirred on a magnetic stirrer for 30 mins till clear solution of the precursors was formed. The mixed solution was oven dried at 80°C for 20 hrs. The fluffy form of material obtained after cooling (Fig. 1b) was crushed and 0.309 g of H₃BO₃ was added as a reflux [16] and further annealed at 1000℃ for 2 hrs. Fig. 1b photographer was obtained under the same condition (same order of preparation, calcination temperature & time, and characterization). Within few minutes, reaction starts giving vellowish flame, this continues for few seconds and it is over. The mixture froths and swells forming foams, which rupture with a flame and glows to incandescence. The white powder obtained was crushed into powder for characterizations. A flow diagram describing the preparation is shown in Fig. 1a.



Fig. 1. Schematic diagram showing synthesis of SrAl₂O₄:Eu³⁺-(PVP; PVA; CMC) phosphors

The phase identification of synthesized powder samples was carried out using X'PertPro, PANalytical XRD spectrometer (CuK α :1.541Å) at 40 kv, 40 mA and a scan rate of 0.02°/_c in the 2 hours range from 10° to 70° for the verification of the crystal stru cture and the average size of the particles at Sheda Science and Technology Complex, Abuja-Nigeria. The photoluminescence emission and excitation measurement was done using Photoluminescence Spectrometer, Perkin-Elmer LS-55 Fluorescence at CSIR Pretoria, South Africa.

 $2\text{Al}(\text{NO}_3)_3. \ 9\text{H}_2\text{O} + \text{Sr}(\text{NO}_3)_2 + 6\text{CO}(\text{NH}_2)_2 \rightarrow \text{SrAl}_2\text{O}_4 + 16\text{O}_2 + 20 \ \text{NH}_3 + 6\text{CO}_2$

3. RESULTS AND DISCUSSION

$$d = \frac{0.897}{B \cos \theta}$$

3.1 Crystallinity of the Samples

Fig. 2 illustrates the combined X-Ray Diffraction (XRD) patterns of the different passivized strontium aluminate samples. Sample(s) was ground to fine powder, and powder X-ray diffraction was taken with X'PertPro, PANalytical made in Netherland XRD with CuK α (1.541Å) radiation. All the peaks could be indexed to orthorhombic phase of strontium aluminate [15,16]. The XRD pattern of PVP passivized nanoparticles has reflection of (021), (121), (211) and (311) planes [15]. The reflection planes for CMC and PVA are (210), (211), (112), (113).

The average grain size of the powder was estimated using the Scherrer's formula:

where

d is the average grain size,

 λ is the wavelength of Cu K α (λ =0.154056 nm),

 β is the full width at half maximum intensity (FWHM),

And θ is the Bragg's angle. All conversion was done in radian.

The grain size calculated from Sherrer formula was 42.01 nm, 41.45 nm and 38.64 nm for PVP, PVA and CMC respectively agreed with that by Nathan et al. [15].

3.2 Luminescence Studies

Fig. 3 shows emission spectra of the three samples under consideration synthesized by direct chemical combustion techniques. The emission characteristics were recorded at 285 nm wavelength excitation. Five observed emission peaks associated to PVP are 541 nm, 592 nm, 648 nm, 674 nm, and 712 nm basically within the yellow-red colour band. Sample passivized by PVA shows broad emission at 648 nm and 699 nm; CMC passivized sample only has a broad emission peak at 648 nm. The intensity of PVP at 648 nm peak relative to the others at that emission wavelength is the highest

[15]. PVP sample which has the highest crystal size of 40 nm also gave the highest luminescence intensity, indicating it's more luminous for LED and other display usage under the said conditions.

These PL spectra results confirmed the incorporation of europium in the strontium aluminate lattice within the +3 state. Eu³⁺ transition are given by ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J=0,1,2,3,4) are undoubtedly pronounced in these spectra¹⁷ but these relative intensities of Eu³⁺ transition varied from sample to sample. The emission peak at 648 nm which is the major peak in these spectral, ascribed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transition,



Fig. 2. XRD of SrAl₂O4:Eu³⁺-(PVP; CMC; PVA) sample prepared by chemical combustion reaction



Fig. 3. PL emission spectra (λ_{Exc} 285 nm) of polymer passivized strontium aluminate synthesized through combustion techniques and annealed at 1000°C

which operates by electric dipole interaction [18]. The other peaks at 541 nm and 590 nm $({}^{5}D_{1} \rightarrow {}^{7}F_{1})$ having a very weak intensity sensitive to ligand environment of the magnetic dipole; 674nm, 699 nm and 712 nm $({}^{5}D_{0} \rightarrow {}^{7}F_{4})$ are electric dipole transition [18,19].

The trivalent europium ion is non-degenerate ground state ${}^{7}F_{0}$ and non-overlapping ${}^{2S+1}L_{J}$ multiplets [20]. These emission wavelengths are all in the red light region. The crystal fields are affected by these transitions.

4. CONCLUSION

Trivalent Europium activated polymer passivized Strontium Aluminate nanoparticle having ~39.00 nm -42.00 nm crystal size was successfully prepared by direct combustion methods. These exhibit broad emission bands at 648 nm with PVP having the highest luminescence intensity. These materials are likely to have a high efficiency of conversion in the LED and display industries.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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