THE EFFECT OF EXCITATION WAVELENGTHS ON THE EMISSION SPECTRUM OF $SrAl_2O_4:Eu^{3+}$ NANOPARTICLES

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Abstract

The effect of photoluminescence excitation wavelength on the intensity distribution of the luminescence peaks of the strontium aluminate in solution-combustion technique and calcined at 1000^{O}C for 2hrs was investigated. The photoluminescence spectral shows several emission wavelengths at various excitations (ranging from 285nm to 468nm) under same condition of phosphor preparation. All excited wavelength produces emission spectrum within the blue colour range majorly except for excitation wavelength of 365nm, 345nm and 320nm which produced Cyan colour. Only excitation of 385nm and 285nm produced the highest emission wavelength of 693nm and 652nm respectively at the red colour range, hence these excitation wavelength are recommended for LED and displayed unit material. At 468nm and 385nm excitation, green colour was observed. The general emissions observed were attributed to the dependent of intermolecular reaction on the excitation wavelength.

Keywords: *Strontium Aluminate, Excitation, Emission, Wavelengths, Photoluminescence.*

1. INTRODUCTION

Florescence and phosphorescence luminescence are fascinating optical phenomena that drew attention of many materials researcher and optical scientist globally[1,2,3,4].The puzzle/mystery associated with persistent luminescence phenomenon remains unsolved over time as no clear explanation to it mechanism still remain. The luminescence of lanthanide ions has a large technological importance in a variety of materials like phosphor lamps, displays, laser and optical amplifiers.

Trivalent Europium as also applied to the case of many lanthanides ions are known for their special optical properties resulting from the fact that the electrons of the partially filled 4f-shell are often shielded completely from the surrounding filled 5S and 5P shells. Electric dipole transitions are forbidden because energy levels of the 4f-shell have equal parity. An outer electronic configuration $5S^2\ 5P^6\ 4f^n$, where n varies from 1 (Eu^{3+}) in trivalent lanthanides ions indicating the number of electrons in the 4f-shell unfilled.The optical transitions are caused by the valence electrons of $4f^n$.Valence shell of atom made up of the 4f 5d and 6S electron are chemically similar elements[5]. The crystal field has almost no effect on the $4f^n$ energy due to the effective shielding of the 4f electron.Figure 1 shows the energy levels diagram of trivalent lanthanides ions.

1.1 Theory

A spectrum is an assembly of energy levels in the form of radiation emitted by an atom in its excited state. Each electron in an atom has a definite minimum energy required to get excited, which is called the threshold energy or work function or ionization energy. Each line in the spectrum corresponds to a specific wavelength and it is unique to a given element. The spectrum obtained from white light shows seven different colours; each colour in the spectrum is associated with a certain wavelength i.e. when an atom get excited, it emits light of certain wavelengths which correspond to the different colours. For the transition of electron from lower energy level to higherenergy level, it absorbs some amount of energy in the form of radiation.

Excitation is the process of an electron in an atom absorbing a photon, hence, after absorbing a photon the electron/atom is said to be excited. Electron in this excited state is not stable, it radiates some amount of energy in the form of radiation and return to the ground state (electron occupy its lowest energy level). The energy of an electron in a certain energy level is expressed as:

$$E_n = -R_H/n^2 \qquad 1$$

Where, R_H= Rydberg constant, n= Energy level of the electron.

In transition of electron, the photon energy is given as:

$$E_{photon} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad 2$$

Where, n_i is Initial energy level of the electron, and n_f is the final energy level of the electron. But energy is always proportional to the frequency of the emitted photon, therefore,

$$v_{photon} = (E_i - E_f)/h \qquad 3$$

Where, E_i is the initial energy of the electron, E_f is the final energy of the electron and h the Planck constant.

Emission spectrum is when an electron of an atom emits radiation while returning from excited state to its original state and is recorded on a spectrometer.

The objective of this work was to find out the effect of different excitation wavelength on a single phosphor sample towards the emission of various colours.

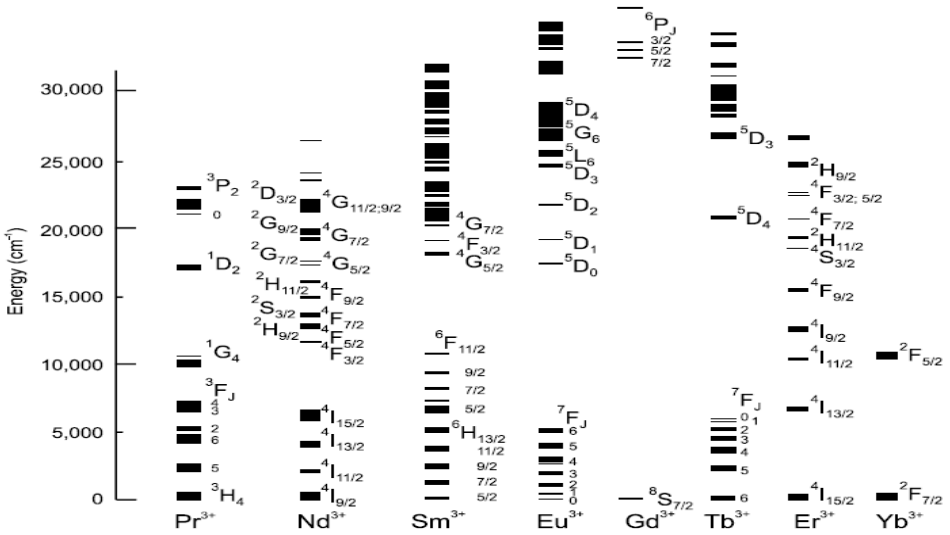

Fig.1. $4f^n$ Energy levels diagram of trivalent lanthanides ions culled from reference 12 and 13

2. EXPERIMENTAL DETAILS

Eu^{3+}-doped $SrAl_2O_4$ was synthesized by a solution combustion method using $Sr(NO_3)_2$(Kermel), $EuCl_2.6H_2O$ (Sigma-Aldrich),$Al(NO_3)_3.9H_2O$ (Sigma-Aldrich), H_3BO_3 and CH_4N_2S as starting materials, these were dissolved in deionised water and stirred well for 30 minutes at a temperature of 80°C on a magnetic stirrer. The quantities of the various precursors $Sr_{1-x}Eu_xAl_2O_4$ (where x=0.02g), 2g of $Al(NO_3)_3{\cdot}9H_2O$, 0.98g $Sr(NO_3)_2$; 3.90g CH_4N_2S and 0.02g $EuCl_2.6H_2O$were taken. The formed nanoparticles solution was oven dried at 90°C for 24hrs. The dried sample was then poured into a crucible;the crucible containing the paster was introduced into a muffle furnace maintained at 1000°C for 2hrs, and allowed to cool gradually.The obtained phosphor was then characterized using Scanning Electron microscopy, X-ray Diffraction, and Photoluminescence studies.

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM) and EDS result

The surface morphology of the sample was studied using PhenomProX-Scanning Electron Microscopy (SEM) and EDSanalyserat Chemical Engineering Department A.B.U. Zaria Nigeria. The particles are agglomerated with irregular size distribution, fig 2a, while the elemental composition analysis using energy dispersive X-rays spectroscopy (EDS) shows the presence of Strontium, Aluminium and Europium Fig. 2b; indicating that the synthesized $SrAl_2O^4$:Eu^{3+}nanophosphors are sulphur and nitrogen deficient.

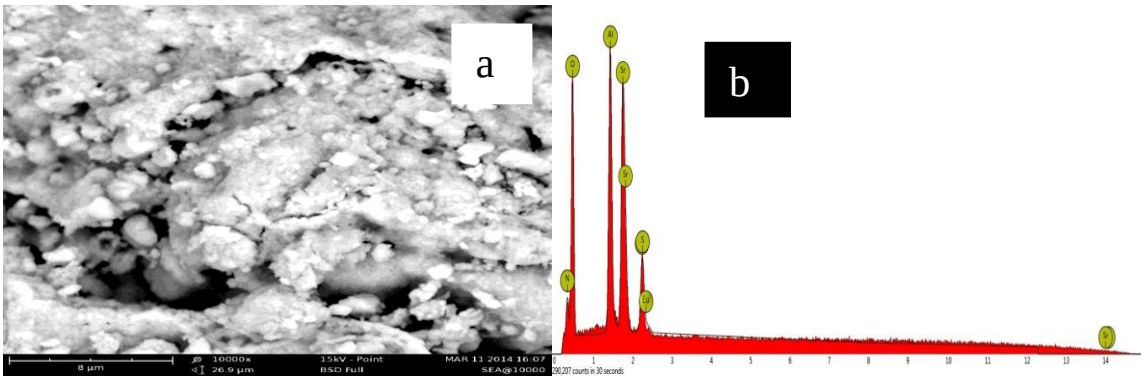

Fig. 2: SEM/EDS micrograph of SAE

3.2 Structural Studies

X-rays diffraction in crystalline solid takes place because the atomic spacing is in the 10^{-10m} range .i.e. the wavelength[6]. The energy E of an X-ray photon is related by the equation 1 below where h the Planck's constant and v the frequency.

$$E = hv \qquad 4$$

W.L. Braggs developed a simple way to understanding and predicting diffraction phenomenon from crystal[7];

$$2dSin\theta = n\lambda \qquad 5$$

The X-ray diffraction pattern of the sample is shown in Figure 3. The five diffraction peaks in the sample match well with those of the Monoclinic Al_2O_4Sr reported in ICCD powder diffraction file No. 00-034-0379. Five diffraction peaks at 2θvalues of about 19.45, 28.36, 29.49, 29.47 and 36.52 correspond to (-220), (-321), (330), (510) and (141) lattice planes respectively. Impurity peaks such as Eu^{3+} ions was detected. The mean crystalline sizes were calculated from the full-width at half-maximum (FWHM) of the five prominent peaks in the XRD pattern using the Debye Scherrer formula.

$$D = \frac{0.94\lambda}{\beta cos\theta} \qquad 6$$

where, $D$is the crystallite size, $\lambda$is the wavelength of X-ray, $\beta$is the FWHM and θ is the Bragg's angle. The result of crystallite sizes calculated from XRD patterns using Scherrer's equation is presented in Table 1. From the result, the average crystallite size of the nanoparticles is in the strong quantum confinement regime.

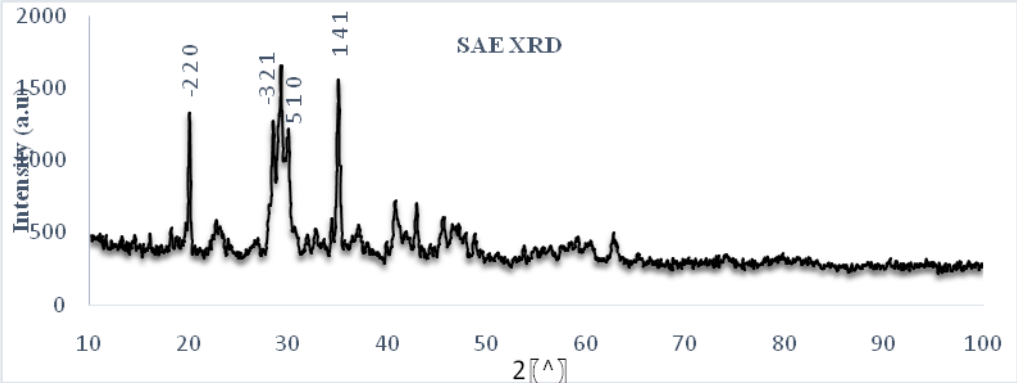

Fig. 3.XRD pattern of $SrAl_2O_4:Eu^{3+}$

Using Sherrer's equation, the calculated average crystal size is presented below:

Table 1. Crystallites size calculated from the XRD

SAMPLE	OBSERVED $2\theta^0$	MACHINE $2\theta^0$	h k l	FWHM β^0	CRYSTAL SIZE (nm)	AVERAGE CRYSTAL SIZE (nm)
SAE	19.966 28.408 29.941 29.949 35.041	19.451	-2 2 0	0.1978	39.71283888	35.74
		28.364	-3 2 1	0.1978	39.71302705	
		29.495	3 3 0	0.1978	39.71305050	
		29.475	5 1 0	0.2637	29.78911586	
		36.527	1 4 1	0.2637	29.78923013	

3.3 Photoluminescence Studies

When an atom or an ion undergoes a transition from a higher energy state to a lower energy state the difference in the energies of the two states is given out as a photon. When the transition occurs in the

outermost states of the atom, the ones that are split due to LS coupling, and the photon that is given out is in the visible range of the electromagnetic spectrum. It is called an optical transition as the photon given out is in the visible range of the electromagnetic spectrum.[8,9,10,11]

Infig 4, the peaks at 320-347nm from 285nm excitation are assigned to the band edge excitation of $SrAl_2O_4$nanocrystals, since Eu^{3+} has negligible excitation cross-section at 347nm,[14] these results in weak peaks which causes the emissions of the red light associated to intra configuration of Eu^{3+} at 612nm, 613nm ($^5D_0 \rightarrow {}^7F_2$) also to be weak. The broad emission peak at 481nm from excitation wavelength of 468nm with the highest PL intensity (21754500a.u) is associated to aluminate vacancy.

Upon excitation at 468nm, 385nm, 345nm, 330nm, the emission spectrum was predominantly dominated by ($^5D_1 \rightarrow {}^7F_1$); also at 385nm, 365nm, 285nm emission wavelength yield ($^5D_0 \rightarrow {}^7F_2$), ($^5D_0 \rightarrow {}^7F_3$), ($^5D_0 \rightarrow {}^7F_4$) all associated to Eu^{3+} ions. The presence of high intensity of the hypersensitive electric dipole transitions ($^5D_0 \rightarrow {}^7F_2$), ($^5D_0 \rightarrow {}^7F_3$) and ($^5D_0 \rightarrow {}^7F_4$) indicates low symmetry of the Eu^{3+} ions sites.[15] It is clear from fig.4 (385nm, 285nm) that the intensity of red light emission is dependent on the Eu^{3+} ions excited wavelength. Excitation wavelength of 285nm sample is found to be the best red light emitter with the highest intensity.

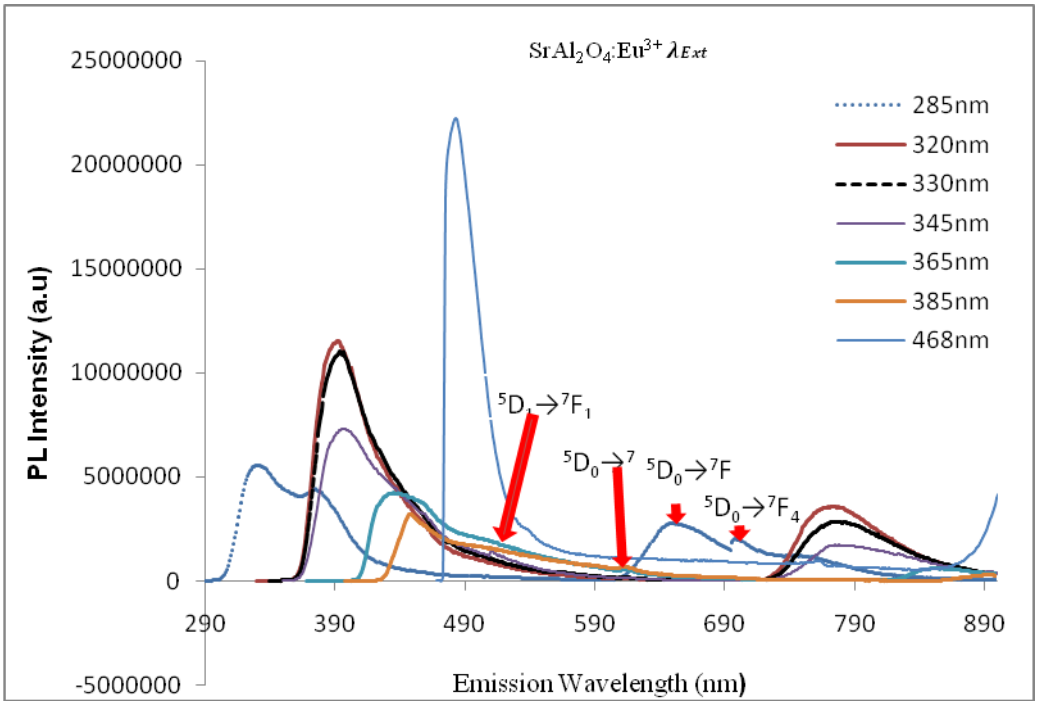

Fig.4 PL Spectrums of the various excitation wavelengths

TALBE 1 PL Emission Wavelength at Different Excitations from Fig. 4

Sample	Excitation (nm)	Emission (nm)	Colour	PL intensity (a.u)	Frequency intensity

SAE	**468**	***484***	Blue	21 754 500	750-670THZ
		541	Green		
	385	***450***	Blue	3 173 700	670-610THZ
		491	Cyan		
		534	Green		
		612	Orange		
		693	Red		
	365	***441***	Violet	4 208 700	610-580THZ
		613	Orange		
	345	***398***		7 224 400	580-540THZ
		513	Green		
	330	***392***		10 884 000	540-510THZ
		474	Blue		
		480	Blue		
		562	Yellow		
	320	***394***		1 1451 800	510-480THZ
		402	Violet		
		437	Violet		
	285	***335***			
		372			
		450	Blue	5 539 600	480-430THZ
		649	Red		

TALBE 2 Major characteristics of Eu^{3+} Transition

Sample	**Excitation (nm)**	**Spectral Region (nm)**	**Transitions**	**Relative intensity**	**Remarks**
SAE	**468**	***484***		Nt.Eu.Trans	
		541	$^5D_1 \rightarrow {}^7F_1$	Very weak	Int.Sen. L.E
	385	***450***		Nt.Eu.Trans	
		491		Nt.Eu.Trans	
		534	$^5D_1 \rightarrow {}^7F_1$	Very weak	Int. Sen. L.E
		612	$^5D_0 \rightarrow {}^7F_2$	Very Strong	Elect Dip. Tra
		693	$^5D_0 \rightarrow {}^7F_4$	Medium Strong	Elect Dip. Tra
	365	***441***		Nt.Eu.Trans	
		613	$^5D_0 \rightarrow {}^7F_2$	Very Strong	Elect Dip. Tra
	345	***398***		Nt.Eu.Trans	
		513	$^5D_1 \rightarrow {}^7F_1$	Very Weak	Int. Sen. L.E
	330	***392***		Nt.Eu.Trans	
		474		Nt.Eu.Trans	
		480		Nt.Eu.Trans	
		540	$^5D_1 \rightarrow {}^7F_1$	Very Weak	Int. Sen. L.E
	320	***394***		Nt.Eu.Trans	
		402		Nt.Eu.Trans	
		437		Nt.Eu.Trans	
	285	***335***		Nt.Eu.Trans	
		372		Nt.Eu.Trans	

450		Nt.Eu.Trans	
649	$^5D_0 \rightarrow {}^7F_3$	Strong	Str. Mag. Dip. Tra

* Elect Dip. Tra = Electric dipole transition
* Nt.Eu.Trans = Not Europium Transition
* Int. Sen. L.E = Intensity sensitive to ligand environment
* Str. Mag. Dip. Tra = Strong magnetic dipole transition

4. CONCLUSION

The synthesis of Eu^{3+}-doped $SrAl_2O_4$ nanoparticles whose dimensions are comparable to the exciton Bohr radius of $SrAl_2O_4$ was successfully carried out. The photoluminescence (PL) spectra of $SrAl_2O_4:Eu^{3+}$ nanoparticles have been measured using a Xenon lamp source spectrophotometer of an excitation wavelength 285nm, 320nm, 330nm, 345nm, 365nm, 395nm and 468nm.The wavelengths produced depend on the internal crystal structure of the material. The glow intensity depend on the particles size.[3] The report of this work clearly showed that photoluminescence intensity with the excitation wavelength of 285nm and 385nm has the better red colour emission intensities of 649nm and 693nm respectively; 618nm for orange, 520nm for green, and 450nm for blue colours. Exciting $SrAl_2O_4:Eu^{3+}$ phosphor at 385nm and 330nm give more emission of various colour bands. The desired colours from these results will be determined by the wavelength to be excited. There is clear evidence that energy transfer from the $SrAl_2O_4$ host to Eu^{3+}, though the emission intensity is weak.

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