International Journal of Luminescence and applications
Vol6 (4) January, 2017, **ISSN 2277 – 6362**

Novel photoluminescent behavior of Gd^{3+} ion in LAG host phosphor Prepared via solid state reaction method

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Abstract -- The present paper reports on the synthesis, characterization and photoluminescent studies of LAG host and Eu^{3+} doped LAG phosphors. LAG stands for ($La_2Al_2Gd_2O_9$). As per the reported literature, the possible PL emission peak of Gd^{3+} ion, in most host lattices is at 316nm wavelength (UV region) and in the few host lattices is around blue region also. But we observed for the first time and reporting the novel photoluminescent behavior of Gd^{3+} ion, from UV- red region in the LAG host phosphor. The Gd^{3+} rare earth ion emissions are observed from UV – red region under 254 and 275nm excitation wavelengths. In order to understand these emissions, we doped with the Eu^{3+} ion in the host lattice at 0.1, 0.2, 0.5, 1.0, 1.5 and 2.0 mol% concentrations. The phosphors were synthesized using the standard solid state reaction technique. To enlarge the fundamental understanding of the phosphors was done by PL, XRD, SEM, FTIR and CIE are determined.

Keywords: Photoluminescence, wavelength, phosphor, doping, host lattice, novel

1. INTRODUCTION

Lanthanide compounds have attracted much attention in the field of luminescence spectroscopy. The excited state behavior of lanthanide ions Ln^{3+} have been investigated extensively [1–6]. The electronic spectra of Ln^{3+} with f^n (n=1-13) electron configuration are dominated by electronic transitions between f-orbitals. Transitions between f-orbitals of Ln^{3+} are strictly parity forbidden. In addition, many f-f transitions are also spin forbidden although spin orbit coupling facilitates a mixing with spin allowed transitions. Light absorption by Ln(III) complexes can be enhanced by suitable ligands which transfer the excitation energy to emissive Ln^{3+} ions.

However, the f-f states of Gd^{3+} are located at exceptionally high energies owing to the extreme stability of its half-filled f-shell (f7). The emission line appears at 312nm is assigned to lowest energy f-f transition. Accordingly, Gd complexes are frequently characterized by emissive intra-ligand (IL) states at lower energies. Owing to its heavy atom effect and para-magnetism, Gd^{3+} induces a strong singlet/triplet mixing in the ligands [7]. It follows that the IL fluorescence is largely quenched while the IL phosphorescence is facilitated [8–11]. It follows those IL triplets of gadolinium complexes may generally emit under ambient conditions. We explored this possibility in the LAG phosphor.

The ligands were chosen according to different emission colours (UV, blue, green and red) of the gadolinium complexes. Various applications are conceivable. For example, triplet emissions under ambient conditions could be utilized in light emitting diodes (LED) and sensor technology. The first reported white light LEDs were based on blue InGaN technology, which uses a combination of blue emission from a blue LED and yellow from YAG:Ce^{3+} phosphor coated. Then uses a combination of blue emission from a blue LED and yellow from YAG:Ce^{3+} phosphor and red from Y_2O_3:Eu^{3+}emissions.

In view of YAG and TAG phosphors we thought to synthesize this new LAG phosphor for the first time using solid state reaction method and studied its characterization and luminescent properties in detail.

2. EXPERIMENTAL

The inorganic compounds like La_2O_3, Al_2O_3 and Gd_2O_3 of purity (99.9%) were used as starting materials for the host $La_2Al_2Gd_2O_9$ (LAG) phosphor. All the compounds was weighed, added

International Journal of Luminescence and applications
Vol6 (4) January, 2017, **ISSN 2277 – 6362**

in appropriate proportions and grounded into a fine powder using agate mortar and pestle about an hour. The grounded phosphors were placed in an alumina crucible and heated in air atmosphere at 1200°C for 2 hours in a muffle furnace with a heating rate of 5ºC/min.

In the same way LAG:Eu^{3+} phosphors was synthesized in order to analyze the dopant nature i.e. the effect of concentration and its emission lines in the host phosphor. Europium oxide Eu_2O_3 is used as activator ion at different concentration (0.1, 0.2, 0.5, 1.0, 1.5 and 2.0 mol%). The phosphors was again ground into powder after cooling and done the following characterizations.

The phosphors were characterized by the photoluminescence emission and excitation spectra using (SHIMADZU, model RF-5301 PC) Spectrofluorophotometer using xenon lamp as excitation source. The incident beam was perpendicular to the surface of the sample, and the observation angle was 45º relative to the excitation source. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm. X-ray diffraction (XRD) studied using Rigaku-D/max 2500 using Cu Kα (1.54) radiation at a scanning step of 0.02 degree, continue time 20s, in the 2θ range from 15^0 to 60^0. The microstructures of the phosphors were studied using a scanning electron microscopy (SEM) XL 30 CP Philips. The FTIR studied using an FTIR spectrometer (Perkin Elmer-Spectrum 100) in the range from 500 to 4000cm^{-1}.

3. RESULTS AND DISCUSSIONS

3.1 Photoluminescence excitation study

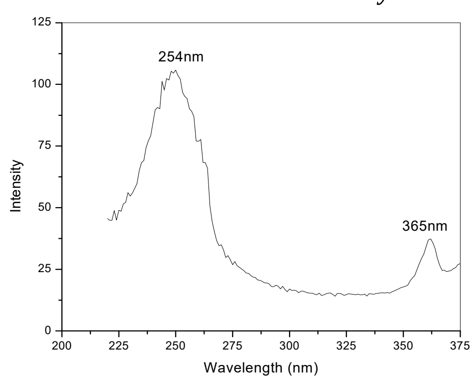


Fig.1a

Fig.1a & b are the excitation spectrums of LAG host phosphor monitored under 400 and 625nm wavelength respectively. The excitation spectrum was characterized by single band. The band was ranging from 220-275nm with peak at 254nm, the second small band at 365nm is assigned to crystal field.

Fig.1b is the excitation spectrum of LAG host phosphor monitored under 617nm wavelength. The excitation spectrum was characterized by two sharp bands. The band was ranging from 220-325nm with peak at 254nm, and 275nm.

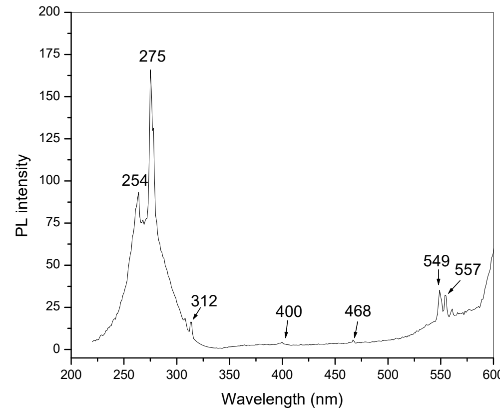


Fig.1b
Excitation spectrums of LAG host phosphor monitered under a) 400nm b) 617nm wavelength

The second sharp band is stronger than first band. It is observed that the excitation is different and intensity is also high when compared with the fig.1 spectrum. The excitation spectra of LAG host monitored under 625nm wavelength may be divided in to two regions (1) the intense broad band centered at 254nm and 275nm were attributed to two types of charge – transfer (CT) transitions i.e. between Al^{3+}– O^{2-} ($^3p_1 \rightarrow ^2p_4$) and Gd^{3+}– O^{2-} ($^5d_1 \rightarrow ^2p_4$). (2) In the range from 380 to 600nm, it shows the characteristic intra configuration 4f – 4f transitions.

3.2 Photoluminescence emission study

Basing on the excitation study it is decided to measure the emission spectrum under 254 and 275nm excitation wavelengths.

Fig.2 shows the emission spectrum of LAG host phosphor. Curve 1 shows the emission under 254nm excitation and curve 2 shows the emission under 275nm excitation. The emission spectrum consists of several sharp peaks in the range from 350 – 650nm. The peaks are at 365, 400, 420, 429, 448, 468, 495, 514, 540, 557, 592, 616 and 624nm. It is observed that under 254nm excitation due to the high crystal field at 365nm the emission peak intensities are decreased as the wavelength increases (curve 1) from 350 – 650nm. Whereas under 275nm excitation due to the less crystal field at 365nm the emission peak intensities are increased as the wavelength increases (curve 2) from 350 – 650nm. It clearly indicates that the crystal field playing an important role, one can get different emission colours from the phosphor by changing the excitation wavelength. The atomic radius of Al^{3+} is 1.82 Å, La^{3+} is 2.74 Å and Gd^{3+} is

2.56 Å, respectively. The molar mass weight of the synthesized phosphor is 790.269 g/mol and the elemental composition is as follows i.e. La=35.15%, Al=6.83%, Gd=39.80% and O=18.22%. In this composition it is observed that the Gd% is more than the La%.

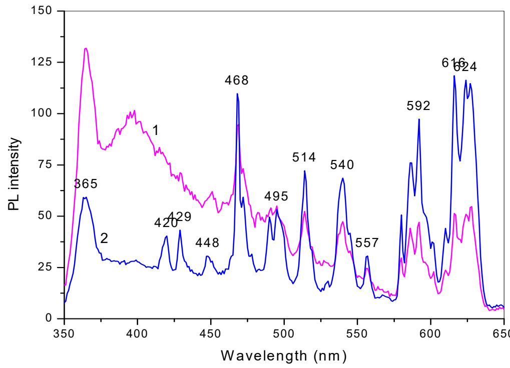


Fig.2

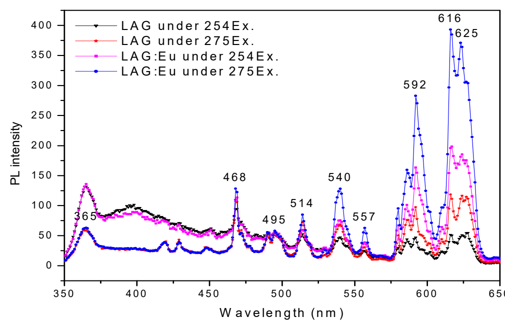


Fig.2a
Emission spectrum of LAG host phosphor under 254 & 275nm excitations

All these emissions are from the excited states of the seven excited electrons which are present in the outer most shell of the Gd ion only. However La ion is not responsible for these emissions since it is not having the free electrons.

Fig.3a & 3b shows the emission spectrums under 254 and 275nm excitations of Eu doped at different concentrations in the LAG phosphor. The emission spectrums consist of several sharp peaks in the range from 350 – 650nm as in the case of LAG host phosphor. The peaks are at 365, 400, 420, 429, 448, 468, 495, 514, 540, 557, 592, 616 and 624nm. It is observed that under 254nm excitation the high crystal field at 365nm when compared to 275nm excitation. Clearly we can conclude that under both the excitations the emission peaks are same except the intensities are changing. When the Eu ion doped in the host phosphor the emission intensity in the red band is almost doubled when compared with the host emission intensity under 254 excitation where as under 275nm excitation it is increased by 4 times. Obviously the charge is transferred from Gd to Eu ion. It is also observed that the emission intensity is high for 2mol% doped Eu ion in the visible band whereas 0.5mol% doped shows high intensity in the UV band.

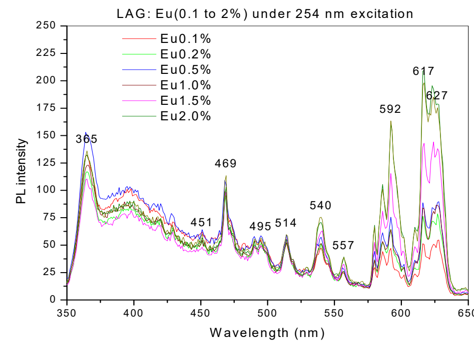


Fig.3a

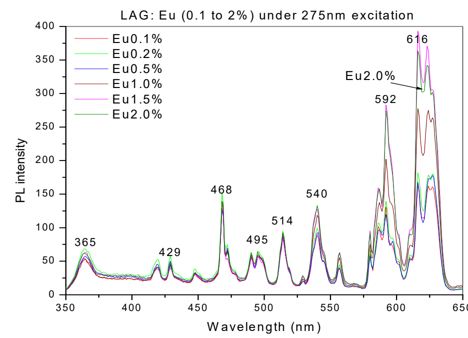


Fig.3b
Emission spectrum of LAG:Eu phosphor under a) 254 & b) 275nm excitations

3.3 X-Ray Diffraction Analysis

The typical XRD pattern of LAG phosphor without flux is shown in fig. 5. Fig.6 shows same pattern with high intensity LAG phosphor with flux. From the XRD pattern the narrow peaks indicates bigger the crystallite size and thereby bigger the particle size. The calculated crystallite size as 68.9nm and 41nm respectively, using Scherer's formula $D = K \lambda / \beta \cos\theta$ where k the constant (0.94), λ the wavelength of the X-ray (1.54 Å), β the full-width at half maxima (FWHM), θ the Bragg angle.

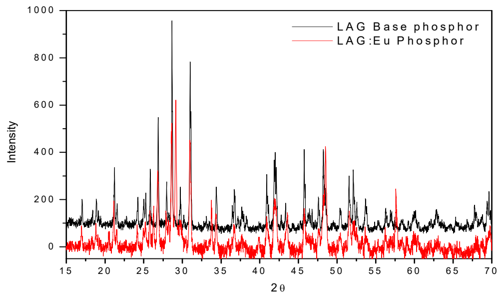


Fig.4 XRD patterns of a) LAG host phosphor b) LAG:Eu phosphor

3.4 SEM Analysis

Fig.5a & 5b shows the SEM micrographs of LAG host phosphor under different magnification for better understanding. The phosphor particles had non-spherical shape and the irregular shaped particles are highly agglomerated

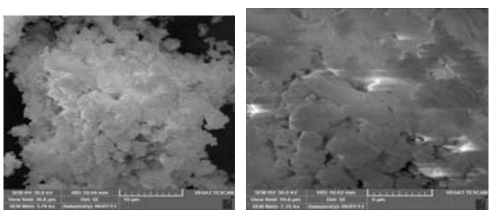
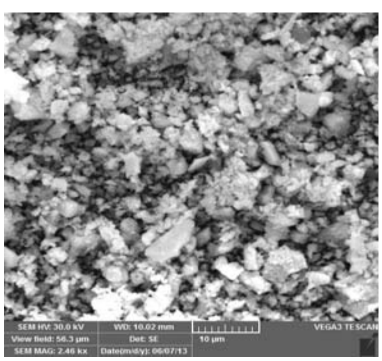


Fig.5a, Fig.5b
SEM micrographs of LAG host phosphor under different resolutions

Fig.6a & 6b shows the SEM micrographs of Eu doped LAG phosphor under different magnification for better understanding. The phosphor particles had nearly spherical shaped particles and are less agglomerated having an average basal diameter less than one micron to few microns.



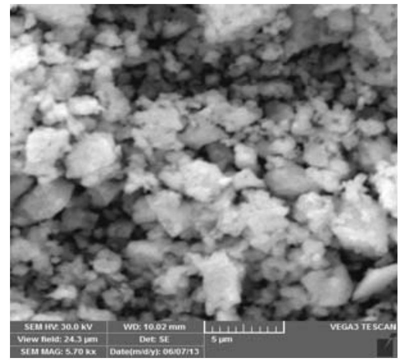


Fig.6a, Fig.6b
SEM micrographs of LAG: Eu phosphor under different resolutions

The LAG host phosphor particle sizes are bigger than that of Eu doped LAG phosphor. From the XRD pattern and calculated crystallite sizes confirms this. From the PL study it confirms that the bigger the particles size lesser the emission intensity and smaller the particles size higher the emission intensity. From SEM micrograph it is observed good particles having mostly diffreent shapes of varying sizes mostly agglomarated together are found.

3.5 FTIR Analysis

Fig.7a & 7b shows the FTIR graphs of LAG host and Eu doped LAG phosphor. From the figures the observed bands are at 3625, 2375, 1425, 850, 650, 500 cm^{-1}. From FTIR it is observed that most of the bonds are due to Gd-O, La-O and Al-O stretching and the O-H stretching band is observed at $3625 cm^{-1}$. The band around $3625 cm^{-1}$ is due to the H-OH stretching of absorbed water molecule from the atmosphere.

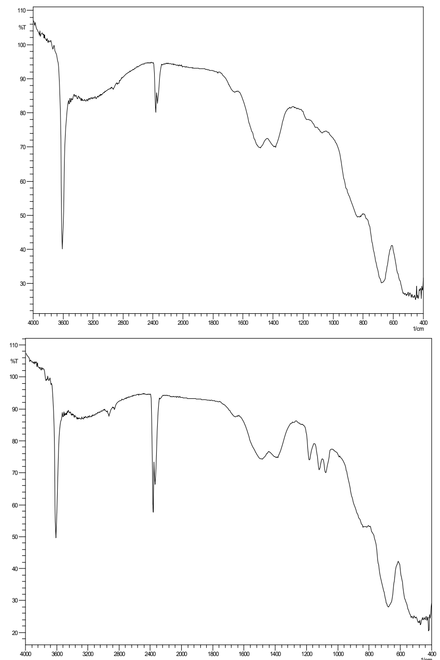


Fig.7a, Fig.7b
FTIR of a) LAG host phosphor b) LAG: Eu phosphor

3.6 CIE analysis

Fig.8 shows the CIE diagram of LAG phosphor Fig.5.13 shows the CIE colour co-ordinates of the Eu (2%) doped LAG phosphor under 254 and 275nm excitation wavelength. The colour co-ordinates of the Eu doped LAG phosphor under 254nm and 275nm are x=0.490, y=0.317 and x=0.571, y=0.348. From the figure the phosphors emitting red colour and are useful in producing white light in the field of lamps and display devices. The calculated correlated colour temperature (CCT) of 254nm excited phosphor is 1692K whereas the CCT of 275nm excited phosphor undefined.

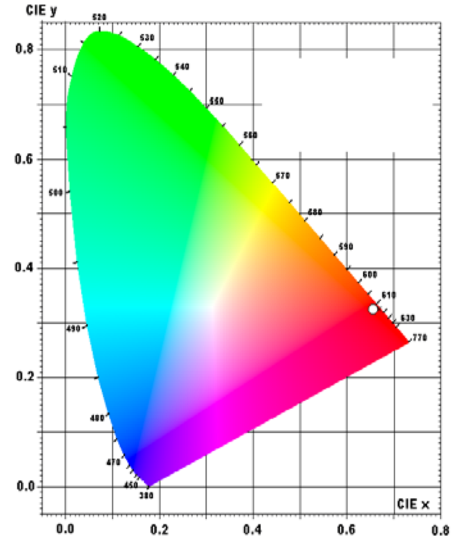


Fig.8
CIE co-ordinates of LAG host & LAG: Eu phosphor

CONCLUSIONS

The Eu^{3+} doped LAG ($La_2Al_2Gd_2O_9$) phosphor is successfully synthesized. The emission spectrum of Eu^{3+} doped LAG phosphors under 254nm excitation consists of several sharp peaks in the range from 350 – 650nm. The peaks are at 365, 400, 420, 429, 448, 468, 495, 514, 540, 557, 592, 617 and 627nm with good intensity. These emissions were assigned to the Gd^{3+} - O^{2-} and Eu^{3+} - O^{2-} bonds stretching's and the emission arises from the un paired electrons in the 4f orbit in Eu^{3+} and seven electrons in Gd^{3+} which are behaving in such a way to tune them self gives rise the combined luminescence leading to generation of near white light from single host which is Eu^{3+} doped LAG ($La_2Al_2Gd_2O_9$) phosphor. The orange – red emission under 592 - 616nm dominates in $La_2Al_2Gd_2O_9$ [LAG] doped with Eu (0.2 -2.0%) when excited with 254 and 275nm.It is interesting to note here the emission around 365nm intensity is decreases as the Eu concentration increases in LAG which is allowing us to conclude the crystal field emission is reducing even the Eu concentration increases in LAG.

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