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Jisha P.K

PREFACE

Nanophosphors were inorganic materials generally doped with transition metal or rare earth ions that efficiently emit light under particle and photon excitation. Nano particles have been found to exhibit some difference in terms of electrical, optical and structural aspects as compared to the existing bulk and these features are the resultant of the quantum confinement effect, caused by an increase in the band gap due to decrease in the quantum allowed state and a high surface to volume ratio that improves the surface and interface effects. Rare earth (RE) ions are particularly effective as luminescent centres in various inorganic host lattices and characterized by partially filled 4f shell that is well shielded by $5s^2$ and $5p^6$ electrons hence, widely exploited to produce high quantum efficiency phosphors. Since, luminescent nanomaterials play an integral role in modern life, with wide applications ranging from cathode ray tube (CRT), high definition television (HDTV), flat panel displays (FPD), plasma display panels (PDP), fluorescent lamps, lighting, sensing, defence security ink applications to medical diagnostics (i.e. positron emission tomography scanners), forensic finger print and nuclear radiation detectors. Hence, it is very significant to explore the full potential of nanophosphor materials.

During past decade, field emission display (FED) has attracted much attention as the most promising flat panel display due to its potential to provide displays with the advantages of thin panel, quick response time, high brightness and contrast ratio, light weight, low power consumption and so on. Compared with the cathode ray tube (CRT), the FED can be operated at the lower excitation voltage (5 kV) and higher current density (10–100 mA/cm^2). Therefore, the phosphors for FED are required to have the properties of high luminescent efficiency and good stability at the low voltage electron excitation and high current density.

The initial phosphors were zinc sulphides (ZnS) doped with copper and later, manganese. Sulphide based phosphors faced a number of issues that significantly limited their application. They were chemically unstable due to the sulphide absorbing moisture from the surrounding environment to form sulphates, resulting in the destruction of the sulphide lattice and degrading their persistence properties will inhibit their potential applications. In the field of display, the pure and mixed oxide nanophosphors have received special attention owing to their high vacuum stability and absence of corrosive gas emission. Later, perovskite structured (ABO_3) materials play an important role for wide range of applications due to their special properties such as low coefficient of thermal expansion, good lattice coordinating, negligible loss at microwave frequencies, relatively high dielectric constant (~25), low leakage current density and good chemical stability.

Among ABO_3 structured materials, gadolinium aluminate (GAP) perovskite is found to be a phosphor host material used for various applications like monitor tube, colour television, fluoroscopic screens, luminescence phosphor, since it has high melting point, high thermal stability, chemically stabile, low thermal expansion, high thermal conductivity etc. Luminescence efficiency of these phosphors can be altered by changing the dopant concentration. Great improvements in luminescence efficiency of phosphors were observed by doping with even very small quantities of dopants/co-dopants. Currently, the research on efficient and inexpensive nanophosphors is a challenging problem for new luminescent materials. Use of those phosphor materials in light emitting diode (LEDs) was a major step in solid state lighting technology. However, white light emitting diodes (WLEDs) are consider to be the next generation lighting system because of their excellent properties such as high luminous efficiency, low power consumption, environmentally friendly features, reliability and long life.

$GdAlO_3$ was prepared using various wet and soft synthesis methods including solid state reaction, polymerized complex method, sol–gel process, EDTA gel route, co-precipitation method, pyrolysis using triethanolamine and solution combustion technique. However, solution combustion synthesis method has been developed and successfully used for the low temperature production of pure and doped aluminates nanoparticles from past few years. This method is most popular due to its simple experimental set up, provides molecular level of mixing, high degree of homogeneity, time saving, more economical, high yield, higher surface area and requires less temperature. In fact high purity and homogeneity are achieved at temperatures as low as 400 °C which cannot be done using conventional solid state method.

Chapter 1: It gives the overview of introduction, classification, properties, importance, various synthesis methods of nanophosphors. It also gives advantages of combustion synthesis over other synthesis techniques. It deals with types of luminescence, phosphors, variety of applications along with scope of the present work and review of literature.

Chapter 2: It deals with pure and RE^{3+} ions (RE^{3+} = Eu, Dy, Tb) and transition metal ion Co^{2+} doped $GdAlO_3$ nanophosphor prepared by solution combustion technique using laboratory prepared **Oxalyl di-hydrazide** (ODH) as a fuel. It also deals with principle and instruments used for characterization such as powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Visible spectrophotometer (DRS), electrochemical work station and photoluminescence (PL) technique.

Chapter 3: Deals with synthesis of different mol concentration of Eu^{3+} doped with $GdAlO_3$ nanophosphor using ODH as a fuel and the obtained sample was calcined at 1000 °C for 3h. The structural characterization was studied by powder X-ray diffraction (PXRD) and confirming single orthorhombic phase with Space Group: Pbnm (No. 62). The average crystallite size (D) was found to be in the range 20-40 nm using Scherer's method and W-H plots. FTIR studies confirm characteristic metal–oxygen (Gd– O or Al –O) stretching vibrations in the host matrix. SEM images clearly shows that, the powders show highly porous, agglomerates with an irregular morphology, large voids and cracks which is common in solution combustion prepared samples, TEM images shows particles were irregular shaped, highly dispersed and the average crystallite size was in comparison with PXRD results. The optical energy band gap of host $GdAlO_3$ and Eu^{3+} doped sample was found to be in the range 4.6–4.8 eV. The phosphor exhibits different PL emissions corresponding to $^5D_0 \rightarrow {}^7F_{j\ (j=0,1,2,3,4)}$ transitions and the transition at 612 nm ($^5D_0 \rightarrow {}^7F_2$) is found to be hypersensitive in nature resulting in a strong and red emission under NUV (395 nm) excitation with excellent colour purity of 98 %. The quantum efficiency (QE) was found to be ~ 63 %. The J–O parameters ($\Omega_2 > \Omega_4$) confirms the covalency existing between the Eu^{3+} ions and surrounding ligands. The CIE chromaticity co-ordinates (0.64628, 0.35338) for $GdAlO_3{:}Eu^{3+}$ (3 mol %) estimated using CIE 1931 diagram were nearer to NTSC standard values for red colour and corresponding CCT value was estimated to be 2418 K .

Chapter 4: The present chapter deals with the synthesis of various mol concentration of Dy^{3+} doped with $GdAlO_3$ nanophosphors using ODH as a fuel. Single orthorhombic crystallite with an average size of 25 nm was confirmed by PXRD. Rietveld refinement analysis was performed by using FULLPROF software. The GOF (goodness of fit) was found to be 0.75, confirming good fitting with experimental and theoretical plots. The optical energy band gap of host $GdAlO_3$ and Dy^{3+} (0.5 - 9 mol %) sample was found to be in the range 5.4–5.9 eV.

The emission spectra show, peaks centered at 480, 572 and 670 nm corresponding to transitions of $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue), $^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow) and $^4F_{9/2}\rightarrow{}^6H_{11/2}$ (red) respectively. The emission intensity decreases due to concentration quenching when the concentration is more than 1 mol % is may be due to dipole to dipole (d-d) interaction. J–O parameters here ($\Omega_2 > \Omega_4$) symmetry shows Dy^{3+} sites is distorted because of the sample size and high rigidity of the sample. The quantum efficiency (QE) of~ 64 % was observed in optimized $GdAlO_3:Dy^{3+}$ (1 mol %) sample. The CIE coordinates of all the samples falls in white region of the spectrum which indicates that the samples exhibit white light emission. Correlated color temperature (CCT) was observed to be around 6276 K comparing to sunshine temperature. It is quite useful for display applications.

Chapter 5: Deals with synthesis, characterization, PL and forensic finger print studies of $GdAlO_3:Tb^{3+}$ (1 -11 mol %) phosphors. PXRD confirmed Single orthorhombic phase and average crystallite size of 15-25 nm was calculated by Scherrer’s formula. The energy band gap value was found to decreases from 5.13 to 5.88 eV as the dopent concentration increases. Emission spectra show, the characteristic emission of Tb^{3+} ($^5D_4$-$^7F_{J=3,4,5}$) in $GdAlO_3:Tb^{3+}$ sample. The strongest emission cantered at 542 nm was due to $^5D_4$-$^7F_5$ transition of Tb^{3+} cations. The dipole–dipole interaction is the major mechanism for the concentration quenching of fluorescence emission of Tb^{3+} ions in $GdAlO_3$ phosphor. The green emission of these phosphors was confirmed by CIE diagram. The photographs of latent fingerprints on variety of surfaces were effectively detected by using $GdAlO_3:Tb^{3+}$ (3 mol %) nanophosphor. The fingerprint is well-defined in terms of finger ridge details without background staining, resulting in good contrast for enhanced detection.

Chapter 6: In this chapter synthesis of $GdAlO_3$ doped with Eu^{3+} and Co^{2+} as similar as the previous study such as Eu^{3+}, $Dy^{3+}$and Tb^{3+} doped $GdAlO_3$ was discussed. The electro chemical studies, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) by preparing carbon paste electrode were discussed in detail. The CV studies clearly indicated that 3 mol % cobalt doped $GdAlO_3$ sample shows greater reversibility by reducing the E_O-E_R value of the electrode reaction. EIS gives R_{Ct} and capacitance of the electrode was recognized by equivalent circuit of EIS spectrum. The impedance spectra of these electrodes show a depressed two dimensional figure ensuring charge transfer resistance within the high-frequency region, and a slope associated with Warburg resistance within the low frequency region. Spectra show electrochemical reaction on electrode 3 mol % of $Eu^{3+}$and Co^{2+}doped $GdAlO_3$ precedes a lot simpler than on electrode with other electrodes. Using the above results $GdAlO_3$:Eu^{3+}.CO^{2+}nanophosphor can be a potential candidate for electrical applications.

Chapter 7: It summarizes the results obtained in the present research work and the scope for the future work.

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Glossary of term

(GAP)$GdAlO_3$	Gadolinium Aluminate
ODH	Oxalyl di-hydrazide
SCS	Solution Combustion Synthesis
PXRD	Powder X-Ray diffraction
FWHM	Full Width Half Maximum
JCPDS	Joint Committee on Powder Diffraction Standards
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
EDAX	Energy dispersive X-ray analysis
EDS	Energy dispersion spectroscopy
HRTEM	High Resolution Transmission Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
DRS	Diffuse Reflectance Spectra
UV-VIS	Ultra violet visible spectroscopy
RE	Rare-earth
PLE	Photoluminescence Excitation
PL	Photoluminescence
ET	Energy transfer
CIE	Commission Internationale de l'Eclairage
CCT	Correlated color temperature
LED	Light emitting diode
WLED	White light emitting diode