Citrate mediated synthesis and tuning of luminescence in Eu$^{3+}$ incorporated Gd$_2$O$_3$ nanophosphors

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Citrate mediated synthesis and tuning of luminescence in Eu\(^{3+}\) incorporated Gd\(_2\)O\(_3\) nanophosphors

R G Abhilash Kumar and K G Gopchandran

Department of Optoelectronics, University of Kerala, Thiruvananthapuram – 695 581, Kerala, India

E-mail: gopchandran@yahoo.com

Abstract. Gd\(_{1.9}\)Eu\(_{0.1}\)O\(_3\) nanophosphors were prepared successfully by a large-scale facile solution based citrate-metal complex controlled combustion method and was systematically studied by varying the citric acid to metal cation ratio. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL) measurements and radiative properties were done to evaluate the crystal structure, phase formation, phase composition, surface morphology, radiative and luminescent properties of the prepared nanophosphors. Photoluminescent emission intensity of the samples can be correlated with the amount of citric acid, improved crystallinity, uniform morphology, particle size, reduced defects, and proper diffusion of Eu\(^{3+}\) in to the crystal structure of Gd\(_2\)O\(_3\). Higher asymmetry results in intense red emission (612 nm) due to \(^{5}D_{0}\text{–}^{7}F_{2}\) forced electric dipole transition and found that photoluminescence intensity is highest for the sample prepared with citric acid to metal cation ratio of 2:1. The existence of strong red emission from Gd\(_{1.9}\)Eu\(_{0.1}\)O\(_3\) nanophosphor corresponding to \(^{5}D_{0}\text{–}^{7}F_{2}\) transition (612 nm) of Eu\(^{3+}\) under UV light excitation make it a promising candidate for applications in bio assays, magnetic resonance imaging, deep uv LED’s, solid state lighting, fluorescent lamps and flat panel displays.

1. Introduction

Phosphors, especially rare earth ion doped nanophosphors have been widely used in display devices, optical fibers, solid state lighting, amplifiers and in medical fields as imaging, biolabels, immunoassays etc. because they posses excellent luminescent properties as a result of their inner shell electronic transitions between the 4f-4f energy levels. The f-f transitions of trivalent rare-earth ions (except Ce\(^{3+}\) ion) is forbidden by the parity selection rule, so the emission of trivalent rare-earth ions (except Ce\(^{3+}\) ion) doped phosphors yield sharp lines in the optical spectra and a good color rendering index [1]. The rare earth sesquioxide gadolinium oxide (Gd\(_2\)O\(_3\)) isostructural to Y\(_2\)O\(_3\) with high density (7.64 g/cm\(^3\)), superior chemical durability, superior colour purity, thermal stability, thermal conductivity and low phonon energy has been shown to be a good host for the luminescent rare earth ions and Eu\(^{3+}\) and Tb\(^{3+}\) ions are particularly used as efficient luminescent centres especially in display applications. Eu\(^{3+}\) doped Gd\(_2\)O\(_3\) nanocrystals have shown very rich luminescent features due to the possible paths of activating the trivalent rare-earth ion Eu\(^{3+}\) through different sensitization processes, viz. the host Gd\(_2\)O\(_3\) absorption, Eu-O charge transfer, the Gd\(^{3+}\) ion absorption, and the Eu\(^{3+}\) ion self-excitation. Due to a \(^{5}D_{0}\text{–}^{7}F_{2}\) transition within europium, Gd\(_2\)O\(_3\):Eu\(^{3+}\) shows red luminescence at 612 nm.

It should be noted that a morphology controlled synthesis by a single technique is of special importance, but remains as a challenge in the field of engineering of particles. The grain size, chemical homogeneity, morphology, agglomeration, and/or surface passivation are well-known factors which should influence phosphor efficiency [2]. Spherical shaped particles posses high packing fraction and also minimize light scattering for practical display applications. In the present study, we report a cost effective way to synthesis almost uniform spherical shaped Gd\(_{1.9}\)Eu\(_{0.1}\)O\(_3\) nanophosphors by a large-scale and facile solution based citrate-metal complex controlled combustion method and was systematically studied by varying citric acid to metal cation ratio. In this synthesis method, citric acid...
acts as a chelating agent of metal cations via the hydroxyl and carboxyl groups. Polymerizing ability of citric acid is effectively utilized for the formation of metal-citrate complex in diethylene glycol medium, where the metal ions are uniformly distributed. Apart from that, citric acid is also performed as a fuel and caused controlled exothermic reaction with nitrates to result in the formation of nanophosphors.

2. Experimental

Materials used were Gadolinium oxide (Gd$_2$O$_3$, 99.99%, Aldrich), Europium oxide (Eu$_2$O$_3$, 99.99%, Aldrich), Conc. HNO$_3$ (70%), Polyethylene glycol 200 (PEG, 99%, Merck), Diethylene glycol (DEG, C$_4$H$_9$O$_3$, Merck, 99%) and Citric acid monohydrate (C$_6$H$_8$O$_7$.H$_2$O, A.R. grade) and were used without further purification. Stoichiometric amounts (Gd$_{1.9}$Eu$_{0.1}$O$_3$) of Eu$_2$O$_3$ and Gd$_2$O$_3$ were dissolved in concentrated nitric acid and deionized water (1HNO$_3$:1H$_2$O) to make their respective nitrate solution. The two solutions were then mixed under magnetic stirring to assure uniform mixing and then citric acid in DEG was added slowly into the prepared aqueous nitrate solution to chelate metal ions to form metal-citrate complex with continuous stirring. In order to study the effect of citric acid, molar ratio of citric acid to metal cation (CM) ratio is varied as 0.5:1, 1:1, 2:1 and 3:1. About 2 ml of PEG is also added to this complex solution as a mineraliser. The mixed solution was then maintained at ~100 °C with continuous stirring in a water bath for about 5 h to form a highly transparent viscous solution. The resulting viscous solution is then subjected to heat treatment in a muffle furnace at 180 °C for 1h and then the temperature is raised to 400 °C for 2h to result the greyish precursor. The precursor powder thus obtained were fully ground and was then subjected to sintering in a muffle furnace at 800 °C for 2h at a heating rate of 4 °C/min to obtain the Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphors.

Phase formation, phase analysis and microstructural characterizations of the phosphor samples were done on a X-ray diffractometer (Philips X’pert Pro) in the angular range (2θ) 10°-70° with CuKα1 (λ =1.54056 Å) radiation employing X’celerator and monochromator at the diffracted beam side. The morphology of the samples was investigated using a Field Emission Scanning Electron Microscope (FEI-FEG, Sirion) operating at 5 KV in SE mode and by a transmission electron microscope (FEI Tecnai F20) operating at 200 KV equipped with a Gatan CCD camera. Jobin Yvon Horiba Fluorolog III (FL3-11) Spectrofluorometer equipped with a 450W Xenon lamp as excitation source and a photomultiplier tube in photon counting mode (Hamamatsu R928P) as detector is employed to record the excitation and emission photoluminescence spectra at room temperature.

3. Results and Discussion

3.1. Phase, Structure and Morphology Studies

X-ray diffraction (XRD) patterns of Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor prepared with different citric acid to metal cation ratio (CM ratio) and heat treated at 800 °C for 2h is shown in figure 1. All the diffraction patterns observed can be indexed to cubic Gd$_2$O$_3$ (JCPDS File No. 43-1014, Ia3 (206) space group). No additional peaks of other phases have been found, which shows that Eu$^{3+}$ has been effectively incorporated in to the Gd$_2$O$_3$ host lattice in all samples. It is found that the intensity of XRD peaks increase and width of peaks decrease with increase of CM ratio. This indicates an improvement of crystallinity and increase in crystallite size of the samples with increase of citric acid to metal cation ratio.

The crystallite size (D) of the phosphors were calculated from XRD patterns using the Scherrer equation

$$Crystallite\ size\ (D) = \frac{K\lambda}{\beta\cos\theta}$$

where, K is a constant (=0.9), λ is the wavelength of X-rays (0.15406 nm), β is the diffracted full width at half maximum (FWHM) in radian, θ is the Bragg diffraction angle.
Figure 1. XRD patterns of Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor prepared with CM ratio (a) 0.5:1, (b) 1:1, (c) 2:1 and (d) 3:1.

Figure 2 depicts the variation of lattice constant, cell volume and the evolution of crystallite size of the Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor as function of CM ratio. Lattice constant obtained are in agreement with the standard JCPDS File No. 43-1014 (a = 10.813 Å). It can be seen that at lower CM ratio, there is no appreciable change in the crystallite size, but it increases more rapidly when CM ratio crosses 2:1. This is in agreement with the sharpening of X-ray diffraction peaks observed.

Figure 2. Variation of (a) lattice constant, cell volume and (b) the evolution of crystallite size of Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor as function of CM ratio.

Figure 3. presents the typical scanning electron micrograph (SEM) and transmission electron micrograph (TEM) of the Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor synthesized using the CM ratio of 2:1. From the SEM, it can be seen that almost spherical shaped morphology is observed. The size distribution of
these nanoparticles is uniform with regular shape. TEM pattern reveals that the nanoparticles are monodisperse and uniform with almost spherical shape. The size of the nanoparticles measured from the TEM images was around 25 nm in diameter, which is consistent with XRD results. It is well known that spherical shaped grains are of greater importance because of their high packing density, lower scattering of light and better luminescence properties [3] for display applications.

![Figure 3](image)

**Figure 3.** Typical (a) scanning electron micrograph and (b) transmission electron micrograph of the Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor synthesized with a CM ratio of 2:1.

### 3.2. Photoluminescence Studies

The photoluminescent excitation spectrum consist of a strong broad band in the wavelength range 230-300 nm with a maximum at 265 nm and superimposed with weak lines. Strong broad band is due to the charge transfer (CT) electronic transition from the 2p orbital of O$^{2-}$ to the empty 4f orbital of central Eu$^{3+}$ ions [1]. Weak lines observed at 276, 279, 280 (5S-6I) and 314 nm (5S-6P) are related to internal f-f transitions of Gd$^{3+}$ ion, indicates that there exists an energy transfer from Gd$^{3+}$ to Eu$^{3+}$ [4]. Photoluminescent (PL) emission spectra of Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor (under 265 nm CT excitation) prepared by different CM ratio is shown in figure 4 (a). All the emission spectra have similar emission profiles and there are five groups of distinctive emission peaks between 550 and 720 nm are observed corresponding to the transitions from excited $^5$D$_0$ to $^7$F$_J$ (J =0, 1, 2, 3, 4) levels of Eu$^{3+}$ ions [5] and are assigned to $^5$D$_0$-$^7$F$_0$ (581 nm), $^5$D$_0$-$^7$F$_1$ (588,593,599 nm), $^5$D$_0$-$^7$F$_2$ (612, 630 nm), $^5$D$_0$-$^7$F$_3$ (651 nm) and $^5$D$_0$-$^7$F$_4$ (707 nm) transitions, respectively. The strongest red emission peak at 612 nm corresponds to the hypersensitive forced electric dipole $^5$D$_0$-$^7$F$_2$ transition of Eu$^{3+}$ ion with the selection rule $\Delta J = 2$ [1], induced by the lack of inversion symmetry and the $^5$D$_0$-$^7$F$_1$ is due to the magnetic dipole transition. Integrated photoluminescent intensity (PL) of the nanophosphors as a function of CM ratio is shown in figure 4 (b) and found that the highest emission intensity was observed when CM is 2:1. This may be due to the fact that high citric acid concentration brought about a higher carbon impurity left in the samples which is not favourable for luminescence while lower CM ratio accelerated the rate of hydrolysis which may yield in the formation of inhomogeneous nanoparticles. Thus the observed results showed that a CM ratio of 2:1 shows high luminescent intensity may be due to homogeneity, improvement of doping, good activation between host and activator, better crystallinity and lesser surface defects.
4. Conclusions

An efficient method for the synthesis of Eu$^{3+}$ incorporated Gd$_2$O$_3$ nanophosphors using metal-citrate complex method is established and studied the effect of citric acid to metal cation ratio on the structure, morphology and luminescent properties of nanophosphors. Photoluminescent emission intensity of the samples can be correlated with the amount of citric acid, improved crystallinity, uniform morphology, particle size, reduced defects, and proper diffusion of Eu$^{3+}$ into the crystal structure of Gd$_2$O$_3$. Higher asymmetric environment around europium results in intense red emission (612 nm) due to $^5$D$_0$ - $^7$F$_2$ forced electric dipole transition and found that photoluminescence intensity is highest for the sample prepared with a CM ratio of 2:1. The present study reveals that emission intensity can be tuned by suitably selecting the amount of citric acid during synthesis, which can be employed for other phosphor systems. The existence of strong red emission from Gd$_{1.9}$Eu$_{0.1}$O$_3$ nanophosphor corresponding to $^5$D$_0$ - $^7$F$_2$ transition (612 nm) of Eu$^{3+}$ make it a promising candidate for applications in bio assays, magnetic resonance imaging, deep uv LED’s, solid state lighting, fluorescent lamps and flat panel displays.

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