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Synthesis and characterization of $ZnGa_2O_4:Eu^{3+}$ nanophosphor by wet chemical method

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ABSTRACT

Quantum dots of $ZnGa_2O_4:Eu^{3+}$ was successfully synthesized by simple wet chemical method. This easy synthesis technique at low temperature, in aqueous medium resulted in the cubic spinel structured $ZnGa_2O_4:Eu^{3+}$ quantum dots, confirmed from x-ray diffraction (XRD) and transmission electron microscopy (TEM). The photoluminescence (PL) spectrum consists of electric and magnetic dipole transitions of Eu^{3+}, and there exist a quenching behavior with respect to concentration of activator. This is the first time report on the synthesis of red emitting phosphor by aqueous solution route and the pure, efficient PL emission may find applications in imaging techniques as well as in display technology.

In the present scenario, nano-rare earth luminescent materials have significant attraction due to their remarkable utilization in the fields like optoelectronic devices, flat panel displays, biomarker, sensor etc. Recently more attention is given to the activator incorporation into the metal oxide semiconductors due to their wide direct band gap, which give rise to fruitful results. The stability in thermal and chemical properties, in comparison with sulfides also induce their practice in low voltage cathodoluminescent devices.

Zinc gallium oxide/zinc gallate ($ZnGa_2O_4$) is a binary oxide compound which come under the group of inorganic spinels. They posses crystal structure in the form $A^{2+}B^{3+}{}_2O_4$ in which both of the cation (A═Zn and B═Ga) belongs to the fourth period. Here Zn^{2+} and Ga^{3+} ions occupy the tetrahedral and octahedral sites of the cubic spinel respectively with Fd3m space group. This particular spinel structure improves their use in sensing applications [1]. The wide band gap of 4.4 eV and good transparency over the visible spectrum aids their use in the applications like reflective optical coatings [2], transparent conducting oxide [3] etc. Rare earth [RE] doped zinc gallate results in better quantum efficiency and sharp luminescence which enrich the phosphor applications. Here the shielding effect generated by the 5 s and 5p electrons of RE helps in the competent emissions from the 4f shell and are insensitive to the surrounding effect. $ZnGa_2O_4:Eu^{3+}$ is an excellent red phosphor, where the red emission is generated from the 4f shells of Eu^{3+} ion [4]. This sharp red emission by Eu^{3+} doping can be utilized in lasers, light emitting diodes [LED], display boards etc. In conjunction with this pure red emission, nontoxic nature of zinc gallate can be effectively exploited for the cell imaging purposes in the biological field [5].

A variety of synthesis techniques like solid state reaction [6], hydrothermal [4,7–9] and citrate solgel method [10], which require high temperature for the synthesis or annealing purpose, were used for $ZnGa_2O_4:Eu^{3+}$ production. The volatilization of ZnO at these temperatures, instigate the synthesis of zinc gallate at low temperature with fewer chemicals. Here we adopted a simple, cost effective synthesis of $ZnGa_2O_4:Eu^{3+}$ at a low temperature of 90 °C by using an aqueous solution route. This is the first time report by this method, for the synthesis of red emitting zinc gallate and the observed pure, intense red emission can be utilized in optoelectronic devices and in bio markers.

To the aqueous solution of gallium nitrate [$Ga(NO_3)_3$, Sigma, 99.9%], required molar concentration of europium acetate [$Eu(OOCCH_3)_3$, Alfa aesar, 99.99%] was added. Keeping the molar ratio of Zn^{2+}: (Ga^{3+} + Eu^{3+}) as 1:2, zinc acetate [$Zn(CH_3COO)_2$, Sigma, 99.9%] was prepared in distilled water and mixed with the above solution. After complete dissolution, 6 g urea [$CO(NH_2)_2$, Merck, 98%] was also added to the above mixture. The final solution was taken in a standard capped bottle and transferred to a conventional laboratory oven and kept for 24 h at 90 °C. The resultant solution with white precipitates was filtered centrifugally using 2-propanol and dried in the oven, with the same temperature for another 24 h to get the final $ZnGa_2O_4:Eu^{3+}$ powder.

The resultant powder was analyzed structurally and optically. Rigaku MiniFlex 600 X-Ray Power Diffractometer was used for the XRD analysis. The crystal structure and morphology of the particles were studied using Jeol JEM 2100 transmission electron microscope. Diffuse reflectance spectra were recorded with Varian, Cary 5000 UV-VIS-NIR spectrophotometer having an external diffuse reflectance accessory consisting of a 150 mm diameter integrating sphere with

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