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Ultrasonic-assisted wet chemical synthesis and characterization of Eu^{3+} doped SnO_2 nanoparticles

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ABSTRACT

Nanocrystals of europium doped tin oxide have been prepared under ultrasonication using the precursors $SnCl_2{\cdot}2H_2O$ and $Eu(NO_3)_3{\cdot}6H_2O$ in the ethanol solvent. The crystalline structure and grain size of Eu doped SnO_2 were determined from the powder X-ray diffraction (XRD) pattern. The elemental composition of SnO_2:Eu^{3+} was analysed by Energy Dispersive X-ray (EDX) spectrum. The surface morphology and size of the particles of the synthesized nano semiconductor were discussed through the images taken by Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscope (HRTEM). The photoluminescence emissions at 583, 623 and 653 *nm were absorbed in the emission spectra due to the dopant Eu^{3+}.*

Keywords: SnO_2:Eu^{3+}, SnO_2, Eu^{3+}, semiconductors, nanoparticles, ultrasonication.

INTRODUCTION

SnO_2 is an n-type semiconductor with a wide band gap energy (Eg = 3.6 eV at 300 K) has been widely investigated due to its high sensitivity for detection of combustible gases at low concentration levels [1]. In recent years, rare earth ions as luminescence centers incorporated into different hosts have attracted more attention due to promising applications in many fields, solid lasers [2], high-density frequency domain optical data storage [3], planar waveguide [4], transparent conducting electrodes for dye sensitized solar cells [5], catalyst for oxidation of organic compounds [6] etc. Based on these potential applications, rare earth ions especially, trivalent Eu^{3+} ions incorporated into oxides and glass hosts, which exhibit narrow band red light emission from the Eu^{3+} ions arising from intra-4f parity forbidden transition ($^5D_0 \rightarrow {}^7F_2$), have deserved extensive research [7]. In this work, Eu^{3+} dopped SnO_2 nano particles were synthesised by ultrasonication using the solvent ethanol.

MATERIALS AND METHODS

Synthesis

0.01 mole of $SnCl_2{\cdot}2H_2O$ (Merck, GR) was dissolved in 100 ml absolute ethanol in a 250 ml beaker and sonicated in a bath-type ultrasonicator (157 W, 20 KHz Maxwell seller) for 10 minute. 1 m % of $Eu(NO_3)_3{\cdot}6H_2O$ (Sigma-Aldrich, 99.9%) was dissolved in 10 ml of ethanol and added drop by drop in the solution under sonication. The solution was further sonicated for 5 minute. The precipitate was filtered and washed several times by ethanol. The powder was dried at 100 °C for 3 h. Then it was ground and calcinated at 400°C for 2 h in air.

Characterization

The synthesized nanopowders were characterized by a X-ray diffractometer RAYOS-X with monochromatic CuK_α (λ=1.5406 Å) radiation and taken over the 2θ range 20° – 70° at the scanning rate of 0.04° per second. The average crystalline size *D* of the nanocrystals was estimated using Scherrer's [8] equation as follows,

$D = 0.9 \lambda / \beta \cos \theta$,

Where β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle. FESEM image was taken by F E I Quanta FEG 200 operated at 15 kV. The HRTEM image was taken by JEM-2100F operated at 200 kV. The photoluminescence emission spectra were recorded by Jobin Yvong flurolog-3-11 spectrofluorometer.

RESULTS AND DISCUSSION

The powder XRD pattern of $SnO_2:Eu^{3+}$ in the Fig. 1 shows several diffraction peaks assigned to the tetragonal rutile crystalline phase of cassiterite SnO_2 (JCPDS 41-1445) without any indication of Eu_2O_3 or Eu_2SnO_7. This indicates that the doped europium ions probably replaced tin atoms in the crystal structure [9]. The average crystallite size of the nanocrystals was calculated as 11 nm by Scherrer's formula and further verified in the HRSEM and HRTEM images in the Figures 3 and 4. The obtained product is appeared as spherical and ellipsoidal nanoparticles in the electron microcopy images. The EDX spectrum in the Fig. 2 reveals the presence of Eu^{3+} in the SnO_2 lattice structure.

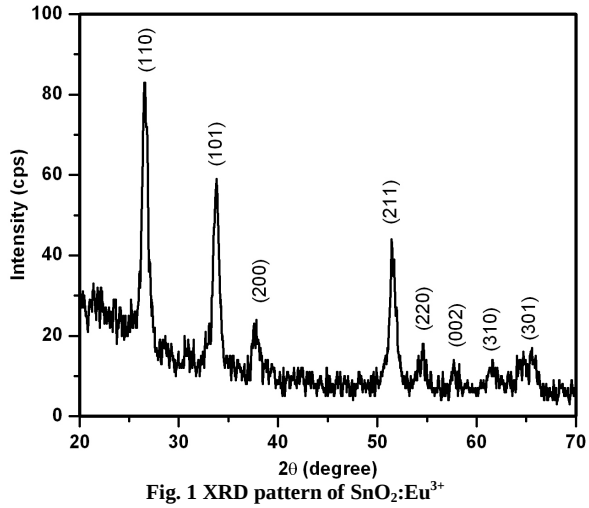

Fig. 1 XRD pattern of $SnO_2:Eu^{3+}$

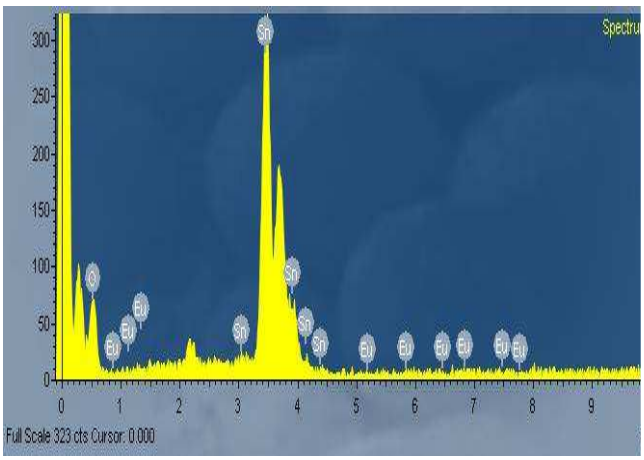

Fig. 2 EDX spectrum of $SnO_2:Eu^{3+}$

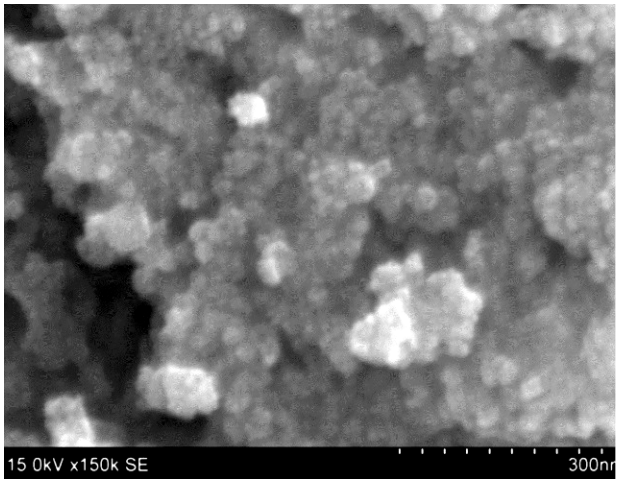

Fig. 3 HRSEM of $SnO_2:Eu^{3+}$ nanopaticles

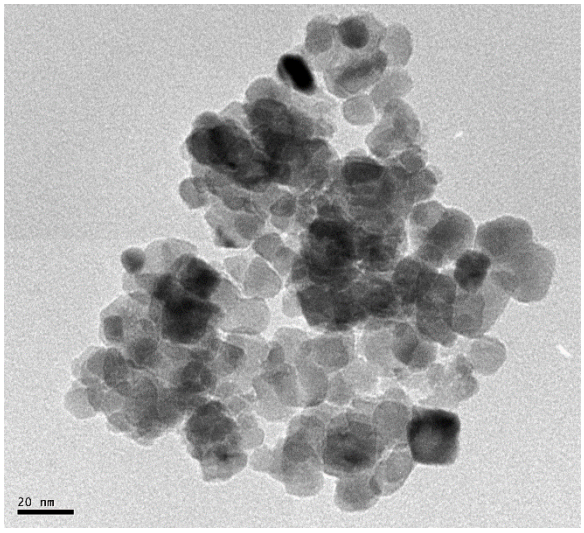

Fig. 4 HRTEM of $SnO_2:Eu^{3+}$ nanopaticles

The Fig. 5 shows the photoluminescence emission spectrum for the excitation wavelength 280 nm. The peak at 335 nm is corresponding to the band gap energy of the SnO_2 (3.7 eV) which is greater than its bulk form. The blue shift in the band gap energy is due to the quantum confinement effect of the nanoparticle [10]. The peak at 423 nm is due to tin interstitials or dangling present in the SnO_2 nanocystals [11]. The emission peaks at 469 nm and 484 nm corresponding to $^7F_0 \rightarrow {}^5D_2$ and $^7F_0 \rightarrow {}^5D_1$ transition of Eu^{3+} [12]. The emission at 538 nm is due to oxygen vacancies on the surface of the SnO_2 nanocrystals [13]. The PL spectrum in the Fig. 6 for the excitation wavelength 325 nm

has the emission peaks at 583 nm, 623 and 653 are due to $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ transition of Eu^{3+} respectively [14]. In the synthesis process, sonication produces acoustic cavitations that reduces viscosity and increases dispersibility [15] which is favor for nanoparticle formation at room temperature and reduces synthesis time.

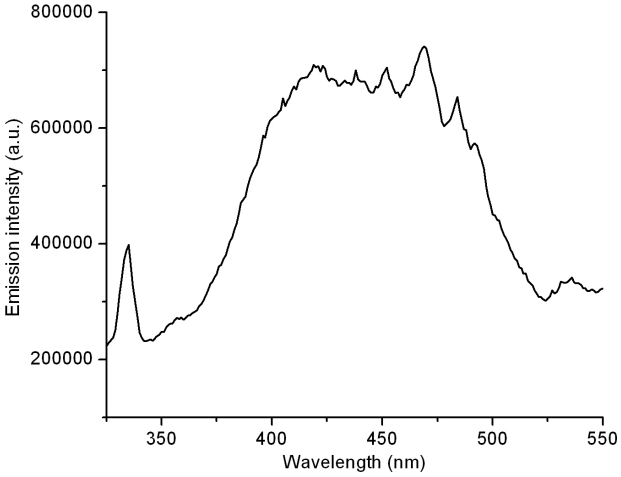

Fig. 5 PL spectrum of SnO_2:Eu^{3+} nanopaticles at the excitation wavelength of 280 nm

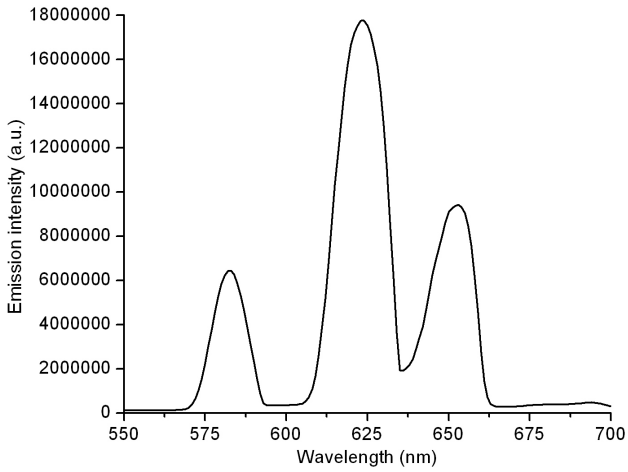

Fig. 6 PL spectrum of SnO_2:Eu^{3+} nanopaticles at the excitation wavelength of 325 nm

CONCLUSION

In this paper, the rare-earth Eu^{3+} ion doped SnO_2 nanoparticles were successfully prepared by ultrasonication assisted wet chemical method. The photoluminescence emission spectra, EDX and XRD results of the synthesized particles can be used to conclude that the Eu^{3+} replaces Sn in the SnO_2 nanocrystals.

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