



ENHANCEMENT OF LUMINESCENCE IN $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ NANOPHOSPHOR Shougaijam Dorendrajit Singh*, Konsam Reenabati Devi, Sanoujam Dhiren Meetei

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Abstract

Indium oxide is an attractive metal oxide as it has a wide band gap (direct gap of 3.55–3.75 eV). In this work, undoped and europium doped indium oxide nanocrystal were synthesized by simple precipitation method. X-ray diffraction (XRD) pattern confirmed the presence of cubic phase for both undoped and europium doped samples. Further transmission electron microscopy (TEM), photoluminescence (PL), electron paramagnetic resonance (EPR) studies were done to characterise the samples. The average size of the doped samples was found to be 21.9 nm from the XRD analysis. PL analysis of the samples is the core of the present research. CIE (Commission Internationale de l'éclairage) co-ordinates of the samples were calculated to know color of light emitted from the samples. On doping europium to In_2O_3 lattice, substitution of In^{3+} by Eu^{2+} and evolution of singly ionized oxygen vacancy are observed. PL emission intensity is found to enhance due to the +2 oxidation state of doped europium ion. This causes the enhancement in the host blue-green emission.

Keywords: Metal oxide semiconductor; Photoluminescence; Oxygen vacancy; Blue-green emission

PACS Code:

1. INTRODUCTION:

Among the semiconducting metal oxides, indium oxide an n-type semiconductor is very attractive as it has a wide band gap [1,2]. It is highly transparent in the visible range and possesses high free carrier mobility. It finds applications in diverse fields such as UV photo-detection, thin film transistors, optoelectronic devices, and tunnel barriers in spintronic devices, solar cells, gas sensor etc. Wu *et al* [3] have synthesized indium oxide nanowires by carbothermal reduction reaction and studied their photoluminescence (PL) property. They reported that the prepared nanowires emitted blue light at 416nm and 435nm due to the presence of vacancies in the material. Emission of light in the visible region due to its defects is one of the interesting factors in studying the material. In general, vacancy in the material may be either In or O vacancy and defects in the material such as anti-site O or In or interstitial oxygen can also induce emission in the visible region [3,4]. Seetha *et al* [1] also reported blue emission for their indium oxide samples.

Generally, rare earth ions are incorporated in semiconductors to improve the luminescence efficiency. However, there are very few reports on synthesis and optical of rare earth doped In_2O_3 nanophosphor [5]. Keeping this in mind, undoped and europium doped indium oxide were synthesized by simple precipitation method. The nanoparticles

have been characterized and studied thoroughly. Results of this work are reported herein.

2. EXPERIMENTAL:

Indium nitrate (99.999%, Aldrich) and Europium nitrate (99.99%, Aldrich) were used as starting materials without further purification. The reagents were made to dissolve in distilled water and stirred for 10-15 minutes. NaOH pellet was added to the solution and stirred for 30 minutes and the precipitate was collected by continuous washing with distilled water and acetone. The precipitate so obtained was dried, ground and annealed at 900°C. Similar procedures were performed for synthesis of other samples (1at.%, 2at.%, 4at.%, 5at.%, 6at.%). XRD data of the samples are recorded in X'Pert PAN analytical diffractometer at 40kV and 30mA. Wavelength of the x-ray used is 1.54Å ($\text{CuK}\alpha$). The TEM images and SAED pattern were recorded using a JEM-2100 microscope (JEOL) (200kV), JES-FA200 ESR spectrometer is used to identify the nature of oxygen vacancy. Photoluminescence (PL) emissions are recorded on LS55 Fluorescence Spectrometer (PerkinElmer).

3 RESULTS AND DISCUSSION:

3.1. XRD studies:

Fig.1 shows the XRD patterns of In_2O_3 and $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ (1at.%, 2at.%, 4at.%, 5at.%, 6at.%) samples. X'pert HighScore's search and match

analysis showed the presence of cubic phase (ICDD-00-006-0416) for both undoped sample and doped samples. The crystallite sizes were calculated using Scherrer formula $t = 0.9\lambda/\beta\cos\Theta$, where λ is the wavelength of the X-ray, 0.9 is shape factor, β is full width at half maximum (FWHM) and Θ is Bragg angle. The crystallite size was found to be 36.5nm for undoped sample. Moreover, with the increase of doping concentration, the shift in diffraction peaks position towards the lower diffraction angle was observed as shown in fig.1. These are attributed to the substitution of In^{3+} (ionic radius=94pm) by Eu^{2+} (ionic radius=94.7pm).

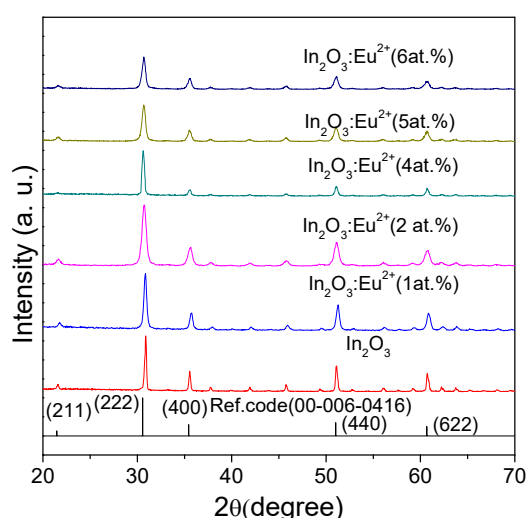


Fig. 1: XRD patterns of undoped In_2O_3 and doped $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ (1,2,4,5,6 at.%) with its reference stick patterns .

Unit cell volume and lattice parameter are found to increase gradually from undoped In_2O_3 nanocrystal to europium doped In_2O_3 nanocrystals as shown in Table 1.

Table 1: Crystallite sizes and cell volume of the samples along with the references.

Sl. No.	Sample	Size(nm)	Unit cell Parameters	
			a (Å)	Cell volume (Å) ³
1	In_2O_3	36.5	10.094	1028.42
2	$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ (1at.%)	26.0	10.097	1029.43
3	$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ (2at.%)	25.2	10.098	1029.67
4	$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ (4at.%)	21.3	10.10	1030.29
5	$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ (5at.%)	18.9	10.12	1033.34
6	$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ (6at.%)	19.0	10.14	1042.50
7	Ref code (00-006-0416) In_2O_3	—	10.118	1035.82

3.2 TEM analysis:

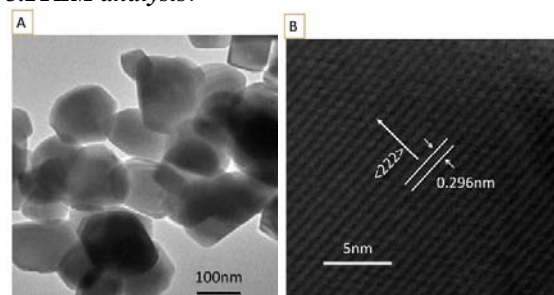


Fig.2 A) TEM image, B) HRTEM image (showing the interplanar spacing) of undoped In_2O_3 .

The TEM images of undoped indium oxide and doped $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ are shown in fig.2 (A, B) and 3(A, B,) respectively. The average crystallite size of undoped nanoparticle estimated from TEM micrographs (nm) are in range from 30-50nm which is consistent with that obtained from XRD line broadening analysis i.e. 36.5nm. The clear fringes

observed in HR-TEM image demonstrate that the synthesized In_2O_3 and $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ particles are single crystalline. The separation between the lattice fringes is 2.96 \AA (fig.2 B), which is in good agreement with the lattice plane spacing $d_{222}(2.92 \text{ \AA})$ of body centred cubic indium oxide(Ref. code: 00-006-0416).

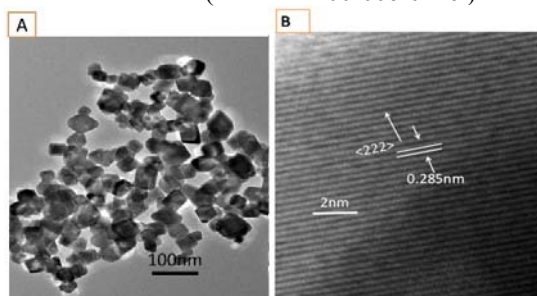


Fig.3 A)TEM image, B)HRTEM(showing the interplaner spacing)of 2 at.% doped $\text{In}_2\text{O}_3:\text{Eu}^{2+}$.

Similarly the average crystallite size of 2 at. % doped $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ estimated from TEM micrographs (nm) are in range from 20-40nm, which is in close agreement with that obtained from XRD line broadening analysis i.e. 26nm. Further the separation of lattice fringes 2.85 \AA (fig.3 B) is in agreement with the lattice plane spacing $d_{222}(2.92 \text{ \AA})$ (Ref. code: 00-006-0416).

3.3.Photoluminescence(PL)studies:

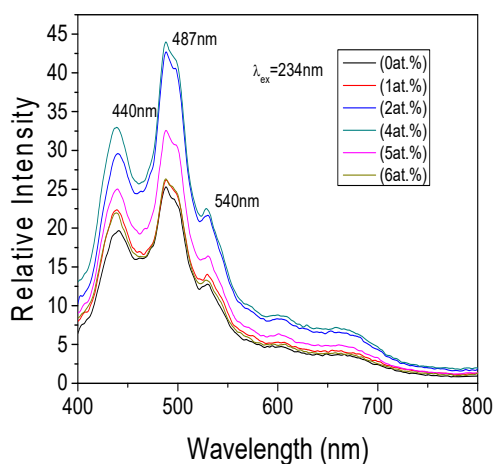


Fig.4 PL emission spectra undoped and (1 at.%,2at.%,4at.%,5at.%,6 at.%)doped $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ excited with 234nm.

While exciting the undoped sample with 234nm, a broad emission at 440nm (blue), 487nm (blue), and a

weak emission at 540nm (green) were observed (Fig.4). The emission peaks of the present work can be referred to the deep level (DL) or trap state emissions due to oxygen vacancies [2]. That is, oxygen vacancies induce the formation of new energy levels in the band gap and as a result, the emissions involving these trap states attribute to the radiative recombination of a photo-excited hole with an electron thereby emitting light at room temperature. In the present case, oxygen vacancies might be formed while calcinating the sample in static atmosphere i.e. box type muffle furnace. During calcination the hydroxyl group in the indium hydroxide lattice will be removed in the form of water. Some of the lattice oxygen may also release in the form of oxygen gas, thus leaving oxygen vacancies.

To identify the type of oxygen vacancy present in the synthesized samples, electron spin resonance (ESR) or electron paramagnetic resonance (EPR) analysis was performed. The EPR /ESR spectra (Fig.5) revealed that the nature of oxygen vacancy is singly ionized oxygen vacancies with $g=1.9985$ [2,6,7] because other oxygen vacancies are not paramagnetic.

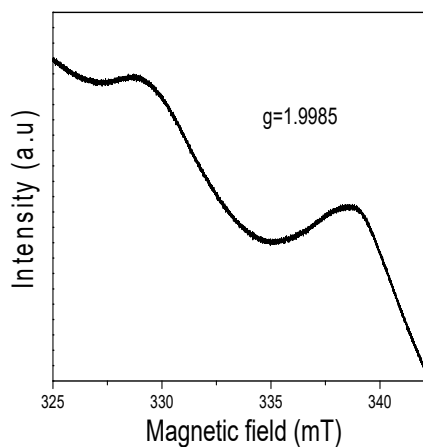


Fig.5 EPR spectra of undoped indium oxide sample.

In the emission spectra of (1 at.%,2 at.%,4at.%,5 at.%, 6 at.%) doped $\text{In}_2\text{O}_3:\text{Eu}$ excited by 234nm, there is no distinct peak around 610nm . However, the emission intensity of the host is found to increase after doping europium. Fig.6 shows that intensity of

EPR signal ($g=2.0448$) is found to increase for 4 at. % doped sample. This may be due to increase of oxygen vacancies in the doped sample resulting to the enhancement of host emission intensity. The enhancement of emission around 450-560nm and almost negligible emission around 600-650nm reveals the doped europium ion is in +2 oxidation state (Eu^{2+}). It is also suggested that Eu^{2+} replaces the In^{3+} in $\text{In}_2\text{O}_3:\text{Eu}^{2+}$ lattice thereby creating singly ionized oxygen vacancies[8]. And this additional oxygen vacancies helps in enhancing the emission around 450-560 nm.

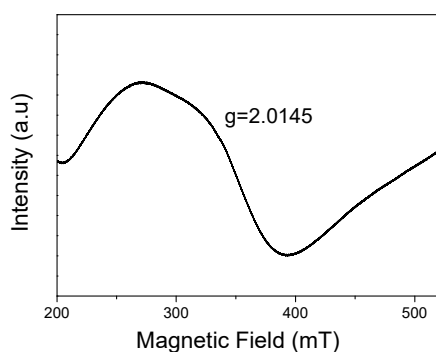


Fig.6 EPR spectra of 4 at. % doped sample.

From Fig.4, it is clearly observed that the intensity of the PL emission decrease on increasing the concentration of Eu^{2+} after 4at.% doping. This can be attributed to luminescence quenching. At low concentration of Eu^{2+} ions within the indium oxide host, the ions are distributed randomly and the distances between Eu^{2+} is larger. Therefore, the probability of energy transfer between Eu^{2+} ions is low. However, as the concentration increases, the distance between the Eu^{2+} ions are shortened and hence the probability of energy transfer between the Eu^{2+} ions increase. Consequently, concentration quenching of luminescence occurs i.e., some amount of excitation energy is dissipated non-radiatively which results in decrease of luminescence intensity. Besides the concentration quenching discussed above, the decrease in emission intensity can also be explained due to decrease in crystal size or size quenching. It is clearly observed from Table 1.that the crystal sizes decrease on increasing the doping concentration. As a result, the surface areas of the nanocrystals increase on decreasing the crystal size. And therefore, increase in surface area of the nanocrystals can also lead to significant increase in non-radiative decay and hence decrease in the emission intensity [8, 9].

3.4. CIE (Commission Internationale de l'eclairage) chromaticity study:

The Commission Internationale de l'eclairage (CIE, 1931) co-ordinate is calculated in order to evaluate the phosphors' performance of the synthesized nanocrystals, as shown in the table. All the co-ordinates (x,y) in the Table 2 falls in greenish blue region.

Table 2

Sample Concentration	x	y	Color
In_2O_3 0 at. %	0.21	0.27	Greenish blue
$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ 1at. %	0.21	0.28	Greenish blue
$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ 2 at. %	0.23	0.28	Greenish blue
$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ 4 at. %	0.22	0.27	Greenish blue
$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ 5 at. %	0.20	0.27	Greenish blue
$\text{In}_2\text{O}_3:\text{Eu}^{2+}$ 6 at. %	0.21	0.26	Greenish blue

4. CONCLUSION:

Undoped indium oxide and europium doped indium oxide were synthesized by simple precipitation method. Crystallite size was found to be 36.5 nm for undoped sample and average crystallite size was found to be 21.8nm doped samples. Characterizations of the samples were done by XRD, TEM, PL and EPR studies. EPR analysis revealed that the doped europium is in +2 oxidation state. This causes to the increase of singly ionized oxygen ion concentration in the doped sample and hence enhancement of host emission intensity (blue-green emission) occurs. However this emission intensity again decreases after 4at. % doped concentration which may be due to concentration quenching and non-radiative decay.

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