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Optical Properties Of Europium Ion Doped Zno Nanomaterial

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Abstract**: Rare-earth ions doped materials have been intensively studied for their potential use in integrated optoelectronic devices like visible (blue, green, and red), infrared luminescent devices and laser materials. The optical properties of rare earth ions mainly depend on the local environment or symmetry of the host materials. However, manipulating the concentration of the dopants and controlling the aspect ratio of the one-dimensional nanostructures are still remain challenges to the nanotechnology community.**

Euoropium ion doped ZnO nanomaterials were prepared by Chemical synthesis method. The materials were characterized by XRD, SEM, TEM and FTIR. Their absorption spectra were measured in 300-900 nm regions at room temperature. Six absorption bands have been observed. Various spectroscopic parameters such as Slater-Condon, Racah, spin-orbit interaction, Nephelauxetic ratio, bonding and Judd-Ofelt parameters have been computed from the observed band. The Fluorescence spectra have been recorded of Eu^{3+} doped ZnO nanomaterial using with intense absorption bands (400 nm) at room temperature in visible region.Radiative properties viz. spontaneous emission probability (A), fluorescence branching ratio (β), radiative life time (τ) and stimulated emission cross- section (σ_p) have been computed. The size range of the generated Eu^{3+} doped ZnO nanomaterial was approximately 200-20nm.

Keywords: Europium doped ZnO Nanomaterial, Absorption Spectra, Fluorescence Spectra and Radiative properties

I. INTRODUCTION

Nanotechnology is a rapidly developing branch of material science which has been attracting a large number of scientists and technologists throughout the world since the last part of the twentieth century.The progress of this technology is mainly due to its potential benefits in varieties of fields including food, medicine, energy, optical, electrical, textile, and such others. ZnO is an inorganic compound and is a white powder[1]. Many report, for example, about the applications of nanoparticles in biophotonics [2], luminescent nanomaterials for biological labelling [3], functionalised europium nanorods for in vitro imaging [4],development of new ink materials based on luminescent nanomaterials for the security labels of printing products such as passport and visa documents has encouraged research in this direction [5].

Several reports are available on the synthesis and studies of the luminescent properties of europium doped semiconductors in various morphologies [6,7]. Cheng and Wang reported the synthesis and phosphorescence of europium-doped ZnS nanowires [8]. Okuyama and coworkers observed the energy transfer from the ZnO to the Eu^{3+} ions in europium-doped ZnO/poly(ethylene glycol) nanocomposites [9]. Europium doped ZnO thin films are also reported.Kanemitsu and coworkers reported the synthesis of Eu-doped ZnO nanorods by a microemulsion method [10].

In this paper we present, the nanomaterial and doping concentration of rare earth ions to produce suitable nanomaterial which prepared by the chemical synthesis method. Their spectral characterization i.e. absorption and fluorescence spectra have been studied. Optical property of nanoparticles is an important property which gives specific information of size, shape, concentration, agglomeration state, etc., near the surface of the particles. These particles interact with specific wavelength of light and show maximum absorption at a

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wavelength. To the best of our knowledge Laser properties of Eu-doped ZnO Nanomaterial has not been reported.

II. EXPERIMENTAL DETAILS

The nanomaterial with rare earth ions will be prepared by chemical synthesis method [11]. ZnO nanoparticles will be tried in alcoholic media like ethanol, methanol or propanol. In alcoholic media growth of oxide particles is slow and controllable [12]. Different solutions will be prepared by dissolving 0.2725 g of $ZnCl_2$ (10^{-1} M, 20 ml), 0.525 g NaOH (10^{-1} M, 100 ml) and *X* M glycerol in ethanol. Glycerol slowly added to NaOH solution while it will be continuously stirred. The resulting solution will be stirred for one hour before adding $ZnCl_2$ and Eu^{3+} solution to it. After three hours of constant stirring a milky white solution will be obtained. Size selective precipitation will be carried out using acetone as a non-solvent. The precipitate will be washed in methanol and ethanol will be allowed to evaporate at room temperature to obtain ZnO nanoparticles in white powder form.

III. RESULTS AND DISCUSSION

Structural and morphological properties

X-Ray Diffraction (XRD)

The X-ray diffraction pattern of typical ZnO: Eu^{3+} nanoparticles is given in **Fig. 1**.It can be noted that all of the diffraction peaks could be well indexed to the Hexagonal Wurtzite crystal structure. In this Eu^{3+} doped sample, no additional phase was observed, indicating that manganese was successfully doped in the ZnO crystalline lattice. The width of the diffraction lines is broadened because of the small size of the crystallites.

Transmission Electron Microscope (TEM)

A TEM image of ZnO: Eu^{3+} is presented in Fig.2**.** It can be seen from the figures that the ZnO: Eu^{3+} sample occurs through the aggregation of the nanocrystals exhibiting sizes of about 20 nm.

Fourier Transform Infra Red (FTIR)

A FTIR image of ZnO: Eu^{3+} is presented in Fig.3and table 2**.** The FTIR spectra of Eu^{3+} doped ZnONM consists of several peaks which are broad and moderate in band width. The peaks in the range 665-683 cm^{-1} are due to metal–oxygen bonds Eu/ZNO. The peak around 1650 cm^{-1} is assigned to the asymmetric stretching vibrations of Zn–O bonds from metal-oxygen group. The broad band in all the ZnONM matrices around 3410-3500 cm^{-1} is corresponding to the fundamental stretching vibrations of O–H indicating the presence of hydrogen groups. The band positions and their assignments for observed FTIR bands are reported in Table 2 for Eu^{3+} doped ZnONM. [13-16].

UV-visible study

The UV-visible study of Euoropium doped Zinc Oxide nanomaterial has been done by recording optical absorption using Spectrophotometer (2375 Double Beam Spectrophotometer and Varian Carry). The absorption spectra of Euoropium doped Zinc Oxide nanomaterial is shown in Fig. 4 and table 3-5. It has been observed that the absorption peaks appears at wavelengths 372 380, 388, 410, 480 and 544nm as the concentration of dopant varies as 0.1mol%, 0.2mol% and 0.3 mol% in Euoropium doped Zinc Oxide nanomaterial matrix respectively. The shifting occurred in the spectra may be due to the polarity of solvent used in the synthesis or may be due to the dispersion of rare earth oxide particles in the Euoropium doped Zinc Oxide nanomaterial matrix. Some research papers on Neodymium are available for Laser studies [17].

Fluorescence study

Fluorescence spectra of Euoropium doped Zinc Oxide nanomaterial samples are shown in Figure 5 and table 6-7. Fluorescence study of Euoropium doped Zinc Oxide nanomaterial in which the concentration of dopant varies as 0.1mol%, 0.2mol% and 0.3 mol% shows emission peaks at wavelength 600, 626 655 and 720nm. It has been observed from fluorescence spectra that the emission peak has maximum intensity at concentration 0.3mol% corresponding to wavelength 400nm. A slight shifting has been observed in the spectra as concentration of dopants changes in the host matrix. The spectra show narrow emission peaks resulting from 4f-4f transitions within Eu^{3+} ions, with the most intense peak at 626 nm corresponding to the $^5D_0$–$^7F_2$ transition. Three other peaks are observed at 600 nm ($^5D_0$–$^7F_1$), 720 nm ($^5D_0$ –$^7F_4$), 618 nm ($^5D_0$–$^7F_3$), respectively.

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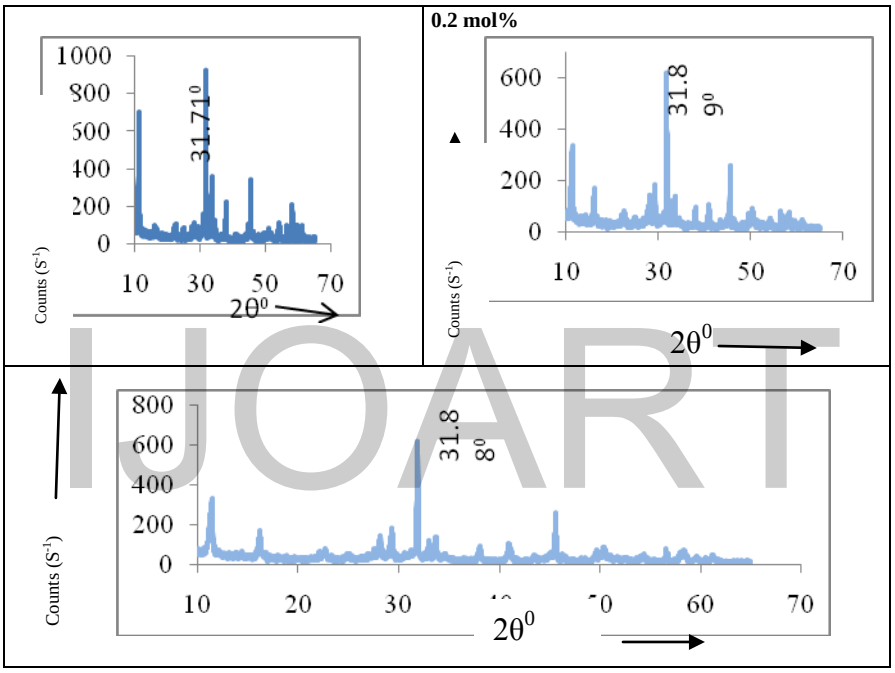
IV. CONCLUSION

ZnO: Eu^{3+} nanomaterial were successfully prepared by Chemical synthesis method. The crystal structure and surface of nanomaterials were analyzed by X-ray diffraction, TEM, FTIR, Absorption and Fluorescence characters were studied by high-resolution Fluorescence with 400nm excited wavelength. The X-ray diffraction and TEM results show that our samples are nanomaterials with particle size about 50–10 nm. The spectroscopic properties of RE ions doped ZnONM have been analyzed on the basis of Judd-Ofelt theory. Judd - Ofelt intensity parameters Ω_2, Ω_4 and Ω_6 have been computed Eu^{3+} doped Zinc Oxide Nanomaterial specimens. Fluorescence spectra were studied in detail. They have strong PL intensity and their colour can be modified by concentration of Eu^{3+}. The promising material for imaging technology, excited by He-Cd laser, ZnO: Eu^{3+} also be excited by a 400nm diode. The optimal concentration of Eu^{3+} is 0.3mol%. ZnO:Eu^{3+} Nanomaterial have been the subject of much research due to their wide application in semiconductor-electronic technologies. The influence of concentration has been discussed. ZnO: Eu^{3+} was used to prepare red or green labels under 365-nm lamps to control money or 400-nm diode to easily recognize green or red emissions.

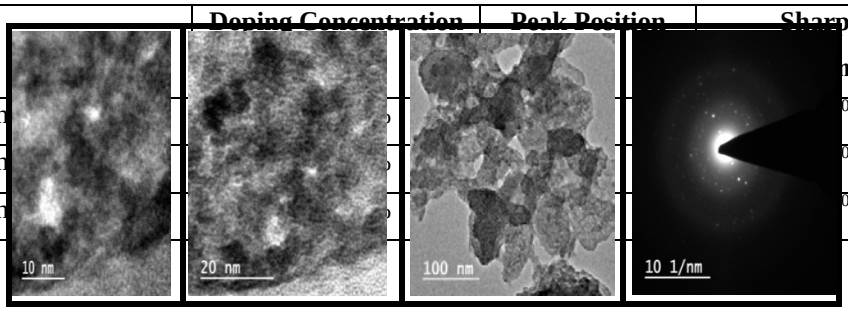
TABLE 1:- Observed peak height and sharp diffraction of Eu^{3+} doped ZnOxide



Nanomaterial with different concentrations.

Fig.1:-XRD pattern of ZnO Nanomaterials with of Eu^{3+} ion.

	Doping Concentration	Peak Position	Sharp n($2\theta^0$)
Zn			
Zn			
Zn			



0.1mol% **0.2mol%**
0.3mol% **HR-TEM**

Fig.2:-TEM micrograph Zinc Oxide Nanomaterial with 0.1mol% Eu^{3+} ion.

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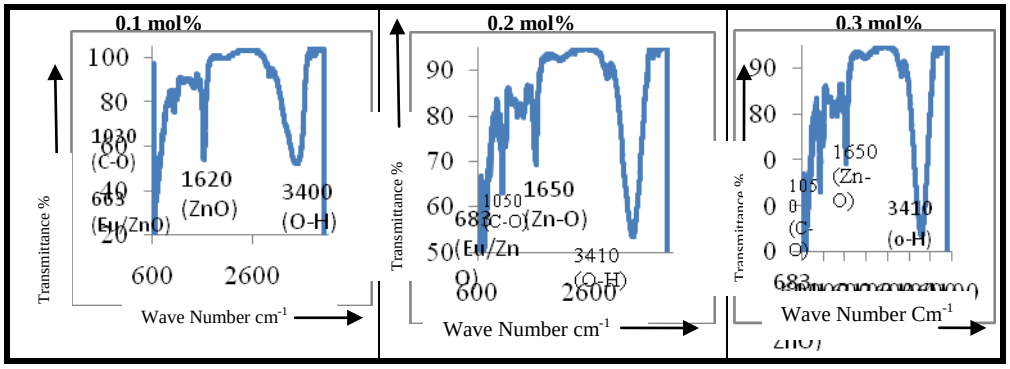

Fig. 3:- FTIR pattern of ZnO Nanomaterial with Eu^{3+} ion.

TABLE 2:-Observed band of Eu^{3+} doped Zinc Oxide Nanomaterial with different Concentrations

S.No.	ZnONMEu01	ZnONMEu02	ZnONMEu03	Assignment
0.1 mol%	Wave Number	0.2 mol% Wave Number	0.3 mol% Wave Number (cm-1)	BONDS

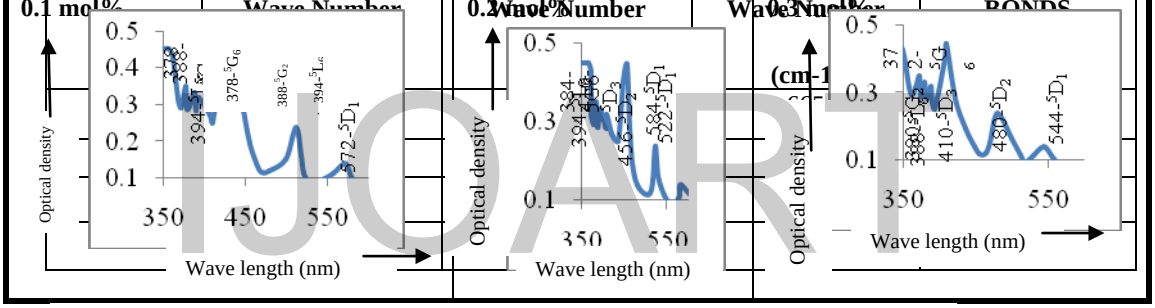

Fig. 4:- Absorption spectrum of ZnO Nanomaterial with Eu^{3+} ion

TABLE 3:- Experimental (S_{exp}) and Calculated (S_{cal}) with their Differences (ΔS) for various absorption levels of 0.3mol% Eu^{3+} doped Zinc Oxide Nanomaterial.

Absorption levels	$S_{exp}(10^{-20})$	$S_{cal}(10^{-20})$	ΔS
$^5D_0$	0.01	0 .002	0.01
$^5D_1$	0.04	0.12	0.17
$^5D_2$	0.18	0.09	0.08
$^5L_6$	0.28	0 .002	0.28
$^5G_2$	0.17	0.03	0.14

TABLE 4:- Experimental (S_{exp}) and Calculated (S_{cal}) with their Differences (ΔS) for various absorption levels of 0.3 mol% Eu^{3+} doped Zinc Oxide Nanomaterial

Absorption levels	$S_{exp}(10^{-20})$	$S_{cal}(10^{-20})$	ΔS
$^5D_0$	0.01	0 .002	0.01
$^5D_1$	0.04	0.12	0.17
$^5D_2$	0.18	0.09	0.08

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$^5L_6$	0.28	0 .002	0.28
$^5G_2$	0.17	0.03	0.14

TABLE 5:-Judd-Ofelt intensity parameters for Eu^{3+} doped Zinc Oxide Nanomaterial

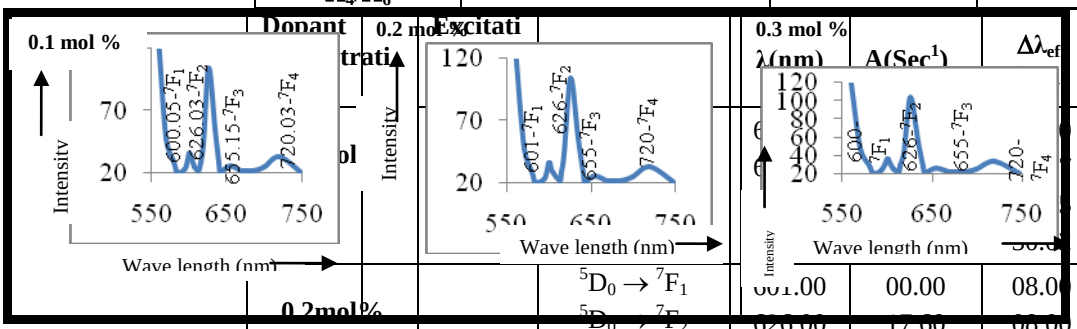
TABLE 6:- Matrix elements (U^{λ}) for absorption levels of Eu^{3+} ion [13]

Absorption level	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$
$^5D_0$	0.00000	0.00000	0.00000
$^5D_1$	0.00000	0.00000	0.00000
$^5D_2$	0.00080	0.00000	0.00000
$^5D_3$	0.00000	0.00000	0.00000
$^5L_6$	0.00000	0.00000	0.01550
$^5G_2$	0.00060	0.00000	0.00000

Fig.5:- Fluorescence spectrum of ZnO Nanomaterial with Eu^{3+}ion

TABLE 7:- Spontaneous emission probability (A,) Fluorescence Braching ratio (β) Radiative time(τ) for various fluorescence peaks for Eu^{3+} doped Zinc Oxide Nanomaterial with different doping concentrations

Omega parameters	ZnONMEu01	ZnONMEu02	ZnONMEu03
	0.1mol%	.2mol%	0. 3mol%
$\Omega_2(10^{-20})$	1.23	2.42	1.56
$\Omega_4(10^{-20})$	3.27	3.17	1.89
$\Omega_6(10^{-20})$	2.38	4.73	2.22
Ω_4/Ω_6	1.37	0.67	0.84



Dopant concentration	Excitation wavelength (nm)	Transition	λ(nm)	A(Sec^{-1})	$\Delta\lambda_{eff}$	β	τ (μ sec)
						00.00	00.00
						00.05	00.11
						00.00	00.00
						00.94	00.00
0.2mol%	400	$^5D_0 \rightarrow {}^7F_1$	601.00	00.00	08.00	00.00	00.00
		$^5D_0 \rightarrow {}^7F_2$	626.00	17.00	08.00	00.10	00.05
		$^5D_0 \rightarrow {}^7F_3$	655.00	00.00	15.00	00.00	00.00
		$^5D_0 \rightarrow {}^7F_4$	720.00	151.00	30.00	00.89	0.006
0.3mol%	400	$^5D_0 \rightarrow {}^7F_1$	600.0	00.00	08.00	00.00	00.00
		$^5D_0 \rightarrow {}^7F_2$	626.0	11.30	08.00	00.10	00.08
		$^5D_0 \rightarrow {}^7F_3$	655.0	00.00	15.00	00.00	00.00
		$^5D_0 \rightarrow {}^7F_4$	720.0	90.10	30.00	00.89	00.01

TABLE 8:- Emission Cross Section for various fluorescence peaks of Eu^{3+} doped Zinc Oxide Nanomaterial with different doping concentrations

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Dopant concentration	Excitation λ(nm)	Assignment	$\sigma_p(10^{-22})$
0.1mol%	400	$^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_4$	0.00 1.03 0.00 1.13
0.2 mol %	400	$^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_4$	0.00 1.93 0.00 1.09
0.3 mol %	400	$^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_4$	0.00 1.24 0.00 6.49

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