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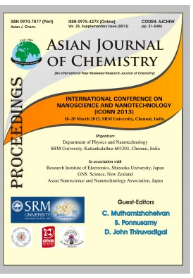

Synthesis and Characterization of Gd Doped ZnO Nanocrystals†

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Rare earth doped semiconductor nanocrystals are of great interest due to their applications in optoelectronic and display devices. By introducing the rare earth ions into semiconductor crystal at nano scale, the luminescence of semiconductor host crystal gets affected due to the interaction between these dopant ions and host crystal. Nanocrystals of zinc oxide with gadolinium doping were prepared by sol-gel method. Systematic structural studies on Gd^{3+} ion doped ZnO nanocrystals were carried out using X-ray diffraction, high resolution transmission electron microscopy. Steady state photoluminescence spectroscopy was also carried out to understand the excited state energy redistribution between the band to band transitions and the defect states (surface states) transitions. It was observed that by incorporation of Gd^{3+} ion into ZnO, the UV and visible emission of ZnO gets affected. Since luminescence of the host can be modified by incorporation of Gd^{3+} ions, display devices of required luminescence can be developed.

Key Words: ZnO nanocrystals, Gadolinium doped ZnO nanocrystals, Photoluminescence of semiconductors.

INTRODUCTION

Semiconductor nanocrystals are interesting as they have various applications in the field of photonics, such as opto-electronic devices, display devices, light emitting diodes (LEDs)[1] *etc*. Optical properties such as absorption and luminescence can be modified compared to bulk due to their size effect. When the size of nanocrystal is less than or of the order of exciton Bohr radius, their charge carriers are confined in dimensions. Due to this quantum confinement, band gap gets increased and absorption shifts towards the blue side of the spectrum[2]. Since nanocrystals have large surface to volume ratio as compared to bulk, surface defect state which originates from unsatisfied vacancies at surface (defect states) are increased and due to the interaction between the excitonic states and surface defect states, lifetime of carriers gets modified.

The group of II-VI semiconductors are of great interest out of which Zinc oxide (ZnO) is important due to its various properties like wide band gap, high exciton binding energy (60 meV) and because of this it has significant excitonic emission at room temperature. ZnO is also exploited as display device because of its UV and surface defect state emission that occurs in visible region[3]. The origin of UV emission is from band to band transition and surface defect state emission is due to unsatisfied vacancies present at surface. There have been attempts for controlling of excitonic and surface defect states emission in ZnO. Surface defect state emission is found to decrease by passivation of surface[4]. The controlling of emission from surface defect states can be done by two ways: one is by passivation of surface and other is by introducing rare earth ions in nanocystals. These rare earth ions are important as they have their filled energy levels but on incorporation into the host crystal they can interact with the host crystal as their parity states gets mixed. ZnO is a good host for rare earth ions because zinc ionic radius size is comparable to rare earth ions so that they can replace the zinc without distorting too much the crystal structure of ZnO nanocrystals. When rare earth ions are doped into ZnO nanocrystals then there can be structural change (size and shape) in the host material. The extent of this change depends on the distribution of rare earth ions since the rare earth ions may be distributed in the core of nanocrystals and on the surface. Rare earth ions which are present on the surface of nanocrystals affect the surface defect state transitions. Thus energy redistribution between band to band and surface defect states occurs due to structural change. The energy redistribution between rare earth ions and ZnO can also be further modified due to the energy level position of rare earth ions with respect to ZnO nanocrystals. Rare earth ions like terbium[5], europium[6], dysprosium[7] have been doped into ZnO nanocrystals. It has been observed that on incorporation

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of Tb^{3+} ions into ZnO nanocrystals, the emission due to surface defect states increases up to a certain concentration of Tb^{3+} ions and with higher concentration it gets decreased[5]. Gadolinium (Gd^{3+}) has also been doped into ZnO nanocrystals[8]. It was observed that when Gd^{3+} ions were doped in lower concentration, the surface defect state emission increased up to a certain concentration with no significant change in structure as in the case of Tb^{3+}, while on higher concentration of Gd^{3+}, crystallinity was found to be weak with smaller particle size and decreased surface defect state emission. However, the origin of this energy redistribution is not clear because the possibility could be due to the structural change or position of Gd^{3+} ions in ZnO nanocrystals. Rare earth ions like Tb^{3+}, Eu^{3+}, Dy^{3+} all have their energy levels within the band gap of ZnO nanocrystals. They are in vicinity of the surface defect states of ZnO nanocrystals thus interaction takes place between the surface defect states and rare earth ions levels. On the other hand, Gd^{3+} is specific because it possesses energy levels lying in the conduction band of ZnO nanocrystals, thus energy distribution between the Gd^{3+} and ZnO nanocrystals can be different as compared to other rare earth ions. The main aim of this work is to correlate the modification of the UV and visible emission of this coupled system by studying its optical and structural properties.

EXPERIMENTAL

Zinc acetate dihydrate was purchased from Dhawal Enterprises, Mumbai. Gadolinium acetate hydrate was purchased from CDH New Delhi. All the chemicals were used without any further purification. De-ionized water was used throughout the procedure.

Procedure: Sol gel method was used for the preparation of nanocrystals[5]. In the synthesis method 1.1 g zinc acetate dihydrate was refluxed with 50 mL ethanol. In a separate flask 0.29 g NaOH was sonicated with 50 mL ethanol at room temperature for 0.5 h. After this, NaOH was added drop wise to zinc acetate solution for 10 min and then whole mixture was left for stirring and then sonicate for 1 h. For removing the reaction by-products, sample was mixed with hexane and left for several hours. Then this supernatant was removed and again it was dispersed in ethanol with addition of hexane, this procedure was done for ten times. After then the product was air dried and collected for measurement. For Gd^{3+} doping a weight % of Gd acetate/Zn acetate was added to zinc acetate precursor solution keeping total metal ions concentration constant and rest of the procedure was same.

Detection method: Structural characterization was studied by high resolution transmission electron microscopy (HRTEM) and XRD. For HRTEM it was done by first dispersing nanoparticles in methanol solvent and then drop casted on Cu-grids. For XRD study powder samples were used, using Cu-K_α radiation. For element detection and relative concentration of Gd and Zn inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was done for which samples were diluted with de-ionized water with addition of dilute HCl. For optical properties, the steady-state absorption spectra was recorded by a Jasco V530 absorption spectrophotometer. Photoluminescence was done at 325 nm excitation with He-Cd laser source and an Acton monochromator attached with a cooled CCD camera was used to obtain the spectra. To study the decay dynamics time resolved photoluminescence was done with a tunable dye laser output at an excitation wavelength of 295 nm which was pumped by second harmonic (532 nm) of pulsed Nd-YAG laser (LITRON). Photoluminescence measurements were done under atmospheric conditions at room temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of ZnO and Gd doped ZnO nanocrystals (sample 1, sample 2, sample 3, sample 4 as given in the Table-1). All the diffraction peaks correspond to hexagonal wurtzite phase of ZnO. No diffraction peak due to impurity has been found. Particle size was calculated from Debye-Scherrer formula $d = 0.89\lambda/\beta\cos\theta$, where 0.89 is Scherer constant, λ is wavelength of X- rays, θ is Bragg diffraction angle and β is the full width at half maximum (FWHM) of diffraction peak. Particle size was found to be 12.7, 12.1, 11.0 and 10.6 nm for sample 1, sample 2, sample 3 and sample 4, respectively. It is clear from XRD pattern that with increased concentration of Gd^{3+}, particle size gets reduced due to confinement produced by Gd^{3+} ions in ZnO nanocrystals. Fig. 2 shows the TEM images of ZnO nanocrystals doped with Gd^{3+}. Particle size (Table-2) was found to be decreased with more Gd^{3+} concentration due to weak crystallinity as lattice fringes became smeared (Fig. 3) in the diffraction pattern. Fast Fourier transform (FFT) of the image associated with one of the particles is shown in the inset of the Fig. 2. FFT pattern in the inset confirms that ZnO nanocrystals were in the hexagonal wurtzite structure. The quantity of Gd^{3+} in ZnO was determined by energy dispersive X-ray analysis (EDX) for all the Gd-doped ZnO nanocrystals samples (not shown here) and the feature of Gd^{3+} suggests the association of Gd^{3+} with the nanocrytals. Variation of Gd/ZnO ratio with taken quantities of Gd acetate/Zn acetate is shown in Fig. 4. It was found that amount of Gd^{3+} in ZnO nanocrystals was in consistent with the taken quantities of Gd acetate/Zn acetate. It is also supported by the ICP-AES data for Gd/Zn given in Table-1. Fig. 5 shows the normalized absorption spectra obtained for ZnO and Gd doped ZnO nanocrystals. Average band gap has been calculated at energy at which absorption is half of its peak value. In each case band gap was found to be higher as comparison to ZnO (3.32 eV),which shows that confinement is affected when Gd^{3+} is incorporated in the ZnO nanocrystals. In the inset of Fig. 5, the variation of band gap with increased concen-tration of Gd^{3+} is shown according to which confinement increased with increament of Gd^{3+} ions in ZnO nanocrystals. In Fig. 6, photoluminescence spectra of Gd^{3+} doped ZnO are shown. It has two emission peaks , the first peak in range of 360-380 nm is UV emission due to band to band transition and second broad peak (550-650 nm) is due to surface defect states transitions in visible range. With Gd^{3+} ions doping, the visible emissions is found to be changed. In the inset of Fig. 6 the variation of visible emission normalized by UV normali-zation with respect to Gd^{3+} concentration is plotted. Surface defect state emission intensity increases with a concentrationof Gd^{3+} ions (sample 3) and with higher concentration it gets decreased. At lower

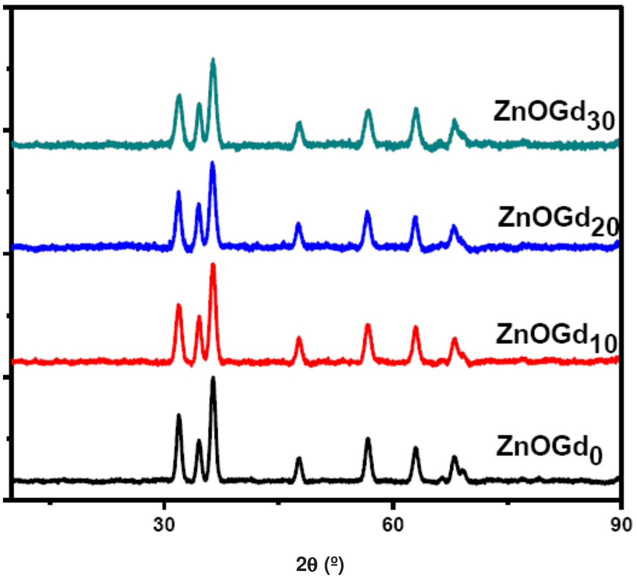


Fig. 1. XRD patterns of ZnO and Gd doped ZnO nanocrystals

TABLE-1
SAMPLE DETAILS WITH THE TAKEN AMOUNT AND DETERMINED WITH EXPERIMENTS

Sample	Sample detail	Gd/Zn (ratio %) as taken	Gd/ZnO (%) from (EDX)	Gd/Zn (ICP-AES)
Sample1	$ZnOGd_0$	0	0	0
Sample2	$ZnOGd_{10}$	10	1.47	0.18
Sample3	$ZnOGd_{20}$	20	1.87	0.28
Sample4	$ZnOGd_{30}$	30	2.9	0.43

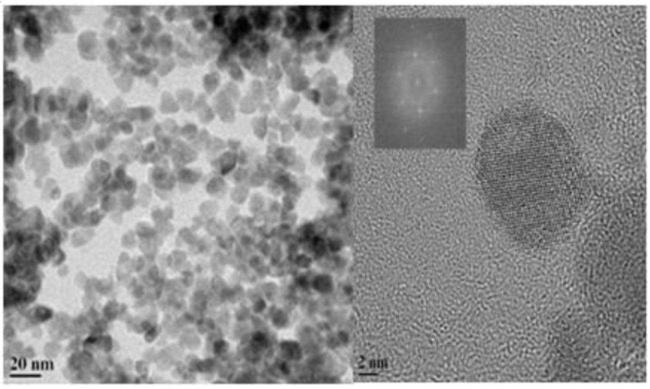


Fig. 2. TEM images of Gd doped ZnO nanocrystals

TABLE-2
SIZE OF NANOPCRYSTALS OBTAINED FROM VARIOUS EXPERIMENTS

Sample	Size (nm) from XRD	Size (nm) from TEM
$ZnOGd_0$	12.7	11.6
$ZnOGd_{10}$	12.1	10.8
$ZnOGd_{20}$	11.0	9.2
$ZnOGd_{30}$	10.6	8.9

concentration the reason for the increment of surface defect state emission could be due to increment of density of states. This increment of density of states may arise due to the incorporation of some oxides of Gd which mayreside on the surface of ZnO nanocrystals[9]. When the Gd concentration was further

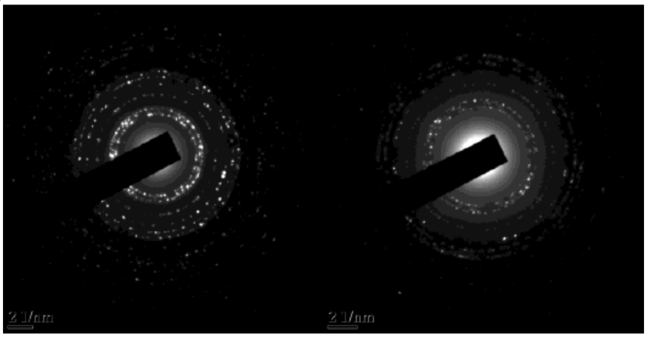


Fig. 3. Electron diffraction pattern of $ZnOGd_{10}$ and $ZnOGd_{30}$ nanocrystals

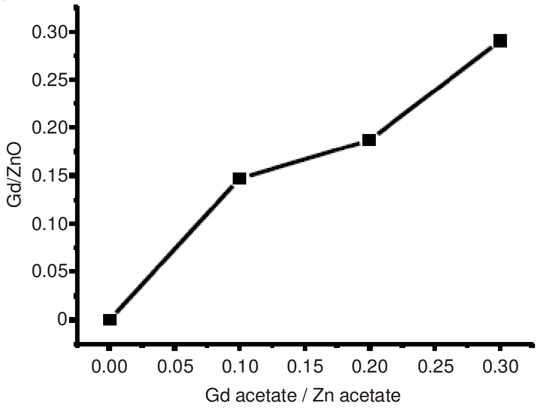


Fig. 4. Variation of Gd amount in ZnO confirmed by EDX

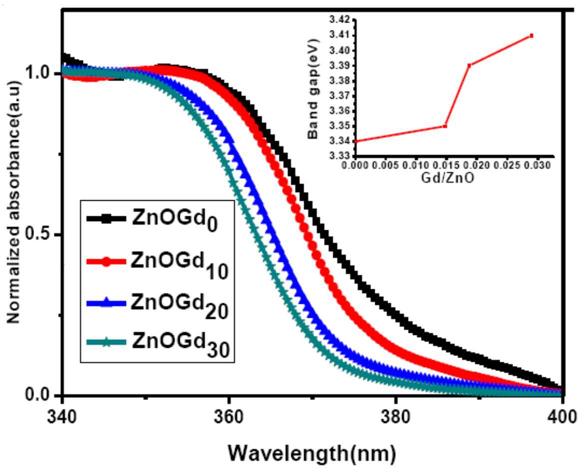


Fig. 5. Normalized absorption spectra for ZnO and Gd doped ZnO nanocrystals

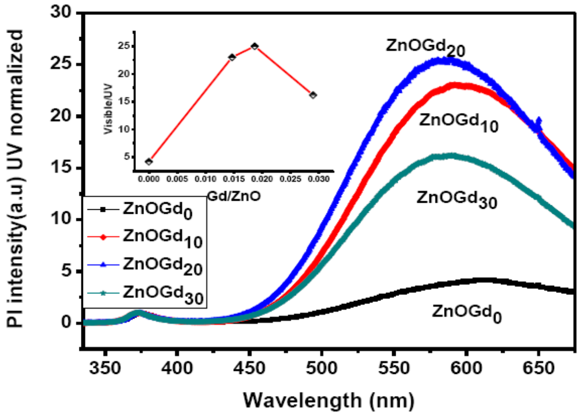


Fig. 6. Photoluminiscence spectrum at an excitation of 325 nm with respect to UV normalization

increased the emission of the surface defect states decreased due to the formation of Gd complex with ZnO nanocrystals. In this case the Gd^{3+} ions enter the core of the nanocrystals and do not affect the surface state emission. However since the size of the nanocrystals decreases as Gd^{3+} ions concentration increases, the surface defect states decrease and hence the emission decreases. Thus the two opposite effects, one introduction of surface states by Gd^{3+} ions and the other reduction of size by the incorporation of Gd^{3+} inside the core determine the increment and decrement of surface states emission with respect to Gd^{3+} ion concentration. The UV and surface defect state emissions in ZnO nanocrystals have different decay time. UV emission has fast decay time as compared to surface defect state as shown in Fig. 7 for sample 4. The reason is that band to band transition is allowed transition on the other hand surface defect states are forbidden in nature and thus decay time is larger for defect states. Time resolved photoluminescence has also been done for ZnO nanocrystals and Gd^{3+} doped ZnO nanocrystals (sample 4) to study the decay dynamics. In the Fig. 8 (a) and (b) time resolved photoluminescence for ZnO nanocrystals (sample 1) and Gd^{3+} doped ZnO nanocrystals (sample 4) are shown. As the delay time of the measurement increases, the percentage change of UV emission is more than that percentage change of defect states emission. After a delay of 15 ns, no UV emission is found.

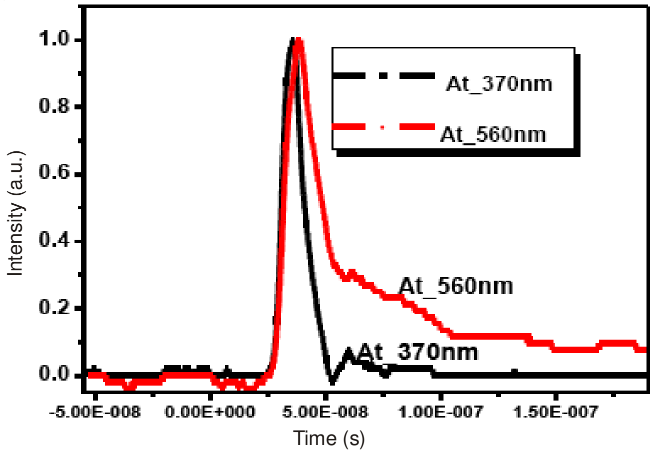
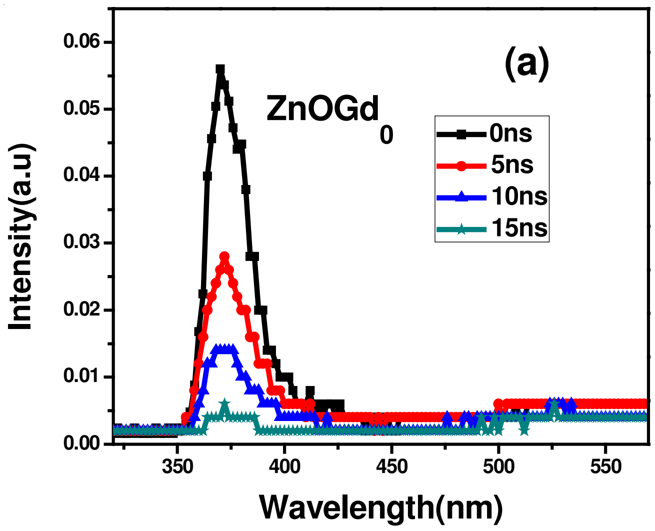


Fig. 7. Decay profile of UV and visible emission in $ZnOGd_{30}$ nanocrystals



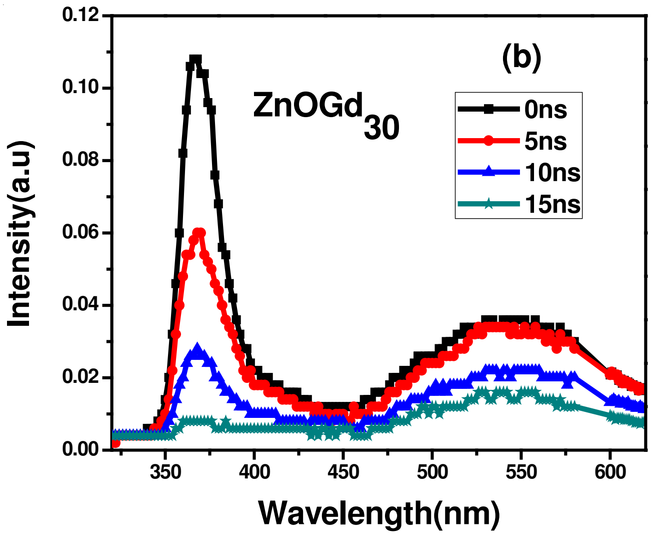


Fig. 8. (a) Time resolved photoluminiscence at an excitation of 295 nm for ZnO and (b) Gd doped ZnO nanocrystals

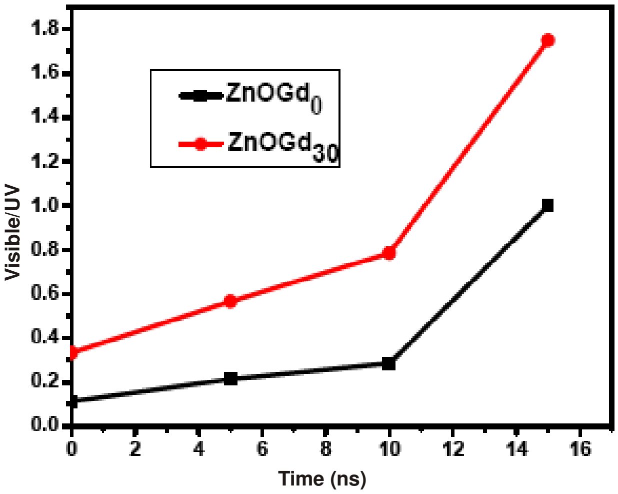


Fig. 9. Variation of visible/UV emission ratio with respect to time for ZnO and Gd doped ZnO nanocrystals

Fig. 9 shows the ratio between visible and UV emission with respect to time delay. As seen the visible/UV is more when Gd^{3+} is incorporated. At delay time of 15 ns since the difference of ratio is more, it is concluded that the lifetime of defect state emission is increased as Gd^{3+} is incorporated into the ZnO nanocrystals.

Conclusion

From our systematic structural, steady state and time resolved optical studies, it was observed that the emission ratio between the visible (defect states) and excitonic states (UV) can be modified by suitably incorporated Gd^{3+} ion in the ZnO nanocrystals. This coupled system can be exploited cleverly for suitable photonic devices.

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