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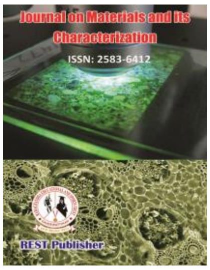

Defect Assisted Efficient Energy Transfer from ZnO host lattice to Eu ion in ZnO porous nanostructures

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Abstract: *In the present work, Eu doped ZnO porous nanostructures have synthesized using one step simple solution combustion method. Incorporation of Eu ion in ZnO nanostructures has been confirmed by XRD analysis. The photoluminescence spectra of pure ZnO nanostructures shows broad defect related emission in orange region. The orange emission is less commonly reported and it arises from optical transitions in the single negatively charged interstitial oxygen ion (O_i). Eu^{3+}-doped ZnO nanostructures, which emit in the visible light region and are non-toxic, have great potential for applications in photonic devices, light-emitting diodes, and bio imaging.*

1. INTRODUCTION

Owing to a direct wide band gap (3.37) with large binding energy (about 60meV) at room temperature, and peculiar optical properties, ZnO is a promising candidate for optoelectronic applications [1] A relevant number of studies indicate ZnO as one of the most efficient oxide-based phosphors in both photoluminescence (PL) and electroluminescence (EL), either in the form or powder [2-4]. In many cases, under proper excitation conditions, ZnO shows a green band, centered at about 500nm, and a UV band at about 370 nm. The UV band has an excitonic nature [5], whereas the origin of the greem emission still represents a matter of debate and is mainly attributed to the presence of electronic defects in the ZnO band gap and/or to surface states [6-10].

Now days, Nanostructured ZnO have attracted much attention for both fundamental and technological reasons [11-15]. However, it has been realized that controlling the morphology or size is not always well suited. As it is well known that doping in with a selected element(s) can offer the possibility to adjust the optical property of the semiconductor, the luminescent properties of ZnO nanostructures have also been shown to be sensitive to many external dopants. By doping with luminescent centers such as transition or rare-earth ions, the emission properties of ZnO can be tailored toward selected wavelength in the visible region, which is of interest for a variety of applications including multicolor emission in light emitting devices [8, 16]

Rare-earth ions possessing special 4f intra-shells are recognized as excellent candidate for luminescent centers due their many optical advantages, such as sharp fluorescent emissions via intra-4f or 4f-5d transition, large stoke shift, no photo bleaching and long luminescent lifetime. Further research predicts that an energy transfer process from excited semiconductor host to doped rare-earth ions helps to circumvent low absorption of optically center ions with showing remarkably improved luminescent properties [17, 18, 29, 30].

Doping of trivalent rare-earth ions into ZnO lattice remains disappointing and could be attributed to two difficulties. The first one is the low saturated concentration of rare-earth ion in ZnO lattice due to large difference in ionic size and charge imbalance [19]. The second difficulty is the inappropriate energy level position of rare earth ion relative to the valence band and conduction band of ZnO host [20]. However, a lot of work has been done on rare-earth ion doped ZnO films and nanocrystals [21-24]. In these studies, it was shown that rare-earth ions can be incorporated in ZnO and exhibit intra-shell 4f transition under direct or indirect excitation. In the case of indirect excitation, intra-shell 4f transition of rare-earth ions always accompanied with defect related visible emissions. A few papers reported the luminescence of rare-earth ions adsorbed at the nanostructure semiconductor surface [25] or nanostructure semiconductors adsorbed on rare-earth ion containing species [26]. Therefore, an important issue needs to be addressed whether rare-earth ions are really being incorporated in the nanocrystalline structure or are they adsorbed at the nanoparticle's surface, and their effect on optical properties.

In recent years a variety of methods have been used to synthesize rare-earth doped ZnO nanostructures. In the present work, Eu doped ZnO sample was synthesized by using a very simple, one step solution combustion method with 0.1% doping. A number of characterization techniques have been employed to understand effect of doping on the optical and microsrtuctural properties of ZnO. Contrary to number of reports, an efficient energy transfer from ZnO host to Eu, with complete quenching of defect related emission has been reported in the case of sample synthesized by solution combustion method with nominal doping concentration.

2. EXPERIMENTAL DETAILS

2.1 Chemicals: Zinc Nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and anhydrous ammonium carbonate [$(NH_4)_2CO_3$] from Merck (Mumbai, India) were used as precursors for ZnO. Europium Nitrate [$Eu(NO_3)_3.6H_2O$] was used as the starting material for doing. Urea from Merck (Mumbai, India) is used as fuel for solution combustion method. All the chemicals were of analytic grade and used as received without any further purification.

2.2 Sample Preparation: A stoichiometric ratio of Zn $(NO_3)_2.6H_2O$ and urea was mixed with little amount of water. 0.1% Eu was added. After mixing, the starting materials, placed in a crucible, were then introduced into a muffle furnace at 550^0C for 15 min. As the ignition occurred, the reaction went on vigorously for few seconds. A fluffy product is obtained after the combustion reaction.

2.3 Characterization: All the measurements for characterization were performed at room temperature. The X-ray diffractometry (XRD) for the crystal structure of the dried powder samples was carried out at Rigaku D/MAX-2200 H/PC diffractometer. The emission measurements were carried out using 355 nm Nd- YAG pulsed laser (Litron lasers, Nano TRL system) as excitation source. An iHR320 (Horiba Jobin Yvon) spectrometer was used to disperse and detect the signal.

3. RESULTS AND DISCUSSION

3.1 SEM Analysis

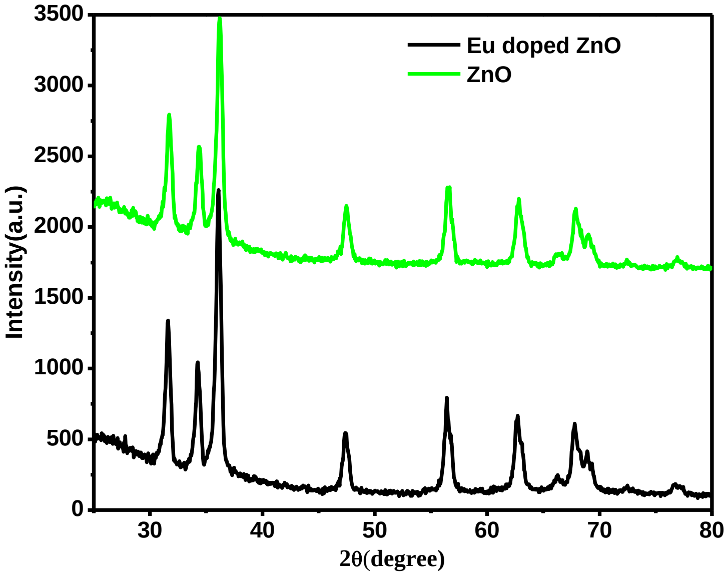

FIGURE 1. XRD patterns of pure ZnO, Eu doped ZnO nanostructures

Figure 1 shows the XRD patterns of pure, Eu doped and Eu, ZnO nanostructures. It is interesting to see that all the diffraction peaks of pure ZnO and Eu doped ZnO nanostructures could be readily index to wurtzite type ZnO (hexagonal structure; JCPDS Card No. 79-0207). No diffraction peaks from any other chemical species such as europium oxides are detectable in these samples. The shifting in XRD (101) peak positions for higher diffraction angle has been observed for Eu doped ZnO samples. The calculated lattice constants are shown in Table 1.

TABLE 1. The calculated lattice parameter for pure and doped ZnO nanostructures

	(101) peak position	*d*-spacing	Lattice parameter, *a* (Å)	Lattice parameter, *b* (Å)
ZnO	36.1755	2.4815	3.24332	5.28661
ZnO:Eu,	36.1159	2.4849	3.24776	5.29386

The observed increase in lattice parameters for ZnO:Eu, can be attributed to large ionic radius of Eu^{3+}(0.95 Å) as compared with Zn^{2+} (0.74Å), indicating that incorporated Eu^{3+} ions occupy the lattice sites of Zn^{2+} and lead to the increase in inter-atomic distance and expansion in lattice constants.

3.2 SEM Analysis

Figure 3 shows the SEM images of Eu doped porous nanostructures. It is clear from SEM images that as synthesized samples have large surface to volume ratio. This indicates that Eu doped porous nanostructures are rich in surface related states.

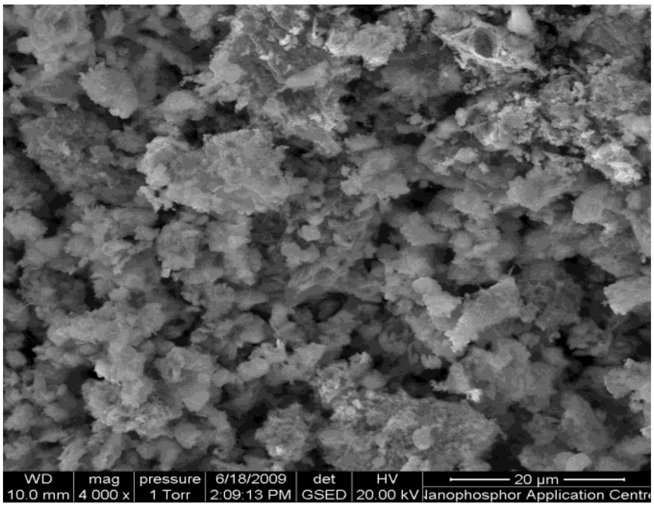

FIGURE 3. SEM image of Eu doped ZnO porous nanostructures synthesized by solution combustion

3.4 Photoluminescence Study

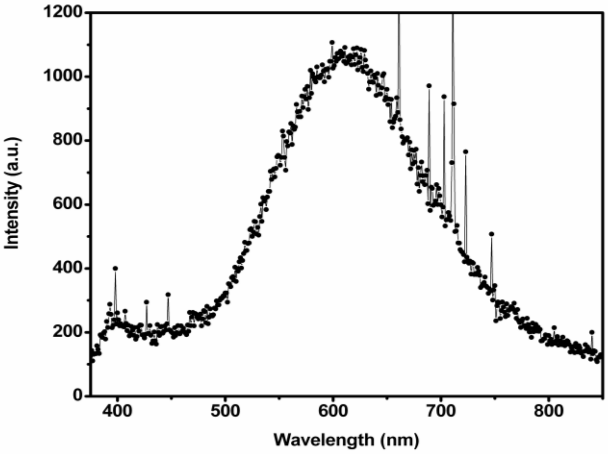

FIGURE 4. photoluminescence spectra of porous ZnO nanostructures synthesized by solution combustion under 355 nm excitation.

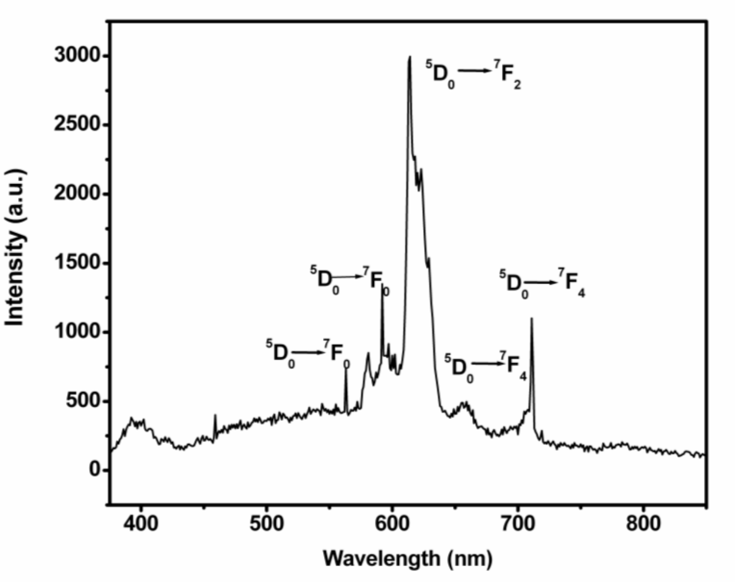

FIGURE 5. photoluminescence spectra of Eu doped porous ZnO synthesized by solution combustion under 355 nm excitation

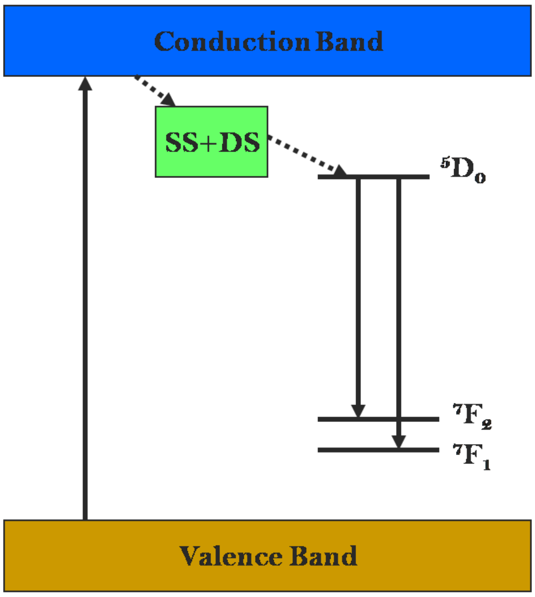

FIGURE 6. Schematic diagram of energy transfer from ZnO to rare-earth ions.

The photoluminescence spectra of Eu doped porous ZnO (Figure 5) shows efficient energy transfer from ZnO to Eu ion, with complete quenching of defect related emission. The photoluminescence spectrum of porous ZnO shows the presence of large amount of defects and large density of surface states and can be expected due to large surface area of porous ZnO (Figure 4). Here, it can be expected that the surface and defect states assist the energy transfer from ZnO to Eu ion. Schematic diagram of energy transfer is shown in Figure 6.

This type of energy transfer process have been reported previously [28] but in that case defect related emission is also observed in addition to 4f-4f intra shell transitions.

4. CONCLUSIONS

Eu^{3+} doped porous ZnO synthesized by solution combustion method exhibit strong Eu related 4f-4f transition with complete quenching of defect related emission. This shows that rare-earth ion can be incorporated in ZnO and efficient energy transfer from ZnO to rare-earth is possible. The result highlights the potential of Eu^{3+}-doped ZnO nanostutures for applications in photonic devices, light-emitting diodes (LEDs), and bio-imaging due to their tunable optical properties and efficient energy transfer mechanisms.

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