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# A study of structural parameters and photoluminescence of Tb doped ZnO nanoparticles

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#### ABSTRACT

Systematic structural studies on  $Tb^{3+}$  ion doped ZnO nanoparticles were carried out using X-ray diffraction, X-ray photoelectron spectroscopy and photoluminescence studies. Our XRD study shows a contraction effect as the dopant ion concentration is increased. The dislocation densities and the surface area calculation also show an increase up to a certain concentration of Tb, which reveals the increase in the surface defects when Tb is incorporated in ZnO host lattice. PL study confirms the presence of band edge as well as defect related transition.

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#### 1. Introduction

ZnO semiconductor nanocrystals are among the nanoscale materials that have been investigated the most in the last few decades, both from the fundamental point of view and for their exploitation as active materials in a wide variety of applications [1–3]. ZnO nanoparticles are of great interest as they can be grown easily which reduces the production costs. In these materials, quantum confinement effects originate when a critical size is reached, which leads to a widening of the band gap. Band gap be tuned by varying the size of the nanoparticles [4,5]. Many interesting aspects of nanostructures are also related to the significant fraction of atoms residing at their surface, which have a profound impact on their optical and electronic properties. Emission from the ZnO nanoparticles can easily be tuned by varying the size or the composition of the nanoparticles without changing their processing properties. ZnO nanoparticles also show great promise for use in optoelectronic properties, owing to their unique optical properties. These nanoparticles have attracted tremendous attention due to their potential for applications in dye-sensitized solar cells, gas-sensors [6,7]. This material also has a lot of prospects for application in light emitting diodes (LEDs) [8,9] especially in UV-LEDs. The prospect for UV-device applications is impaired as the UV luminescence intensity is found to reduce due to the presence of a broad band luminescence in these types of materials [10-12]. Although the broad band luminescence can be utilized for the fabrication of visible light optoelectronic devices but in order to construct UV light devices we need to completely quench the broad band luminescence. In this way, we can utilize both the UV and broad band luminescence to produce ZnO nanoparticles based optoelectronic devices. By reducing the size of these nanoparticles, one can change the electron-phonon coupling strength as well that can influence the quantum efficiency of the nanoparticles. In addition, high fluorescence quantum yield (QY) and photochemical stability can also be achieved by careful modification of the nanostructures surface which may improve the efficiency and stability of the devices [10-14]. A wide variety of semiconductor nanocrystals can be chemically synthesized either in organic or aqueous solutions. Electronic, chemical and surface properties of the host lattice can be altered by the substitution of an appropriate dopant element [15–17]. Rare earth elements are on high demands now a day for being used as dopants for various applications due to their highly magnetic, electrochemical and luminescent properties. Furthermore, for gas sensing applications also, rare earth element doped metal oxides have been proved to be promising candidates for improving sensing behaviour because

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of their effective catalytic nature, fast oxygen ion mobility and high surface basicity [18–27].

The X-ray line broadening is used for the investigation of dislocation distribution. The nanoparticle size and the lattice strain affects the X-ray diffraction peak in different ways and both these effects has an impact on the peak width, peak intensity and shifts the 20 peak position accordingly. The broadening of the diffraction peaks of materials results in the deviation observed when compared with that of the perfect crystal. We can extract the information of nanoparticle size and lattice strain from the XRD peak width analysis. Lattice strain can be defined as a measure of the distribution of lattice constants arising from crystal imperfections, such as lattice dislocation [20-22,28]. X-ray diffraction peak profile analysis is a powerful technique to evaluate the peak broadening with particle size and lattice strain caused by dislocation of ions in the lattice. The average particle size from the XRD profile can be estimated using Debye Scherer's formula.

$$t = 0.9\lambda/\beta_{hkl}\cos\theta \tag{1}$$

The Zn–O bond length (L) is given by Eq. (2).

$$L = \sqrt{\left(\frac{a^2}{3}\right) + \left(\frac{1}{2} - u\right)^2 c^2} \tag{2}$$

where u is the positional parameter in the wurtzite structure and measures the amount with which each atom gets displaced with respect to the next [29,30] and the value of u can be calculated using Eq. (3).

$$u = \frac{a^2}{3c^2} + 0.25 \tag{3}$$

The strain-induced broadening in powders, caused by crystal imperfection and distortion has been calculated using the Eq. (4):

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \tag{4}$$

In order to get an overview of the crystallographic defects or irregularity within a crystal structure Dislocation density can be measured. Hence, we can say that the dislocation density is a measure of the dislocations/irregularities in a crystal which are present in a specific quantity [31,32]. Dislocation density is the length of dislocation lines per unit volume of the crystal. The value of dislocation density is calculated using Eq. (5) [33,34].

$$\delta = 1/D^2 \tag{5}$$

where D is the crystallite size.

Specific surface area is a property of solids which is the total surface area of a material per unit of mass. The values obtained for specific area depend on the method of measurement. The specific surface area calculations can be done using Eq. (6) [35–37].

$$S = \frac{6 \times 10^3}{D\rho} \tag{6}$$

In this work we have used terbium rare earths as a dopant to engineer the surface as it introduces defect which are associated with oxygen vacancies [18–22]. In the present work, ZnO and rare earth doped ZnO has been prepared by following wet chemical route. Here, we present a systematic study of the structural and optical properties of the synthesized ZnO and Tb doped ZnO nanoparticle samples. The X-ray peak profile analysis was also carried out for estimating the nanoparticle size, lattice strain, dislocation density and surface area of the undoped and Tb doped ZnO nanoparticles.

#### 2. Experimental details

Tb doped ZnO nanoparticles were synthesized by a sol-gel technique [38]. In this process Zn acetate and Tb-acetate powders were mixed in 50 ml ethanol at room temperature. The Tb acetate molar ratio is varied from 0 to 30% in order to control the Tb molefraction in ZnO. The mixture is then transferred into a distillation apparatus and boiled under vigorous stirring at 60 °C. Ethanolic solution of LiOH·2H<sub>2</sub>O powder was prepared in a separate container. The LiOH<sub>2</sub>H<sub>2</sub>O suspension was kept in an ultrasonic bath at room temperature for 20 min to obtain a homogeneous solution. The LiOH ethanol solution was then added drop wise to the Zinc acetate solution at 80 °C and subsequently, placed in an ultrasonic bath for one hour at room temperature. To separate Tb doped ZnO nanoparticles from the solution, decantation process was adopted. Hexane was added drop wise to the mixture until a turbid solution was formed. This solution was left at room temperature for 3 h. Hexane dissolved all the by-products and Tb doped ZnO nanoparticles were separated from the solution as precipitate. The precipitate was collected and re-dissolved in ethanol. Hexane was again added to the solution. This process was repeated for several times. Finally, the white precipitate was dried in air and Tb doped ZnO nanoparticles were collected as powder. The structural properties of the nanoparticles were investigated by high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) and X-ray photoelectron spectroscopy. Optical properties were investigated through steady state photoluminescence (PL), UV-VIS Absorption and FTIR spectroscopy.

#### 3. Results and discussion

#### 3.1. Structural characterizations

Fig. 1(a), (b) and (c) shows a typical TEM image of the undoped ZnO and Tb doped ZnO nanoparticles for Tb mole fraction of x = 0.01 and 0.07. Distinct particles with diameter  $\sim 10-12$  nm are visible in the image. The insets in the figure also show the HRTEM image of the same nanoparticles. From HRTEM images the lattice spacing's comes out to be 2.89 Å, 2.7 Å and 2.89 Å for the nanoparticle samples respectively. The EDX patterns for all the nanoparticles are shown in the inset which confirms the presence of Tb in the ZnO nanoparticles. It is observed from Fig. 1(b) and (c) that the Tb peaks increases with respect to the Tb mole-fraction. It clearly suggests that Tb incorporates in the ZnO nanoparticles with the increase in Tb mole-fraction.

Fig. 2 compares the XRD profiles within a smaller range of  $2\theta$  for samples with different Tb mole-fractions. The wide angle X-ray diffraction pattern for ZnO and Tb doped ZnO nanoparticles with Tb mole-fraction of 0, 0.02 and 0.045 are also shown in Fig. 2. All the XRD peaks were indexed by hexagonal wurtzite phase of ZnO (JCPDS Card No. 01-089-0510) [25]. The XRD pattern of the undoped and Tb doped nanoparticles indicates the formation of hexagonal wurtzite phase of ZnO which is in agreement with the electron diffraction results. The peak broadening of the XRD profiles clearly indicates that nanoparticles are present in the samples. There is no evidence of impurity phase in the XRD profiles. A slight shift in reflection peaks of the diffraction pattern of Tb substituted ZnO nanoparticles to higher angle than those of pure zinc oxide nanoparticles is observed. It shows that incorporation of Tb<sup>3+</sup> into ZnO nanoparticles creates some defects which modify the ZnO crystal. However, an insight analysis of the position of the XRD peaks indicates shifting of peaks towards lower angle with further rise in Tb ion content. The change in the position of peaks (100) (002) and (101) clearly shows that Tb ion is modifying the surface either by accumulating on the ZnO nanoparticle to some extent and also getting incorporated for higher Tb mole fraction

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**Fig. 1.** HRTEM image and EDX profile for a (a) ZnO nanoparticle sample (b) Tb doped ZnO nanoparticles with the Tb mole-fraction *x* = 0.01. (c) Tb doped ZnO nanoparticles with the Tb mole-fraction *x* = 0.07. Inset shows a HRTEM image for the same nanoparticles.



**Fig. 2.** X-ray diffraction (XRD) profiles within a 20 range of  $30^{\circ}$ -40° for samples with different Tb mole-fractions. Inset shows the wide angle XRD profile for a Tb doped ZnO nanoparticle sample with *x* = 0.

[26]. The primary investigation doesn't show the traces of Li in the nanoparticle samples

It is a well-known fact that the lattice parameters show a remarkable change after an addition of various dopant ions. In this process of doping, ionic radii plays an important role. According to Vegard's law, if the ionic radii of dopants are higher or lower than the host lattice, then lattice parameters of host increases or decreases respectively to accommodate it. The values of *a* and *c* lattice constants for undoped and all the Tb doped ZnO nanoparticles are obtained from the XRD peak positions. These values of *a* and *c* lattice parameters for ZnO and all Tb doped ZnO nanoparticle samples are plotted as a function of the Tb mole fraction in Fig. 3.

Both the lattice constant decreases with the increase of Tb mole-fraction x upto a value of x = 0.04 but their ratio remains unchanged. Further increase in the Tb mole fraction shows an



Fig. 3. *a* and *c* lattice constants as a function of the Tb mole fraction.

increase in the lattice parameters, which clearly resembles the incorporation of Tb ion in the host ZnO lattice. These results implies that the variation of the lattice constants is due to some strain developed in the ZnO lattice due to the Tb incorporation either on the surface or in the core [31]. It should be clearly noted that the observation of contraction of the lattice is contradictory as Tb has atomic radius larger than that of Zn and thus, an expansion is expected. Hence, this finding suggests that instead of replacing Zn in the core of the nanoparticles, Tb accumulates on the surface by creating defects, for the initial increase in Tb mole-fraction in ZnO nanoparticles which modifies the surface.

The volume of unit cell has been calculated using the Eq. (7):

$$V = \frac{\sqrt{3}}{2}a^2c \tag{7}$$

where a and c are lattice parameters. It has been found that the volume of unit cell decreases with rise in Tb ion content which may be attributed to the decrease in the lattice parameters *a* & *c*. The values

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of unit cell parameters and volume of the unit cell for the undoped and Tb doped ZnO nanoparticles are given in Table 1. It indicates that Tb ions are present on the surface of ZnO lattice for initial increase in Tb content and generating a hydrostatic strain which compresses the lattice showing a reduction in the volume of the unit cell. Beyond Tb content x = 0.04, we can see an increase in the volume of the unit cell clearly indicating the expansion of the lattice. This could be attributed to the incorporation of the Tb in the core as well as on the surface at higher Terbium concentration. Atomic packing fraction (APF) has also been calculated using equation (8) and the values are listed in Table 1.

$$APF = \frac{2\pi a}{3\sqrt{3}c} \tag{8}$$

where *a* & *c* are lattice parameters [32]. It is found from the values that the APF first decreases with increasing Terbium content which may due to the increase of voids in the samples. The APF of bulk hexagonal ZnO lattice is about 74% but in this study the APF of Tb doped ZnO nanoparticles is more than 75% which depicts that APF in nanoparticle samples is slightly greater than that of bulk materials [39,40].

The positional parameters u has been calculated for the undoped and Tb doped ZnO nanoparticles using Eq. (3). It has been observed that the value of u decreases slightly in such a way that the four tetrahedral distances almost remain nearly constant by distorting tetrahedral angles. The Zn–O bond length calculated using eq. (2) for our nanoparticle samples comes in the range of 1.9669 Å–1.9812 Å; whereas the reported Zn–O bond length in the unit cell of bulk ZnO and neighboring atoms is 1.9767 Å [33]. There is a good agreement of the calculated & actual bond length which supports the results of present study. The value of the Zn–O bond lengths (L) and positional parameter value (u) for all the ZnO nanoparticles and is listed in Table 2.

Fig. 4 depicts the variation of strain calculated from the intent  $(1 \ 0 \ 1)$  peak of the undoped and Tb doped ZnO nanoparticles with respect to varying Tb concentration. The strain for all the nanoparticles was estimated using eq. (4). It reveals that the value of strain increases with the increase in Tb concentration up to x = 0.04 while it decreases further for Tb concentration beyond x = 0.04. This observation is in agreement with the results obtained from XRD data. Fig. 2 clearly depicts that FWHM of the reflection peaks changes after addition of dopant ions. There is also a slight shift in

#### Table 1

Volume and APF of the undoped ZnO and Tb doped ZnO nanoparticles extracted from XRD profile.

Tb mole fraction (x)	a (Å)	c (Å)	Volume (Å) <sup>3</sup>	APF (%)
0	3.23	5.18	46.51	75.4
0.02	3.21	5.16	46.04	75.3
0.03	3.2	5.14	45.58	75.2
0.04	3.17	5.12	44.55	74.9
0.06	3.225	5.16	46.48	75.6
0.07	3.248	5.18	47.32	75.8
0.09	3.26	5.2	47.86	76.0

#### Table 2

Positional parameter and bond length of ZnO and Tb doped ZnO nanoparticles.

Tb mole fraction $(x)$	Positional parameter $(u)$	Zn-O bond length (Å)	
0	0.3796	1.9669	
0.02	0.3789	1.956	
0.03	0.3792	1.9492	
0.04	0.3778	1.9346	
0.06	0.38	1.9621	
0.07	0.381	1.974	
0.09	0.381	1.9812	



Fig. 4. Lattice strain calculated from XRD profile for ZnO and Tb doped ZnO nanoparticles as a function of Tb mole-fraction.

peak positions, and their full width at half maximum (FWHM) in the samples having different Tb content as compared to the undoped ZnO nanoparticles. This shift corresponds to the strain generated on the host lattice and replacement of some zinc ions with that of  $Tb^{3+}$  ions. It has been reported in the literature that with addition of foreign particle/dopant in the crystal lattice, a strain and defect(s) is introduced in the lattice which may result in reduction of crystal quality [26,27].

Fig. 5 shows the dislocation density plotted with respect to the Tb mole fraction x. It has been observed that the dislocation density first increases with the increase in Tb concentration and then show a decrease in the value for further increase in Tb concentration.

The dislocation density and the specific surface area of the prepared samples are calculated using eq. (5) and listed in Table 3. The specific surface area values obtained using Eq. (6) (values listed in Table 3) shows an increase with Terbium concentration which clearly suggests that in a given regime the Tb is mostly present on the surface as defects. But at a later stage when Tb is incorporated further, the value of surface area goes down as the Tb now gets incorporated in the ZnO lattice. The value of dislocation densities and specific surface area clearly indicates that the ZnO host lattice gets modified with the incorporation of Tb in it.

Surface energy density  $\gamma$  has to be positive in order to have a compressive hydrostatic strain in the lattice.  $\gamma$  value were also estimated using the *a* and the *c* lattice constants and are reported elsewhere [26]. The values of  $\gamma$  plotted as a function of the Tb mole-fraction clearly show an increase with *x*, which is due to the increase of the Tb coverage on the surface of the nanoparticles



Fig. 5. Dislocation densities of undoped and Tb doped ZnO nanoparticles as a function of Tb mole-fraction.

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 Table 3

 Strain, dislocation density and specific surface area of undoped ZnO and Tb doped ZnO nanoparticles.

Tb mole fraction (x)	Strain	Dislocation density [10 <sup>-3</sup> (nm) <sup>-2</sup> ]	Specific surface area
0	0.00575	4.5	56.32
0.02	0.00585	4.8	60.45
0.03	0.00667	5.9	64.85
0.04	0.00855	8.9	83.6
0.06	0.00717	7.78	71.32
0.07	0.00669	6.5	65.64
0.09	0.00456	2.7	44.03

with the increase of Tb mole-fraction. This surface induced hydrostatic strain is also responsible for the enhancement of the band gap energy with the Tb mole-fraction [26,31].

#### 3.2. Optical characterization

Photoluminescence spectroscopy technique involves the emission of light as a result of excitation by a light source. The sample absorbs photon from a monochromatic source such as a laser or Xe lamp, which results in electron excitation from the valence band to the conduction band. Excited electrons may lose their energy by radiative or non-radiative recombination process. The PL study at room temperature provides information of different energy states available between valence and conduction bands responsible for both the recombination processes.

Fig. 6 shows the PL emission ( $\lambda_{exc}$  = 325 nm) obtained from our undoped and a Tb doped ZnO nanoparticles with x = 0.02.

Fig. 6 clearly shows the presence of two emission bands for both the samples. A weak UV emission band is observed at 3.31 eV for ZnO and at 3.38 eV for Tb doped ZnO nanoparticle (with x = 0.02) respectively. The UV intensity for both the sample is normalized to get an idea about the intensity of broad band luminescence. The UV luminescence band of Tb doped ZnO nanoparticle sample shows a blue shift as compared to the undoped ZnO nanoparticles. The other peak is a stronger and broader visible emission that spans in the range of 2.5–1.7 eV. The UV emission is results from the excitonic recombination corresponding to the near band edge emission of ZnO nanoparticles. The UV emission was found to be

very weak as compared to the broad band luminescence intensity for both the samples. The weak UV emission in this experiment could be due to the high trapping rate of charge carriers at the surface sites relative to the fast radiative recombination rate [18–20]. There are various reports claiming that the visible emissions in ZnO originates from the intrinsic defects such as oxygen vacancy, oxygen interstitial, zinc vacancy, zinc interstitial and antisite oxygen in ZnO crystal [38-42]. Several co-workers have reported that in case of nanoparticles, the intent broad band luminescence is attributed to the presence of defects on the surface in the form of chemical species such as hydroxyl groups, carboxyl groups etc. which are not chemically bonded to the surface [43,44]. We have found that the intensity of broad band luminescence in our Tb doped samples is several times more than that of undoped ZnO nanoparticles. The reason for stronger intensity of broad band in Tb doped ZnO samples could be due to the accumulation of Tb ions on the surface that attaches more number of these chemical groups available as defects on the surface. The stronger intensity of the broad band luminescence resembles the presence of intrinsic (oxygen and zinc vacancies or interstitials) defects as well as the surface defects (physically adsorbed chemical species/accumulation of Tb ions). The intensity of the visible emission thus seems to depend mainly on the surface states. Reports are there which shows that the luminescence properties are entirely dominated by properties of the surface below a certain size [41,42,45]. The room temperature photoluminescence spectroscopy indicates that large amount of surface states related to weakly bonded chemical species are present in the sample.

Fig. 7 show the FTIR spectra recorded for a Tb doped ZnO nanoparticles with Tb mole-fraction x = 0.02 under the atmospheric and vacuum conditions. The figure clearly resembles certain absorption features which are visible under both the conditions. The features appearing between 1390 and 1510 cm<sup>-1</sup> are attributed to the stretching modes of the acetate group (-COOH) [43,44]. This group gets linked to the surface of the nanoparticles during the synthesis of nanoparticles. The absorption peak at 1000 cm<sup>-1</sup> corresponds to C-O deformation mode of the acetate groups. The presence of few peaks appearing at around 2910 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> could be attributed to the presence of C-H bond [43]. The broad peak which appears at  $3400 \text{ cm}^{-1}$  is due to the presence of the hydroxyl (-OH) group [43-45]. FTIR results clearly indicates that the density of the hydroxyl and the acetate groups decreases when the study is performed under vacuum condition, which further infers that these groups are attached to the surface of the ZnO nanoparticles. As these groups are not



**Fig. 6.** Room temperature PL spectra obtained for ZnO and Tb (x = 0.02) doped ZnO nanoparticle sample under the atmospheric conditions.



**Fig. 7.** FTIR spectra for a Tb doped ZnO nanoparticles with Tb mole-fraction *x* = 0.02 under atmospheric condition (Curve 1) and vacuum condition (Curve 2).

Please cite this article as: A. Sharma, V. N. Rai, S. Mani et al., A study of structural parameters and photoluminescence of Tb doped ZnO nanoparticles, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2019.05.377 chemically bonded to the surface, it is easy to remove them by evacuation. FTIR studies performed on undoped ZnO nanoparticles under atmospheric and vacuum condition have been reported elsewhere which shows similar behaviour [45].

XPS study performed on these nanoparticles also gives a confirmation of presence of these groups on the surface of ZnO and Tb doped nanoparticle samples [25,45]. EXAFS study performed on these samples also confirms the presence of Tb in the nanoparticles and the change in Zn-O-Tb and Tb-O-Tb stretching with the change in Tb concentration [46].

#### 4. Conclusion

ZnO and Tb doped ZnO nanoparticle samples were synthesized using sol-gel route. Various parameters such as positional parameter, Zn-O bond length, Dislocation densities and Specific surface areas for the undoped ZnO and Tb doped ZnO nanoparticle samples were calculated from the XRD peak profile of the samples. XRD study clearly suggests that the surface has been modified after Tb was added as a dopant in ZnO host lattice. The structural study reveals that surface here has a major role to play. Tb ion incorporation in the ZnO crystal generates a hydrostatic strain which introduces crystallographic defects in these nanoparticles. All the parameter show a distinct variation from its bulk counterpart which is attributed to the size effect also. PL and FTIR study suggests that the optical properties of these nanoparticles are getting influenced by the attachment of certain adsorbed groups. Under the atmospheric condition, we see that the major part of the broad band luminescence arises due to the presence of the chemical species on the surface of the nanoparticles. It is also found that the density of these defects in the form of surface groups (physisorbed chemical species) is found to increase with the Tb mole-fraction. which results in an increase of the broad band intensity with x under the atmospheric condition. The study also reveals that for high value of Tb concentration in ZnO nanoparticle, the broad band luminescence band results from the surface groups as well as the intrinsic defects.

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