Chapter IV

Europium Doped ZnO Nanoparticles

Results and Discussion
Zinc oxide is a well known conventional phosphor material giving luminescence in UV (band edge luminescence) as well as visible-green (defect level luminescence) emission. One can change these optical properties by incorporating another ion into ZnO lattice, which is called as doping. Doped nanoparticles show different optical properties than that of the bulk host materials [IV.1].

Rare earth elements have incompletely filled 4f shell. Most of them are trivalent elements showing very interesting and important optical properties. These trivalent ions give very intense and sharp fluorescence lines in the visible or neighboring spectral regions due to their 4f intra-shell transitions.

As explained in Chapter I (section 1.5) rare earth doped zinc oxide nanoparticles has become a subject of interest in recent years. Some reports have come on the luminescent properties of rare earth doped ZnO [IV.2-IV.18]. But still it is an open question whether rare earth ions can really be incorporated in ZnO as they have very large ionic radius than that of Zn^{2+}.

In this chapter europium doped zinc oxide nanoparticles will be discussed.

**IV.1 Eu doped ZnO nanoparticles**

Europium doped ZnO nanoparticles were synthesized in methanol as a medium. The detailed synthesis process is discussed in Chapt. II (section II.1(ii)). Zinc acetate [Zn(CH$_3$COO)$_2$] was used as a starting precursor for zinc because the salt of europium was in the form of acetate. We have used similar salts for zinc and europium for the simplicity in the reaction.

Amounts of zinc and europium salts were varied to change the doping percentage of Eu in ZnO. Samples with various Eu doping percentages ranging from 0.3% to 7% were synthesized, discussions about which will be given in following sections. Details of this are given in Table IV.1 which also depicts the percentages of europium measured from Energy Dispersive Analysis of X-rays (EDAX) and Atomic Absorption Spectroscopy which detect the amount of impurity in ppm level.
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For the simplicity samples will be labeled according to wt% of europium salt used for the reaction, though actual europium incorporated is less than it as can be seen from the Table IV.1.

Table IV.1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Eu wt % used for the reaction</th>
<th>Eu wt. % measured using EDAX</th>
<th>Eu wt. % measured using AAS.</th>
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<tr>
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<td>0.1</td>
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<td>1.2</td>
</tr>
<tr>
<td>ZnOEu-7</td>
<td>7.0</td>
<td>5.0</td>
<td>4.0</td>
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</table>

IV.1.1 Optical absorption study

Figure IV.1 gives the UV-Vis absorption spectra for europium doped zinc oxide nanoparticles for doping percentages of 0.3%, 0.5%, 1.0%, 3.0% and 7.0%.

Fig. IV.1: UV-Vis absorption spectra for Eu doped ZnO nanoparticles for various doping percentages ranging from (0.3 to 7.0 %).
As can be seen from the figure all samples show absorption at same wavelength indicating that there is no change in the size due to incorporation of europium into ZnO.

For all the samples excitonic peak could be observed at 300 ± 3 nm which is blue shifted with respect to that of the bulk ZnO value (370 nm). This is due to the quantum confinement effect. Size of the particles was calculated using EMA (eq. III.2) and it came out to be 2.7 ± 0.1 nm and from TB model it came out to be 1.8 ± 0.2 nm.

**IV.1.2 Structural analysis**

X-ray diffraction analysis was carried out for europium doped zinc oxide nanoparticles. Figure IV.2 depicts the XRD patterns for samples with Eu doping percentages of 1%, 3% and 7%. Comparing the patterns with that of undoped ZnO (Fig. III.8) it is clear that samples are having hexagonal wurtzite structure. Diffraction peaks for all the samples are broadened due to small size of the particles.

![X-ray diffraction analysis for ZnO:Eu samples with various doping percentages.](image)
Particle size was calculated using full width at half maximum (FWHM) of diffraction peak and Scherrer formula (eq. II.3). It came out to be 2.0 ± 0.2 nm for all the samples.

Samples were annealed in air for two hours at different temperatures to study the effect of it on the optical properties of ZnO:Eu nanoparticles. Annealing was done at temperatures like 150 °C, 250 °C, 350 °C and 400 °C. X-ray diffraction analysis was carried out for the annealed samples to investigate any effect of it on the particles. Figure IV.3 depicts the XRD patterns for annealed ZnO:Eu samples at various temperatures.

![X-ray diffraction patterns](image)

**Fig. IV.3:** X-ray diffraction for annealed ZnOEu-3 sample. (a-e) depict patterns for as synthesized sample and the same sample annealed at 150 °C, 250 °C, 350 °C and 400 °C respectively.
Figure IV.3 shows that as the annealing temperature is increased, till it reaches 250 °C, there is a little effect on the size of the particles as is evident from the FWHM of the diffraction peaks. But as the temperature was increased above 250 °C, peaks become narrower which is an indication of increase in the particle size. Although there is not much increase in the size as compared to that reported earlier [IV.19]. All the patterns show hexagonal wurtzite crystal structure. XRD pattern does not show any Eu-related peak unlike the previous report in which Park et al. [IV.20] have observed diffraction peaks due to Eu₂O₃ after sintering the europium doped ZnO at temperatures higher than 1000 °C in air and vacuum conditions.

IV.1.3 Investigations using FTIR

Fourier transform infra-red spectroscopy was performed on the as synthesized and annealed samples of ZnO:Eu nanoparticles to check the effect of annealing on the capping of the particles.

![FTIR spectra](image)

Fig. IV.4: FTIR spectra for as synthesized and annealed samples of europium doped ZnO nanoparticles.
Figure IV.4 gives FTIR spectra for europium doped as synthesized samples and after annealing 3% Eu doped sample at 250 °C. This is the temperature till which no much change was observed in the broadening of the diffraction peaks. Annealing data of sample with 3% Eu doping is shown because this sample showed luminescence due to Eu after annealing. A wide band appearing at ~ 3400 cm⁻¹ is due to –OH group which is present in the thioglycerol chain and some contribution in it may come from the hydroxide adsorbed on the surface of the particles. Two sharp bands present at 1430 cm⁻¹ and 1527 cm⁻¹ are attributed to the C=O and C=O stretching vibrations in acetate group [IV.21], respectively. These peaks have appeared as the starting precursor for both Zn and Eu are acetates. The bands appearing at 930 cm⁻¹ and 1105 cm⁻¹ are due to -SH and CH-OH groups [IV.22] present in thioglycerol. A sharp band at ~ 500 cm⁻¹ is due to Zn–O stretching [IV.23].

As can be seen from the figure even after annealing, bands due to thioglycerol ie bands designated to –SH, CH-OH and –OH are present though there is some reduction in their intensity. This confirms that even after the annealing particles are capped with thioglycerol which also reflects in the XRD analysis (Fig. IV.3).

**IV.1.4 Luminescence properties**

As explained in the Chapter I, the main aim of europium doping was to study it’s luminescence properties. Europium is well known for it’s 4f intra shell transitions which gives rise to intense and very narrow lines in the red-region (590 and 615 nm) of visible part of the spectrum and few lines in the near-IR region [IV.4, IV.20, IV.24]. However, it was reported earlier that emission from trivalent rare earth ions in ZnO host are extremely difficult to observe under UV excitation [IV.25]. Photoluminescence measurements were carried out on the Eu doped ZnO samples with various percentages ranging from 0.3% to 7%.

Figure IV.5 depicts PL spectra for 3% europium doped zinc oxide nanoparticles as synthesized and samples annealed at 150 °C and 250 °C. Excitation wavelength used is 320 nm. Spectrum for as synthesized sample shows a broad emission centered around 530 nm. This is a typical green luminescence observed in case of ZnO. An excitonic peak or peak due to band to band transition can be seen
at ~ 390 nm. Intensity of excitonic peak is less than that of green luminescence. As synthesized sample does not show emission due to Eu ions.

Fig. IV.5: Photoluminescence for the as synthesized Zn\textsubscript{0.97}Eu\textsubscript{0.03}O sample and after annealing the same sample for 150 °C and 250 °C in atmosphere for two hours.

After annealing intensity of green band decreases and that of excitonic emission increases as can be seen from the figure. Two more lines, one at ~ 590 nm and another at ~615 nm appear after annealing. These are the characteristic emission lines due to Eu(III) ions. The emission line at 590 nm corresponds to \( ^5D_0 \rightarrow ^7F_1 \) transition (transition a in Figure IV.6) and that at 615 nm originates from \( ^5D_0 \rightarrow ^7F_2 \) transition (transition b in Figure IV.6) in Eu(III) ions [IV.4, IV.20, IV.24]. Energy levels and transitions responsible for the emission lines due to Eu ions are given below in Figure IV.6.
Intensity of the emission lines due to Eu(III) ions was very less. A slight increase in the intensity was observed with increase in the temperature from 150 °C to 250 °C.

Figure IV.7 depicts the PL spectra for annealed samples of ZnO:Eu nanoparticles with two different doping percentages, 3% and 7%. As is evident from the figure, as the doping percentage is increased there is increase in the intensity of emission lines for Eu(III) in ZnO. Inset shows region for Eu(III) emission lines.
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Fig. IV.7: Effect of doping percentage on the luminescence of ZnO:Eu nanoparticles. Inset shows enlarged region of characteristic emission lines due to Eu(III) in ZnO nanoparticles.

Luminescence measurements were also carried out on the samples in which europium percentage was low. No emission due to Eu ions could be detected in samples with doping percentage ≤ 1%. Figure IV.8 depicts PL spectra for ZnO:Eu sample with 0.3% europium as an example. All other low doping percentages viz 0.5% and 1% show similar results except change of intensity. No emission due to europium ions could be observed. This might be due to the small quantity of dopant in the ZnO [IV.21]. A PL spectrum of thioglycerol is given for the comparison. Peaks appearing at wavelengths 378 nm, 404 nm and 428 nm are due to thioglycerol molecules present on the surface of the particle. Inset shows the enlarged region for the visible luminescence (indicated by an arrow) due to ZnO. From the Figure it is clear that after annealing green band disappears.
A sharp peak at ~ 363 nm is a band to band transition or excitonic emission. Intensity of this band is very large in these samples indicating that there are less defects present in the particles.

![PL spectra for 0.3% Eu doped ZnO nanoparticles. Spectra for as-synthesized and annealed samples are depicted along with that for thioglycerol for comparison.](image)

**Fig. IV.8**

**IV.1.5 X-ray absorption spectroscopy analysis**

As discussed in details in Chapter II, X-ray absorption spectroscopy which is broadly divided into two parts, XANES and EXAFS is used to determine 1) oxidation state of the element, 2) co-ordination environment of that particular atom of interest, 3) Position of that element in the host lattice etc.

We have carried out investigations of europium doped zinc oxide nanoparticles using XANES and EXAFS to know whether europium ion is really
incorporated into ZnO lattice or it is present on the particle surface. To know the oxidation state, its co-ordination geometry and if it is incorporated then to know the exact position of Eu ion, whether at substitutional site or interstitial site in ZnO nanoparticles.

XAS analysis was performed on the samples with varied europium doping percentages from 0.3% to 7% before and after annealing. Eu$_2$O$_3$ was used as a standard for the comparison with experimental data. Data was also compared with the simulations done using the FEFF program code. All the samples with varying doping percentages show same results although increasing disorder was seen for higher doping percentages of europium as discussed later in this section.

Figure IV.9 shows a Zn K edge XANES spectra for 3% Eu doped ZnO nanoparticles, that for bulk ZnO and Zn(OH)$_2$ for comparison.
XANES spectra are sensitive to the local surrounding of an atom. The spectrum of the sample in Figure IV.8 compared with that of bulk ZnO and Zn(OH)$_2$, is indicating an intermediate profile between them. Nanoparticle spectrum appears more similar to Zn(OH)$_2$ [IV.26]. However XRD analysis does not give any diffraction peak due to Zn(OH)$_2$. Therefore we propose a core shell model for this in which ZnO core is covered by Zn(OH)$_2$ shell as shown in Fig. IV.10. This may happen as the particles are chemically capped with TG which contains two OH groups. Also some hydroxide may get adsorbed and even during the synthesis hydroxide shell on the surface of particles may have been formed. Earlier reports also suggest the presence of hydroxide on the ZnO nanoparticles which are the main candidates for the defect level luminescence observed in case of ZnO [IV.27, IV.28].

Here we propose that for as synthesized particles Eu ions are present on the surface of the Zn(OH)$_2$ shell. After annealing, thickness of the Zn(OH)$_2$ shell reduces which also reflects in the PL results, and europium ions get diffused in to the shell till surface of ZnO core. This will be discussed in details in the following sections.

Figure IV.11 depicts the fourier transform (FT) to space (distance) of Zn K edge EXAFS for 3% europium doped ZnO nanoparticles compared with that of standard ZnO. The first peak at $R = 1.6 \pm 0.2$ Å labeled Zn – O corresponds to first
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Oxygen coordination shell around Zn. The second intense peak at \( R = 1.9 \pm 0.2 \) (Å) labeled as Zn – Zn is due to Zn nearest neighbours around Zn. The second peak is highly suppressed in case of nanoparticles as compared to that in the standard ZnO sample. This might be due to disorder present in the nanoparticles due to reduced dimensions and doping of europium with high percentages.

All the samples with 1%, 3% and 7% Eu doping, show similar results independent of doping percentages.

Eu L₃-edge XANES spectra are shown in Fig. IV.12, compared with that from Eu₂O₃. There is no peak shift of the white line (peak appearing at 6983 eV), indicating that Eu ions exist as Eu³⁺. Note that the white line is more enhanced and the broad band at ~7010 eV, which is assigned to the \( \sigma^* \) resonance, is shifted to the lower energy side, compared with Eu₂O₃. The former result indicates that the electron charge is more transferred from Eu ion to neighboring oxygen atoms and the latter suggests that the Eu-O bond distance is
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Elongated. Preliminary analysis of Eu L_{III}-EXAFS also indicates the elongation of the Eu-O bond distance.

![Graph showing Eu L_{III} XANES spectra](image)

**Fig. IV.12:** Eu L_{III} XANES spectra for 3% Eu doped ZnO nanoparticles for as synthesized and annealed samples compared with that of Eu_2O_3.

In Figure IV.13 Fourier Transform of Eu L_{III} EXAFS spectra for three different doping percentages are compared with that of Eu_2O_3. The main peak centered at 1.9 ± 0.2 is due to Eu - O first nearest neighbors, is shifted slightly towards higher distances compared to Eu_2O_3 in case of ZnO:Eu nanoparticles and is at same position for all doping percentages. Shape of the curve in 2.5 to 5 (Å) range is different from that of the reference Eu_2O_3. It indicates that local structure around Eu is quite same for all the samples but is slightly different from that of Eu_2O_3.

Fitting parameters used for the analysis of samples with different doping percentages of europium are given in Table IV.2. If europium is substitutionally
doped in the Zn site of ZnO, the co-ordination number should be 4. But it is significantly higher in case of nanoparticles analyzed here.

As the doping percentage increases, there is an increase in the Debye-Waller factor which indicates enhancement in the disorder. The co-ordination number and the bond distance are almost constant regardless of the doping percentage.

These results indicate that the Eu–O bond is more ionized, and Eu$^{3+}$ is more localized than Eu$_2$O$_3$. Although the chemical surrounding of the Eu ions is significantly different from Eu$_2$O$_3$, it is more likely that Eu ions are not substitutionally incorporated, but are outside, may be on the surface of the ZnO particles, which is in the core surrounded by the Zn(OH)$_2$ shell (Fig. IV.10).
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Table IV.2: Fitting Parameters used for the analysis of EXAFS data of europium doped ZnO nanoparticles. (Co-ordination number N, interatomic distance R and Debye – Waller factor σ). r factor is a measure of the quality of the EXAFS fit:

1) Standard Eu\(_2\)O\(_3\) (\(\Delta k=2.7\text{--}8.3\, \text{Å}^{-1}, \Delta R=1.05\text{--}2.4\, \text{Å}\))

<table>
<thead>
<tr>
<th>Eu 1% dope</th>
<th>N</th>
<th>R(Å)</th>
<th>ΔE(eV)</th>
<th>σ \times 10^{-2} , \text{Å}^2</th>
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<table>
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<table>
<thead>
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2) ΔE=-2.88\,\text{eV} is fixed.

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<th>N</th>
<th>R(Å)</th>
<th>ΔE(eV)</th>
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r factor 5.4%

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<th>ΔE(eV)</th>
<th>σ \times 10^{-2} , \text{Å}^2</th>
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<tr>
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r factor 3.2%

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<th>ΔE(eV)</th>
<th>σ \times 10^{-2} , \text{Å}^2</th>
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<td>8.70</td>
<td>2.41</td>
<td>-2.88</td>
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r factor 2.8%
To reduce the disorder observed in case of ZnO:Eu nanoparticles, we made the doping percentage very less, less that 1%. XANES study of 1.0%, 0.5% and 0.3% Eu doped ZnO nanoparticles was carried out. Spectra were recorded for as prepared samples and after annealing them at 250 °C for two hours. All the spectra for as prepared samples (not shown here) are similar to that of Eu₂O₃. Spectra for annealed samples of 1% and 0.5% Eu doped samples do not show any change from that of corresponding as synthesized samples. An interesting thing was observed in case of 0.3% doped sample which was the smallest doping percentage in this set of samples.

Fig. IV.14: Eu L_{III} edge XANES spectra for as synthesized and annealed sample. Spectrum for Eu₂O₃ is given for comparison.

Fig. IV.14 depicts XANES spectra for 0.3% Eu doped ZnO nanoparticles for as prepared and annealed samples at 250 °C for two hours. For comparison XANES spectra of Eu₂O₃ is also given. The sample after annealing gives a shoulder (indicated
by an arrow in the figure) appears at ~ 6975 eV for annealed sample. It corresponds to that of Eu$^{2+}$ species[IV.29]. Spectral analysis was carried out as shown in the Fig. IV.15. Eu$^{3+}$ and Eu$^{2+}$ species are present in the ratio of 85:15 as found out from the analysis.

![Graph showing spectral analysis for Eu LIII XANES spectra for 0.3% Eu doped ZnO nanoparticles annealed at 250 °C for two hours.]

Fig. IV.15: Spectral analysis for Eu LIII XANES spectra for 0.3% Eu doped ZnO nanoparticles annealed at 250 °C for two hours.

The Eu$^{2+}$ ions are present in ZnO lattice. Following explanation can be given for the above result. As the pH of the solution containing Zn and Eu salts was maintained at ~ 8, Eu must be present in Eu(OH)$_3$ form [IV.30] on the surface of the particles as determined from the EXAFS and XANES results described above. After annealing the sample, reduction of some part of Eu is taking place. We have proposed following reaction for the explanation of above result.

$$5\text{Eu(OH)}_3 \xrightarrow{250 \, ^\circ\text{C}} \text{EuO} + 2\text{Eu}_2\text{O}_3 + 7\text{H}_2\text{O} + \text{OH}^-$$
the resultant Eu$^{2+}$ species are diffused into ZnO lattice due to thermal treatment. Thus annealing is playing an important role in the formation of Eu$^{2+}$ species from Eu$^{3+}$ species. Also it is forcing the Eu$^{3+}$ species formed to diffuse in the ZnO lattice. This effect is observed only in case of smallest doping percentage in this set.

Conclusions

Europium doped zinc oxide nanoparticles have been synthesized using a chemical method. Particles are stabilized using an organic capping agent, thioglycerol. Structural analysis shows that particles are of hexagonal wurtzite structure. No peaks related to europium or its oxide were observed in XRD patterns. Annealing of the doped samples was carried out for various temperatures. Presence of capping agent on the surface even after annealing was confirmed using FTIR spectroscopy. Luminescence experiments show emission due to Eu(III) ions in case of samples with higher doping percentages.

XAS analysis shows that ZnO:Eu particles are in the form of ZnO@Zn(OH)$_2$ core-shell structure. Detail analysis shows that Eu(III) ions are present on the surface of the core ZnO and inside the shell of Zn(OH)$_2$ after annealing. Disorder was detected due to nanosize and doping of Eu ions.

XANES study of 0.3% Eu doped samples show that due to annealing Eu$^{2+}$ has converted into Eu$^{3+}$ and has diffused into the particle. Luminescence in this case could not be detected as doping percentage was very low.
References


IV.25 D. Kouyate, J. Lumin. 50 (1991) 205