CHAPTER 7

Eu AND Eu:Si CO-DOPING IN GaN NANOPARTICLES

7.1 Introduction

Doping of gallium nitride (GaN) with Europium (Eu) is very important for light emitting diodes (LEDs) as well as other optical applications. It is also of great interest for applications in biology (Bouzigues et al. (2011)). In contrast to Eu doping in bulk GaN where it costs 1.84 eV energy (Cruz et al. (2012)), doping in its nanoparticles can be significantly different. Due to increase in surface area, a large fraction of atoms lie on the surface where strain can be significantly lower. Also, there could be a reduction in the local symmetry in nanoparticles.

Co-doping of Si with Eu can facilitate Eu doping, and it indeed has been found for bulk GaN (Cruz et al. (2012)). In experiments, Si co-doping has been reported to increase the photoluminescence (PL) lifetime and also the excitation efficiency (Wang et al. (2009)). Recently, co-doping of Mg with Eu in bulk GaN has also been reported. Optimal amount of Mg enhances the Eu$^{3+}$ luminescence by 20 times. With Mg co-doping, Ga vacancy defects have been observed to decrease in GaN (Sekiguchi et al. (2013)). It will also be very interesting to monitor the behaviour of Si co-doping with Eu in GaN nanoparticles. If co-doping could enhance the luminescence in bulk, then it is expected to give even more pronounced results in nanoparticles as they have low symmetries and large surface area, so these combined effects could offer the possibility of strong luminescence.

However, so far there is a little progress in understanding the Eu and Eu:Si co-doping in GaN nanoparticles. These studies have been performed more extensively for bulk GaN from ab-initio calculations [Svane et al. (2006); Gourmi and Kanoun (2008); Sanna et al. (2009); Cruz et al. (2012)]. Small GaN nanoparticles are special as they have fullerene-like empty cage structures and shorter Ga-N bond lengths compared with bulk [Kaur et al. (2012); Shevlin et al. (2008)]. In large GaN nanoparticles also, surface atoms can behave quite differently with significant sp$^2$ bonding character as one finds on an infinite GaN
surface and small nanoparticles. Moreover, the doping could be inside or on the surface and it needs to be properly understood because in nanoparticles surface ligands effects could be more significant. Doping in nanoparticles could also lead to interesting applications. One possibility could be to self-assemble these doped nanoparticles by their ligands coating to generate different nanostructures.

In the present chapter, ab-initio calculations on Eu doping and Eu:Si co-doping in (GaN)$_n$ (for n=12, 13, and 32) nanoparticles have been performed, and we have addressed following questions for these systems:

1. How the Eu doping in GaN nanoparticles will be different from that at the bulk scale?
2. Is the doping of Eu in GaN nanoparticles energetically favourable?
3. Could it lead to structural transition from empty to filled cage structures in GaN nanoparticles?
4. How Si co-doping with Eu in GaN nanoparticles affects their atomic and electronic structure?

In Sections 7.2, 7.3, and 7.4, details of the computational methodology, results and discussion, and conclusions of the results obtained are given, respectively.

7.2 Computational methodology

The calculations have been performed using VASP package (Kresse and Furthmuller (1996a, 1996b)) with projector augmented wave pseudopotential plane wave method [Kresse and Joubert (1999); Blochl (1994)] and generalized gradient approximation (GGA) using PBE functional (Perdew et al. (1991)) for the exchange-correlation energy. The cut-off energy for the plane wave expansion is taken to be 400 eV. The nanoparticles are placed in a cubic unit cell of side 20 Å with periodic boundary conditions. The Brillouin zone integrations have been performed using only the gamma point. The ionic positions are optimized until the force on each ion becomes less than 0.005 eV/Å and the energy is converged within 0.0001 eV. The valence configuration for Ga, N, Si, and Eu atoms is taken to be $4s^24p^1$, $2s^22p^3$, $3s^23p^2$, and $5s^25p^64f^76s^2$, respectively. Due to the
inclusion of 4f electrons we performed spin polarized calculations for the Eu doped systems. Also GGA+U calculations have been done to study the effects of on-site Coulomb interactions. The effective value of U has been taken as 6.0 eV (Cruz et al. (2012)).

7.3 Results and discussion

In the following sections, the results obtained for the atomic and electronic structures of Eu and Eu:Si co-doping in GaN nanoparticles have been discussed. The atomic and electronic structures of rare-earth doped nanoparticles have been studied by GGA as well as GGA+U formalisms within PBE functional.

7.3.1 Atomic structure

For Eu doping and Eu:Si co-doping, both the empty and filled cages of (GaN)$_n$ nanoparticles for n=12, 13 and 32 atomic sizes have been optimized.

7.3.1.1 Doping in small nanoparticles (atomic sizes, n=12 and 13)

Different isomers of small nanoparticles studied in the present work are shown in Figure 7.1. For doping Eu and Si, different sites for each of the cage configuration have been explored as each site leads to different environment, and it is also important from application point of view (Yan et al. (2003)). GaN empty and filled cage structures are composed of hexagonal and rhombus units, so Eu and Si have been substituted on Ga sites in both the hexagons and rhombus environments. These sites have different bonding characteristics. At the hexagonal site, bonding tends to be predominately sp$^2$ type while at the rhombus site, the bonding is more sp$^3$ like. So, it is interesting as well as important to analyze the behaviour of doping on these two sites. For n=12 atomic size, the empty cage structure is highly symmetric and is well studied. It is composed of six hexagonal and eight rhombus units as shown in Figure 7.1 (12a, b). Being symmetric in nature, all the Ga sites on it are equivalent. So, doping of Eu at one or other site will not make any difference. Hence, randomly one Ga atom on it was replaced with Eu atom. Similar was the case for Eu and Si co-doping. Both Eu and Si were substituted at Ga sites randomly which were in vicinity of each other with a common sharing N atom.
Figure 7.1: Different isomers of empty and filled cage structures for Eu and Eu:Si co-doped (GaN)$_n$ nanoparticles for the atomic sizes $n=12$ (a,b) and 13 (a-i). For $n=12$, all Ga sites are equivalent and so only one case is shown for Eu doping. For $n=13$, the lowest energy as well as other higher energy isomers (both empty and filled cages) are shown, and
the energy (numbers in bracket in eV) of other isomers is given with respect to the lowest energy isomer.

In Figure 7.1, 12(a) is the optimized structure of Eu doped (GaN)$_{12}$ nanoparticles. After optimization, the cage structure is slightly distorted due to larger radius of Eu as compared to Ga and N. The Eu-N bond distance is elongated (2.286 Å), it leads to an outward relaxation around the Eu site and in turn a contraction of the nearest neighbor Ga-N bonds that are in the range of 1.876-1.938 Å. However, the bond distances in undoped (GaN)$_{12}$ nanoparticles are 1.879-1.954 Å. This behaviour in nanoparticles is similar to the Eu doping behaviour in GaN bulk system in which case Eu-N bond distance has been reported to be 2.25 Å, which is only slightly shorter as compared to nanoparticles (Cruz et al. (2012)). It indicates that outward relaxation of Eu on Ga site is more in nanoparticles as strain can be released better at the surface of cage.

The co-doping of Si with Eu has also been studied in (GaN)$_{12}$ nanoparticles, and both the Si and Eu have been doped on Ga sites similar to Eu doping such that both Eu and Si lie in the vicinity of each other sharing the same N atom. The optimized cage structure (12b) is shown in Figure 7.1. For Eu:Si co-doping, doping at the same hexagonal unit, rhombus unit as well as Eu doped at rhombus unit and Si doped at hexagonal unit, and vice-versa have been analyzed. It was found that Eu:Si co-doping is most favourable in (GaN)$_{12}$ cage when both Si and Eu are placed at the Ga substitutional sites on the same rhombus unit. As bonding at rhombus sites is more like sp$^3$, so the main reason for this favourable doping configuration could be that Eu prefers to substitute at sp$^3$ bonding site which has longer bond lengths so that it could release its strain energy better. The Si-N bond distance is 1.692 Å and this is perhaps the reason why both Eu and Si favour nearest neighbor Ga sites as Eu and Si combination could kind of compensate the strain induced in the system. After Si co-doping, Eu-N bond distance in (GaN)$_{12}$ changes from 2.286 Å to 2.337 Å due to charge-transfer from Si. Ga-N bond distances which are nearest neighbors to Eu:Si doping sites, are in the range of 1.883-1.928 Å.
Above analysis shows that the outward relaxation of Eu in Eu:Si co-doped system is more significant as compared to in simply Eu doped system. It is also clear from the energy values given in Table 7.1 that for size $n=12$, Si co-doping with Eu in nanoparticles make the system energetically more favourable than the doping of Eu alone in them. It leads to a large energy gain of 4.27 eV. The binding energy per atom of GaN with Eu:Si co-doping also increases indicating enhanced chemical binding of Eu in the co-doped system.

<table>
<thead>
<tr>
<th>Atomic size (n)</th>
<th>System</th>
<th>Energy (eV)</th>
<th>HOMO-LUMO gap (eV)</th>
<th>B.E./atom (eV)</th>
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<tbody>
<tr>
<td>12</td>
<td>GaN</td>
<td>86.186</td>
<td>1.548</td>
<td>3.591</td>
</tr>
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<td>86.582</td>
<td>85.736</td>
<td>0.027 0.165</td>
</tr>
<tr>
<td></td>
<td>GaN:(Eu+Si)</td>
<td>90.849</td>
<td>90.398</td>
<td>0.098 0.927</td>
</tr>
<tr>
<td>13</td>
<td>GaN</td>
<td>91.967</td>
<td>0.956</td>
<td>3.537</td>
</tr>
<tr>
<td></td>
<td>GaN:Eu</td>
<td>92.520</td>
<td>91.804</td>
<td>0.052 0.109</td>
</tr>
<tr>
<td></td>
<td>GaN:(Eu+Si)</td>
<td>96.960</td>
<td>96.398</td>
<td>0.147 0.592</td>
</tr>
<tr>
<td>32</td>
<td>GaN</td>
<td>242.544</td>
<td>1.453</td>
<td>3.790</td>
</tr>
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<td>242.268</td>
<td>0.172 0.389</td>
</tr>
<tr>
<td></td>
<td>GaN:(Eu+Si)</td>
<td>247.519</td>
<td>247.217</td>
<td>0.022 0.887</td>
</tr>
</tbody>
</table>

Table 7.1: The total energy, HOMO-LUMO gap and the binding energy per atom of undoped, Eu doped and Eu:Si co-doped (GaN)$_n$ nanoparticles for the atomic sizes $n=12$, 13 and 32, calculated both within GGA and GGA+U formalisms.

For $n=13$ size, both the empty and filled cage isomers have been optimized exploring the possibilities of different doping sites in them. The optimized structures are shown in Figure 7.1 (13a-c, Eu:GaN; 13d-i, Eu:Si:GaN). Although for (GaN)$_{13}$, empty cage structures are more favourable but both empty and filled cage structures have been
optimized with this intuition that the Eu-N bond is stronger as compared to Ga-N bond, and Eu also prefers to substitute at sp³ bonding site. So, there could be a possibility that Eu will have bonding with four N atoms and hence a filled cage isomer may become more favourable over an empty cage isomer. As shown in Figure 7.1, (13a,b, d-f) empty cage structure of (GaN)$_{13}$ is an elongated one, and (13c, g-i) a filled cage isomer is composed of 13 Ga and 12 N atoms on the cage and one N atom kept inside the cage. So, a Eu atom doped on the surface of cage can make three bonds with neighboring N atoms and one with N atom inside the cage. To begin with, a Eu atom has been substituted on both the hexagonal and rhombus sites in (GaN)$_{13}$ nanoparticles, and the cage structures have been optimized as shown in Figure 7.1 (13a, b). The difference in energy between both the configurations is only 0.06 eV. However, here doping of Eu at hexagon site is more favourable. For (GaN)$_{13}$ nanoparticles, Eu doping in filled cage has also been optimized. Different hexagonal and rhombus doping sites have been explored with Eu atom having three bonds with N atoms on the cage and one bond with N atom inside the cage. The lowest energy isomer is shown in Figure 7.1 (13c). However, its energy is 1.90 eV higher as compared to empty cage isomer (13a). In (GaN)$_{13}$ empty cage isomer, the Eu-N bond distance is 2.336 Å and the Ga-N bond distances nearest neighbor to Eu site, are in the range of 1.878-1.929 Å. It shows that Eu doping in empty cage structures is more favourable than filled cage structures for n=13 atomic size.

The empty and filled cage isomers for Eu:Si co-doping in (GaN)$_{13}$ nanoparticles are shown in Figure 7.1 (13d-i). In this case also, different doping sites have been explored and among all the empty cage structures, the one with Eu doped at rhombus site and Si co-doped at hexagonal site has the minimum energy (13d). The next higher energy isomer is empty cage structure with both Eu and Si doped on the same rhombus unit (13e), and its energy is 0.26 eV higher than the isomer (13d). Filled cage structures have also been optimized (Figure 7.1 (13g-i)), but they have significantly higher energy than empty cage isomers. The Eu-N bond distance for Eu:Si co-doped cage structures is 2.347 Å, Si-N bond distance is 1.691 Å, and Ga-N bond distances nearest neighbor to Eu:Si doping sites, are in
the range of 1.884-1.961 Å. Similar to the case of n=12 atomic size, here also Si co-doping makes the system energetically more favourable, and leads to an enhanced binding energy per atom as well as energy gain of 4.431 eV (see Table 7.1).

**Figure 7.2:** Different empty and filled cage isomers of (GaN)$_{32}$ nanoparticles doped with Eu (a-d) and co-doped with Eu and Si (e-i). Red (violet) balls represent Eu and Si atoms, respectively.
7.3.1.2 Doping in large nanoparticles (atomic Size n=32)

The optimized empty and filled cage doping and co-doping isomers have been shown in Figure 7.2 (32a-i) for the atomic size n=32. At this size also, empty cage structures are more favourable over filled cage structures. For Eu doping in empty cage (GaN)$_{32}$ isomer, the doping at rhombus site has the lowest energy (32a). The Eu-N bond distance is 2.296 Å and the Ga-N bond distances nearest neighbor to Eu site, are in the range of 1.888-1.906 Å. Next higher energy isomer is Eu doped at a hexagonal site in empty cage structure, and is 0.450 eV higher in energy (32b). For the filled cage isomer of n=32, a cubical unit fitted inside the n=28 cage was first optimized (Kaur et al. (2012)) and then the doping of Eu on different Ga substitutional sites was explored, both inside and on the surface of the cage (32c, d). The filled cage isomers have been observed to be 1.50 eV (32c) and 3.54 eV (32d) higher in energy than the minimum energy Eu doped empty cage isomer (32a). It is to be noted that doping of Eu on the surface of filled cage (32d) is significantly higher in energy (3.54 eV) as compared to other doping isomers (32c, 1.50 eV).

Among the different optimized cage structures for the Eu:Si co-doping in (GaN)$_{32}$ nanoparticles shown in Figure 7.2 (32e-i), an empty cage isomer with Eu:Si co-doped at Ga sites on the same rhombus unit is the minimum energy configuration (32e). For this isomer, the Eu-N bond distance is 2.378 Å and Si-N bond distance is 1.680 Å. As compared to Eu doping in (GaN)$_{32}$ nanoparticles, Eu-N bond distance in Eu:Si co-doped case gets elongated from 2.296 Å to 2.378 Å. This characteristic is similar to the one discussed above for n=12 and 13 atomic sizes. The empty cage with Eu doped at rhombus site and Si co-doped at a nearby hexagon site is 0.50 eV higher in energy (32f), and one with both Eu:Si co-doped at the hexagonal site is further 1.34 eV higher in energy (32g). The filled cage isomers for Eu:Si co-doping are also shown in Figure 7.2 (32h,i), and are 1.39 eV (both Eu and Si in the core), and 2.30 eV (Eu in core and Si on the surface) higher in energy than the minimum energy empty cage (32e), respectively. As observed from Table 7.1, Si co-doping with Eu in GaN nanoparticles lowers the energy of the system by 4.573
eV and hence increases the stability. The filled cage isomer (32i) with Eu doped in the core and Si at the surface is 2.30 eV higher in energy than the lowest energy isomer (32e), and also Eu doped at surface (32d) is 3.54 eV higher in energy than the lowest energy isomer (32a). So, intuitively we can say that both Eu and Si doped at the surface of the filled cage will have higher energy.

As observed from Table 7.1, Si co-doping with Eu in GaN nanoparticles increases the stability of the system and it is also energetically more favourable. From the above analysis, it can be concluded that this configuration is more favourable due to the following two reasons:

1. Eu-N bond length is longer and Si-N bond length is shorter, so this particular combination of doping compensates strain in the system.
2. As Si has four valence electrons, so it behaves as an intrinsic donor in the system. It gives its extra electron to Eu atom so that Eu is in +2 state (4f\(^7\) configuration) in GaN nanoparticles, which is energetically more favourable. Eu doping in GaN also lowers the symmetry and facilitates 4f transitions. In addition, Si co-doping in the vicinity of Eu further reduces the symmetry and leads to an increase in the stability of the system.

7.3.2 Electronic structure

The electronic structure of Eu doping and Eu:Si co-doping in GaN nanoparticles has been analyzed in terms of density of states (both within GGA and GGA+U formalisms) and charge density.

7.3.2.1 Density of states

The density of states plots for both Eu and Si co-doped Eu in GaN are given in Figure 7.3. Eu on a Ga site is in a +3 state and the net magnetic moment on this doped system is 6 \(\mu_B\). In Eu doped GaN nanoparticles for each size, spin-up 4f states are close to the GaN valence states and have a hole. On the other hand, spin-down states lie in the conduction band and hybridize with the Ga and N states.
**Figure 7.3:** The density of states for Eu and Si co-doped with Eu in GaN nanoparticles for the atomic sizes, n=12, 13, and 32 within GGA formalism. Vertical line shows the HOMO.
After Si co-doping with Eu in GaN nanoparticles, Eu is in +2 state as Si acts as an intrinsic donor. All the spin-up 4f states are fully occupied and the net magnetic moment of the system is 7 $\mu_B$. All spin-up 4f states lie in the band gap above the valence band of GaN. Eu in GaN nanoparticles is in +3 state and because of a hole in 4f states, they lie at the top of the valence states of GaN. On the other hand, in the case of co-doping with Si, Eu is less positive (+2 state) in GaN and the 4f states shift upward and lie in the HOMO-LUMO gap of GaN. They thus hybridize less and are comparatively sharper.

As the 4f states have localized character so we have also studied the effects of on-site Coulomb interaction within the GGA+U formalism by taking an effective U value of 6 eV for 4f electrons. The densities of states using GGA+U formalism for different clusters are given in Figure 7.4. For Eu doping, the 4f spin-up states shift deeper in the valence states of GaN and the spin-down states shift upward in the conduction states of GaN so that there is more hybridization between Eu 4f orbitals and the GaN states. In the case of Si co-doping, the spin-up Eu 4f states lie close to the top of the valence states of GaN but the down-spin 4f states are shifted significantly upwards as shown in Figure 7.4. The distribution of the 4f states is slightly different in nanoparticles of different sizes due to different local environments but they appear at similar energies and the main features are quite similar.

For the purpose of comparison, total energies, HOMO-LUMO gap and binding energy per atom have been calculated and are given in Table 7.1 for the undoped, Eu doped, and Si co-doped with Eu in GaN nanoparticles by using both GGA and GGA+U formalisms. With GGA, Eu doping in GaN is energetically favourable, but GGA+U calculations show that it costs energy. This result is consistent with those of bulk calculations (Cruz et al. (2012)). In bulk also, with GGA doping of Eu costs 1.84 eV energy and with GGA+U, energy cost increases by 0.18 eV more i.e. overall it costs 2.02 eV energy. However, for nanoparticles the energy cost is less, and is 0.45, 0.16 and 0.28 eV for (GaN)$_{12}$, (GaN)$_{13}$ and (GaN)$_{32}$, respectively. So, Eu doping in GaN nanoparticles is
favourable as compared to bulk. Si co-doping facilitates the Eu doping in nanoparticles as has been observed both with GGA and GGA+U calculations.

Figure 7.4: Density of states plots for Eu and Si co-doped with Eu in GaN nanoparticles for the sizes, n=12, 13, and 32 within GGA+U formalism. Vertical line shows the HOMO.
The binding energy per atom shows an increasing trend with an increase in the atomic size of nanoparticles (Table 7.1). Eu:Si co-doped GaN nanoparticles show higher binding energy per atom indicating enhanced bonding of Eu in GaN. With GGA calculations, binding energy per atom increases for both the Eu and Eu:Si co-doped GaN nanoparticles. However, GGA+U calculations show enhanced binding energy per atom for only Eu:Si co-doped GaN nanoparticles. On the other hand, both GGA and GGA+U calculations predicted a lower value of HOMO-LUMO gap in Eu and Eu:Si co-doped GaN nanoparticles as compared to undoped nanoparticles. It is to be noted that GGA+U calculations have given higher HOMO-LUMO gap as compared to GGA calculations.

Figure 7.5: Charge density plots for Eu doped in (GaN)$_{12}$ nanoparticles with GGA (a), GGA+U (b) and Si co-doped with Eu in (GaN)$_{12}$ nanoparticles with GGA (c) and GGA+U (d), respectively.
7.3.2.2 Charge density

The charge density plots for Eu doping in (GaN)$_{12}$ symmetric cage with GGA and GGA+U formalisms are shown in Figure 7.5. The iso-surface value has been taken as 5. As it can be seen with GGA, most of the polarization is around Eu atom. On N atoms there is down polarization. With GGA+U, hybridization with N has increased a bit; also hybridization of Eu with neighboring Ga atom can be seen. Overall, with GGA+U a little more hybridization is visible. With Si co-doping also, most of the polarization is around Eu atom, up polarization can be seen on N atoms. With GGA+U, polarization is mainly centered on Eu atom and the value of iso-surface has been taken as 10.

7.4 Conclusions

In summary, it has been shown that Eu doping in GaN nanoparticles is energetically favourable compared with Eu in bulk GaN as the strain is easier to relieve. Eu-N bond length is longer than Ga-N, and Eu generally favours sp$^3$ bonding site (rhombus) that has longer Ga-N bond lengths. Si co-doping further facilitates Eu doping with large energy gain due to compensation of strain from an over-sized and an under-sized dopant. Therefore, co-doping is an interesting possibility to stabilize rare earths in GaN and other hosts. These nanoparticles could form an important route to develop luminescent materials. Moreover, Eu occupies less symmetric sites in nanoparticles compared with bulk and this can facilitate intra 4f level transitions. A structural transition from empty to filled cage due to Eu doping in GaN nanoparticles is, however, not obtained due to a strong preference for sp$^2$ bonding that is strengthened due to shorter Ga-N bonds in nanoparticles compared with bulk.