A first-principle density functional study of metal doped ZnO buckyball structure for electronic applications

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Abstract. The nanostructured ZnO Buckyball (ZnOBB) and Al-doped ZnO Buckyball (ZnOBB: Al) has been optimized and their electronic properties were studied using the first-principle density functional theory (DFT) approach. The study includes the structural and electronic analysis of the system, done by observing the variation in the bond length, cell volume, Density of States (DOS) and Partial Density of States (PDOS). The DOS analysis provides information about Fermi level and bandgap while its further study with PDOS furnished an understanding of the orbitals which are contributing to the overall transition of electrons in the material. The optimized structure of ZnOBB: Al consists of dopant Al placed in the position of one of the Zn atoms in the cage of ZnOBB. Undoped ZnOBB showed a bandgap value ~1.5 eV, while ZnOBB: Al showed an increased bandgap value ~3.25 eV, which is attributed to the reduction in the size of ZnOBB after doping. This work proposes a doping mechanism, which may further explain the modifications of the bandgap. ZnOBB structure is itself a very contemporary topic of research and such kind of alteration in the bandgap with doping increases its applications in optoelectronic devices.

1. Introduction
There are diverse research works proceeding in the field of structural variation of the material and its impact on different properties, significantly enhancing their applicability in the field of nanotechnology. The structural variations from quantum dots to nanowires or nanoflowers, etc. Manifest several developments in the optical and electronic properties of that material [1, 2].

Among all different structures, Fullerenes have drawn the attention of researchers towards itself. After finding Fullerenes in 1985, they gathered a lot of appreciation and attention from researchers engaged in science. They have a unique cage-like structure that shows applications in the field of photovoltaics, sensors, portable power devices and biomedicines, etc. [3]. Some of the published works reported the buckyball structures of elements other than carbon. Here one or all atoms of carbon are replaced by any other element's atom, for example, the Buckyball structure of Boron (B80) [4]. The idea of replacing the carbon atoms in a buckyball structure with other element's atom to form a new buckyball structure had engaged our attention to form ZnOBB. We previously performed some simulations to understand ZnO and ZnS buckyball
structures and looked for their structural and electronic properties [5]. In another study, we explored the optical properties after interaction between ZnOBB and Graphene sheets [6]. These theoretical studies enhanced our understanding of stable structures of ZnOBB, its electronic properties and the attainable variations in the properties of ZnOBB with new alterations. The possibilities of bandgap engineering in ZnOBB increased the scope for further study of the system.

ZnO is known for its wide bandgap, better chemical and thermal stability, high electron mobility, non-toxic nature, low cost and easy availability [7,8]. Group III elements are known to be an efficient dopant material with ZnO. Among all the elements in group III, Al is one of the most used materials. It is due to the low cost, non-toxic nature, as well as easy availability of Al. The Al doping in ZnO is known for the production of Transparent Conducting Oxides (TCO). TCOs are widely used in solar cells, LEDs, construction glasses, flat-panel displays, etc. [9]. Mostly Indium Tin Oxides (ITO) and Fluorine doped Tin Oxides (FTO) are known materials for making TCOs. But Al-doped ZnO has proven to be an adequate replacement for ITOs and FTOs, due to its low cost, non-toxic nature, high transparency and low resistivity [10]. Pristine ZnO shows unstable and low electrical conductivity, which might get overcome by using Al as a dopant while maintaining a high level of transparency [11]. Due to the possibility of numerous applications of ZnOBB: Al, we studied its structural and electronic behavior. We also gathered information on structural and electronic changes in ZnOBB after Al doping.

Here, in this work, material modeling is done by using a DFT based technique. Here we expanded our previous study of ZnOBB by replacing one of the Zinc atoms with an Aluminum atom in the cage of ZnOBB. To the best of our knowledge, ZnOBB: Al has been studied for the first time. In the future, we can further investigate the optical properties of the ZnOBB: Al, like conductivity, reflectivity and transparency, etc. And look for its applications in the Transparent Conducting Oxides.

2. Simulation and Theory

Spanish Initiative for Electronic Simulations on Thousands of Atoms (SIESTA) software is used for DFT based study. It is one of the most prominent codes used for interpreting the electronic and optical properties of materials [12]. Here we optimized ZnOBB and ZnOBB: Al individually and looked for the structural variation in ZnOBB: Al as compared to ZnOBB. Along with structural properties, we also studied the electronic properties of the system by obtaining its DOS and PDOS plots. The optimization of the system was carried out by systematically following steps including determination of Cut-off, K-Points and final optimizations. Two types of approximations are considered, Generalized Gradient Approximation (GGA) and local-density approximation (LDA). Here we employed GGA, for exchange-correlation functions [13]. For the modeling of core electrons, Troullier-Martins pseudopotentials were used [14]. The Double Zeta Polarization (DZP) basis set is used here. The system was optimized with sufficient CG steps, mesh cut off was 400 Ry and k-grid value 5x5x5 a.u.

3. Results and Discussion

3.1 Setup and Analysis of Structure

For the structural analysis of ZnOBB and ZnOBB: Al, we optimized the structures first and looked for different parameters to study the system, such as bond length, Fermi energy, cell volume, etc. As shown in figure 1 (a) and (b), initially there are 12 Zinc atoms and 12 Oxygen atoms in the ZnOBB structure, which is fully optimized. Later we replaced one of the zinc atoms (Zn3) with one Aluminum atom (Al3) and optimized the structure again. ZnOBB and ZnOBB: Al, both have a ball-like structure, similar to a carbon buckyball. The changes that occurred in ZnOBB due to Al doping are discussed below.
Figure 1. Optimized structures of a) ZnOBB b) ZnOBB: Al

Table 1. Obtained and Calculated parameters for the study of ZnOBB and ZnOBB: Al structures.

| SN | System used | Atomic volume (Å³) | Cell volume (Å³) | Packing Fraction (%) | Atomic Density (Kg/ m³) | Fermi energy (eV) |
|----|-------------|--------------------|-----------------|----------------------|-------------------------|------------------|
| 1. | ZnOBB       | 149.53             | 395.78          | 37.78                | 4.13 x 10³              | -5.1592          |
| 2. | ZnOBB: Al   | 144.42             | 419.23          | 34.44                | 3.75 x 10³              | -4.1803          |

Table 2. Bond lengths of ZnOBB and ZnOBB: Al structures.

| SN | Name of Compound | Bond Name | Bond Length(Å) |
|----|------------------|-----------|----------------|
| 1. | ZnOBB            | Zn3-O7    | 2.02           |
|    |                   | Zn3-Zn6   | 3.19           |
|    |                   | Zn13-Zn10 | 3.20           |
|    |                   | Zn13-O7   | 1.93           |
| 2. | ZnOBB: Al        | Al3-O7    | 1.79           |
|    |                   | Al3-Zn6   | 3.18           |
|    |                   | Zn13-Zn10 | 3.19           |
|    |                   | Zn13-O7   | 1.98           |

Bond length is one of the most important parameters to understand the system. Under different circumstances, these parameter changes, for instance, a change in bond length leads to a change in binding energy, which implies the change in stress or strain of the system [15]. Here we observed in table 1 and table 2 that, after doping ZnOBB with Al, when one of the Zn atoms is replaced with the Al atom in ZnOBB, a stable symmetric structure is formed. Here, we can see that after doping ZnOBB with Al, restructuring of
the system takes place. Such a kind of restructuring occurs so that the surface energy of the system is minimized and a stable structure is formed [16]. The reformed structure showed no significant changes in the Zn-Zn bonds. Mostly the bond formed by the replaced Al atom with the neighboring Zn atom showed some reduced value as compared to the same bond formed between Zn-Zn in the ZnOBB structure without any doping. This might be due to the smaller size of the Al atom as compared to the Zn atom. Now, in the case of bonds with oxygen, we observed quite visible changes. After replacing Zn with Al and comparing the bonds between Zn-O in ZnOBB with Al-O bonds in ZnOBB: Al, an increase in the bond length was observed. There is a scope to further study such behavior of bond length in detail.

3.2 Electronic properties

Under the study of Electronic properties of a material, we looked for the variations in the electron density and the bandgap of the material and also the participation of different orbitals in the Valence Band or Conduction Band. In the DOS study of material, several different peaks are observed in Conduction and valence bands. These peaks arise as a contribution of s, p, d and f orbitals.

Figure 2 and figure 3 shows the DOS of ZnOBB and ZnOBB: Al and PDOS of ZnOBB and ZnOBB: Al, respectively. Measurement of the bandgap is done by looking at the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [17]. With the bandgap, we can estimate various electronic and optical properties of the material [18].

3.2.1. The Density of States

Figure 2 (a) and (b) shows the forbidden energy bandgap of ZnOBB and ZnOBB: Al, respectively. The Density of States of the material gives the details about the electron states of the system, knowing which we can determine the band structures and hence the bandgap of the material. Here as the structure of ZnO is buckyball, it showed variation in the bandgap as compared to other reported values for bulk structures. The bandgap observed for ZnOBB is around 1.5 eV, though with wurtzite structure in the bulk state it is reported around 3.37 eV [6, 19]. After doping ZnOBB with Al, we observed an increase in the value of the bandgap and DOS plots also showed some discrete peaks as compared to undoped ZnOBB. As shown in figure 2 (b), in the case of ZnOBB: Al band gap value is around 3.25 eV. Such an increase in the value of bandgap of ZnO after its doping with Al has been already reported in some of the experimental research works. In which the average crystallite size of ZnO nanoparticles decreases with increasing concentration of Al which might be due to the compressive strain produced in ZnO after doping it with Al [20]. Also, the bandgap might increase if the stress is increased in the system [15]. In some previous works, the contradictory fact that
even though the bandgap is increased in Al-doped ZnO then also n-type conductivity rises has been reported. This was explained by stating that there might be no local energy levels generated due to Al but the extra electrons observed are transferred directly to the conduction band. The large radius electron polarons enhance n-type electrical conductivity, which is created by doping of Al in ZnO [11]. Such changes in the DOS after doping, where discrete peaks are observed and the bandgap is increased indicates the quantum confinement effect.

3.2.2. The Projected Density of States

![Figure 3. (a) PDOS of ZnOBB (b) PDOS of ZnOBB:Al]

Plots of PDOS give the details about the relative contribution of different atoms and orbitals to the total DOS of the system. For understanding the electron states in detail, PDOS plots of the system are studied here. As shown in figure 3(a), The peak around -23 eV in valence Band, is originating due to the contribution of the O-2s orbital, which majorly showed its contribution in the valence band region. The higher energy region of the Valence band is mainly controlled by O-2p and Zn-3d states. It shows considerably strong interaction in the region from 0 to -13.3 eV, resulting in a strong ZnO bond. The 0-2p and Zn-3d orbitals also showed their maximum contribution in the valence band. The bottom of the CB is controlled by Zn-4s states, which probably had an almost equal contribution in both, conduction band and valence band. As compared to the previously reported results and graph obtained here, the bandgap value of ZnOBB is determined by both O-2p and Zn-4s orbitals [21].

After doping ZnOBB with Al atom, we obtained the PDOS plot for the same. In Al-doped ZnO, the valence band peak at around -23eV is obtained from O-2s states. The range in valence band from 0 to -15 eV is controlled by O-2p and Zn-3d. Zn-4s showed almost equal contribution in both the bands, just as explained for undoped ZnOBB. Here Al-3p showed its major contribution in the conduction band. As observed in figure 3 (b), the maximum contribution in the valence band comes from the Zn-4s, O-2p and Al-3p states. Similarly, in the conduction band, the major contribution comes from the Zn-4s and Al-3p orbitals [11]. It has been reported earlier that the donor levels appear in the conduction band because of the Al atom, which gets hybridized with O-2p orbitals and decreases the resistivity of Al-doped ZnO [22]. This statement holds a correct explanation for our results. The above-mentioned results for ZnOBB: Al matches with the previously reported experimental and theoretical works on Al-doped ZnO.
4. Conclusions

ZnOBB is a unique and contemporary system for research work. It showed some specific changes in the bandgap from existing ZnO structures. When one of the Zn atoms in ZnOBB was replaced by an Al atom, specific changes were observed. That replacement resulted in the restructuring of the system and hence changed the bond lengths. The bandgap of ZnOBB and ZnOBB: Al were calculated by using the DOS plots. Observed bandgap for ZnOBB and ZnOBB: Al was 1.5 eV and 3.25 eV, respectively. After doping ZnOBB with Al, the formation of discrete peaks in the DOS plot and an increased bandgap value indicated the quantum confinement effect in the system. The PDOS plots verified the contribution of different orbitals. These results justify the application of ZnOBB and ZnOBB: Al in the field of optoelectronic devices. In the future, there is scope for further studies of mechanical, optical and electronic properties of ZnOBB and its derivatives and we can further look for their various applications.

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