Theoretical investigation of optical and structural properties of Ba-doped ZnO material

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Abstract. The doping process is a technique widely used for improving the properties of semiconductors. Through insertion of doping controlled amount is possible change drastically the electronic, optical and structural properties of a material. This work focuses on effects of Ba atoms insertion on wurtzite-ZnO structure at 12.5% amount. The results showed that the presence of Ba in low quantity cause increase in the lattice parameters and decrease in band-gap in relation to the ZnO material. In the percentage of 12.5 %, the doping is noted as a potential alternative for application in opt-electronic devices, electronic devices, solar cells and photocatalytic process.

1. Introduction
The doping process consists in adding a controlled amount of impurities in semiconductor structure. This process changes drastically the properties of a semiconductor material without changing its crystalline structure. Through integrated impurities in the semiconductor structure is possible to control their properties. For this reason, the semiconductor materials can be employed at several electronic devices [1, 2]. Among the semiconductors materials, the wurtzite ZnO has attracted interest in recent years because electronic, optical and piezoelectric properties. The ZnO is a n-type semiconductor of direct band-gap of 3.37 eV [3-5], which presents electronic, optical, ferro- and piezoelectric single properties [3, 6-8]. Due to these properties, such material is employed on development of several electronic devices [4, 7-16]. In this crystalline structure, the Zn and O atoms are observed in a hexagonal-close-packed lattice and both atoms occupy the center of tetrahedral site; hence, the wurtzite-ZnO is relatively open, once all octahedral and half tetrahedral sites are empty. Thus, the doping process can be made without the need of complex experimental procedures [6, 10, 11, 17-24]. The incorporation of external dopants improves the materials properties according to impurity type, for instance, group I and II elements causes the improvement of ferroelectric properties and enables a band-gap engineering[25]; while the group III elements provides transparent-conducting-oxide property [10] and transition metals make of ZnO a multiferroic semiconductor.

Nowadays, the ZnO material doped with several elements inserted in the crystalline structure, but there is very low manuscripts focused on Ba-doped materials. In 2013, Haja Hameed and coauthors [26] studies the doping of ZnO materials with alkaline metals and observed the band-gap decrease. At same way, Srinet and coauthors [25] synthetized the Ba-doped ZnO at 5 %. Their results indicate the improvement of electronic, optical and ferroelectric properties of Ba-doped sample regarding to ZnO materials. Others papers showed results for ZnO/BaTiO$_3$ heterojunction [27-30] and BaO/ZnO interfaces [31].

However, DFT investigations about Ba-doped ZnO systems were not found at present moment. Theoretical methods based on quantum mechanical simulations are an important tool to evaluate
material properties, mainly at the molecular level. Studies based on these methods are performance to evaluate the electronic, optical, structural, pyro-, piezo- and ferroelectric properties. Such properties are intrinsically dependent on composition, atomic organization and chemical bonds, once these factors change the charge density on materials. Therefore, we propose theoretical calculations employing the Density Functional Theory (DFT) allied to hybrid functional B3LYP to investigate the effects of barium-doping of 12.5% on electronic, optical and structural properties of ZnO materials.

2. Computational Methodology

Theoretical investigation of 12.5% Ba-doped ZnO (ZnO:Ba) was performed from periodic models analysis. The simulations were based on Density Functional Theory (DFT) allied to B3LYP [32, 33] parametrized hybrid functional, both employed in CRystal09 [34, 35] software package. The model for ZnO was based on wurtzite structure regarding to literature parameters [8]; while the Ba-doped model was developed by unit cell expansion in the direction of a, b and c axes resulting in a 2x2x2 supercell. One Zn atom was replaced by one Ba atom in the supercell resulting in a concentration of 12.5%. In all models, the Zn and O atoms were described by TZVP [36] all electron basis set; whereas, the Ba atoms were described by HAYWSC [37] pseudopotential employed in Zagorac basis set [38].

The calculation parameters applied were: the SCF convergence factor was truncated in 10^-8 Hartree; Mohnkhost-Pach method [39] was defined as eight; whereas, total and partial projected Density of States (DOS) were performed using last five energy levels localized on top of valence band (VB) and the first five bands from bottom of conduction band (CB). Such calculation parameters of computational simulation were performed in CRystal09 software package, the structural analysis was made from XCrysden software package [40, 41]. Both software were used on Ubuntu Linux in computational cluster composed by seven quad-core AMD computers with 32 GB of RAM and data storage capability of 3.5 TB.

3. Results and Discussion

The presence of the Ba atoms in the ZnO crystalline structure is responsible for increasing the lattice parameters (Table 1); such increase for these values is dependent on the largest bond length of Ba – O bonds (2.462 Å) in relation to Zn – O bonds (1.980 Å) and also causes slight variations for unit cell angles (α, β and γ). Such changes show that Ba-doping at 12.5% is possible in wurtzite structure because lattice parameters and cell angles were low changed. Another result that help to indicate a possible phase transition is the tetragonality factor (c/a), which is obtained through ratio between a and c lattice parameters of the primitive cell. In Table 1 is showed a slightly change in the c/a factor indicating that there was no a phase transition.

**Table 1.** Theoretical results for lattice parameters (in Å) and structural angles (in degrees) for ZnO and ZnO:Ba materials.

| Model   | a    | b    | c    | α   | β   | γ    | c/a  |
|---------|------|------|------|-----|-----|------|------|
| Exp. #  | 3.249| 3.249| 5.204| 90  | 90  | 120  | 1.602|
| ZnO     | 3.266| 3.266| 5.279| 90  | 90  | 120  | 1.616|
| ZnO:Ba  | 3.364| 3.399| 5.464| 90  | 90.060| 120.346| 1.624|

#Özgür et al., 2005
The Figure 1 shows total and partial projected DOS analysis for ZnO and ZnO:Ba materials. For ZnO material (Figure 1a), the atomic contribution on top of VB for ZnO was projected between -10 and -5 eV (last five energy levels) been composed by O 2p orbitals and Zn 3d orbitals; whereas, the bottom of CB was described from -2 to 12 eV with contributions of O 2p, 3s orbitals and Zn 4s, 4p orbitals. From doping process, the top of VB was displaced between -6 and -5 eV been composed by O 2p orbitals and Zn 3d orbitals and Ba 4d orbitals; whereas, the bottom of CB was calculated from -2 to 2 eV with contributions O 2p, 3s orbitals and Zn 4s, 4p orbitals. Ba atoms have contributed in VB through 4d orbitals; whereas, 5sp and 6sp hybrid orbitals contribute to CB at -2 to 2 eV range.

![Figure 1. Total and partial projected DOS for (a) ZnO material and (b) ZnO:Ba material at 12.5 %. The hatch range shows the electronic degenerescence of VB and CB from Ba doping.](image)

The energy levels of VB and CB from ZnO are influenced by Ba 4d orbitals, mainly, in band-gap ($E_g$) region (Figure 1). However, another modification from Ba-doping is an electronic degenerescence of these energy levels on top of VB and bottom of CB from ZnO. It is possible to discuss such degenerescence effect because the projected DOS analysis (Figure 1) was performed from equal number of energy levels as VB as CB, the energy levels number chosen was five. For better visualization of such electronic degenerescence effect was used a hatch range in Figure 1. Thus, for ZnO, the energy levels as VB as CB occupy an energy range broader than same energy levels on ZnO:Ba (hatchet range in Figure 1). Such electronic effect is important because the electronic structure was changed through low coordination number (CN) of the Ba atom, CN=4 in wurtzite-ZnO; such CN=4 is unusual for Ba, consequently, the orbitals distribution of Ba is also unusual causing a decrease of $E_g$ (Figure 1). For the ZnO (Figure 1a), the theoretical results exhibit a direct $E_g$ of 3.11 eV ($\Gamma - \Gamma$) in according to experimental results [5, 7, 8]. Nevertheless, from doping process (Figure 1b) was calculated two main $E_g$ values and both are lower than $E_g$ calculated for ZnO material. The lowest
E_g for ZnO:Ba was calculated as 2.85 eV refers to an indirect E_g (L – Γ); whereas, a direct E_g (Γ – Γ) was calculated as 3.01 eV. Such E_g values refer to radiation in the visible ultraviolet making of this material a potential alternative to application in electronics devices and photocatalytic process. The main contribution to change the E_g from Ba-doping was caused by degeneration of energy levels belonging to VB and CB of ZnO. More specific, the electronic degenerescence causes an increase of VB energy and a decrease of CB energy.

4. Conclusion
For ZnO and ZnO:Ba materials, the results indicate that Ba-doping at 12.5% in wurzite-ZnO is a potential alternative to improve the electronic and optical properties of ZnO materials. This improvement is caused by degeneration of energy levels and, consequent reduction of the band-gap.

5. Acknowledgments
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6. References
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