First Principles Research on The Magnetic Properties of Na and Cl doped ZnO

Mauludi Ariesto Pamungkas, Setiawan Ade Putra, Irwansyah, Heru Harsono

Abstract*: *ZnO is considered as a wide bandgap material because it has a 3.4 eV direct bandgap. This wide bandgap characteristic causes good transparency, high electron mobility and luminescence at room temperature.The unique and tuneable properties of nanostructured ZnO shows excellent stability in chemically as well as thermally stable n-type semiconducting material with wide applications such as in luminescent material, supercapacitors, battery and solar cells. To be applied to a variety of needs, price control bandgap is needed. Likewise, control over the magnetic nature. Therefore we need a study related to bandgap modification, one of them is by giving impurity atoms. Atom Na and Cl were chosen as representatives of donors and acceptors. Atomistic calculations use the Functional Density Theory method which is implemented in ABINIT software. Relaxation and convergence research results are used to find the most stable energy value of ZnO.. The results showed Magnetic Properties in ZnO doping Na obtained magnetization values of 1.4802 μB greater than pure ZnO that is 0.9394 μB while ZnO doping Cl obtained magnetization values of 0.8593 μB smaller than pure ZnO. In conclusion the ZnO doping magnetic properties of Na increase magnetization and Cl doping also change the magnetic properties by decreasing ZnO magnetization.

***Keywords* : : First Principle, ZnO, Na, Cl, Magnetic .**

I. INTRODUCTION

Diluted magnetic semiconductors (semiconductors containing small amounts of magnetic impurities) and oxides are interesting for fundamental science and applications[1]. Doping oxides such as zinc oxide (ZnO) are among the best candidates for the DMS industry due to the multifunctional ZnO in opto-magnetic applications. In particular, ZnO-based DMS with properties such as visual transparency and piezoelectricity has aroused great interest in science as a strong candidate for spin-transistor and spin-polarized light-emitting diode fabrication[2].

At room temperature, the ferromagnetism shown in ZnO semiconductors under certain conditions has led to the argument that the defect could be the origin of ferromagnetism [3]. Kittilstved and Gamelin (reported that Mn: ZnO nanoparticles and thin films had ferromagnetic RT (room temperature) conditions only when covered with defective p-type molecules, and vice versa for Co: ZnO films N-type defects the conditions supported RT ferromagnetism. This led to numerous studies to identify the magnetic properties of ZnO with various n- and p-type dopants[4].

N-type doping is relatively well developed by substitution of Group III (Al, Ga, In) elements, resulting in n-type ZnO with high conductivity. All previous attempts to achieve a reliable p-type doping in ZnO, however, remained largely unsuccessful. Some materials whose valence bands are relatively close to the vacuum level have good p-type conductivity. In contrast, materials having a valence band relatively far from the energetic position of the vacuum level, such as ZnO, exhibit good n-type conductivity. In general, elements in group III donate electrons to Zn. While, elements such as Li, Na, K, Cu, and Ag recive electron from Zn [5].

it was reported that the Na-doped p-type ZnO experiment was successfully performed by Piao et al [6][7]. The results show that the magnetic properties of ZnO increased the saturation magnetic properties by 0.008 emu/cc. In DFT (Density Functional Theory), d-type Na doping with ZnO has not yet occurred. Therefore, this study was conducted to determine the effect of magnetic properties on the doping of Na-ZnO using DFT. Na was also chosen because Sodium is the fourth most abundant element that can be found on earth. Sodium is an alkali metal, in group one of the periodic table, because it has an electron in its outer shell that is easily donated, creating positively charged atoms in the form of Na+ cation and is an alkali metal material which may have ferromagnetic properties due to the holes created.

Additionally, in the study by Wang et al [7] doping has been carried out on ZnO with nonmagnetic elements such as Li, Mg, and Al, which make ZnO X (X = Li, Mg and Al). These non-magnetic impurities have reduced the energy formation of ZnO vacancies, which in turn affects the magnetic properties of ZnO. Therefore it is necessary to try impurities instead of magnetic impurities other than these elements. So in this calculation we use the Cl element as a non-magnetic impurity. The Cl element is also the second most abundant halogen atom on earth and is often used in the manufacture of advanced technologies such as processors, semiconductors and electrical components submission to the journal, rectification is not possible.

II. COMPUTATIONAL METHODS

We performed first principles electronic-structure

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calculations based on the spin polarized density-functional theory (DFT) implemented in ABINIT package[8]. An exchange correlation potential was evaluated via a generalized gradient approximation (GGA).

described by the Perdew-Burke-Ernzerhof (PBE) scheme[9]. Plane-wave cutoff energy is set at 400 eV and the Brillouin-zone integration is performed with a k-points mesh which is generated automatically by the Monkhorst-Pack scheme[10].

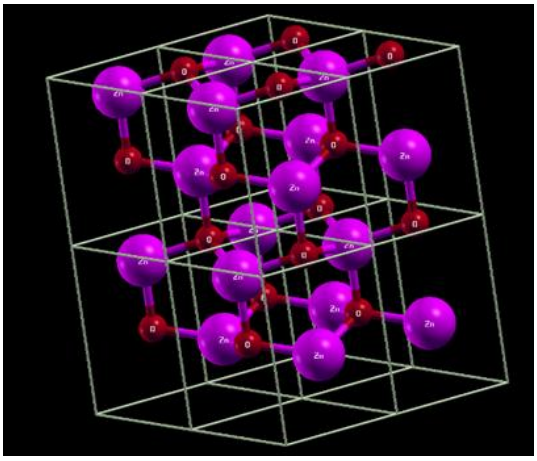


Fig. 1. Crystal structure of pure ZnO

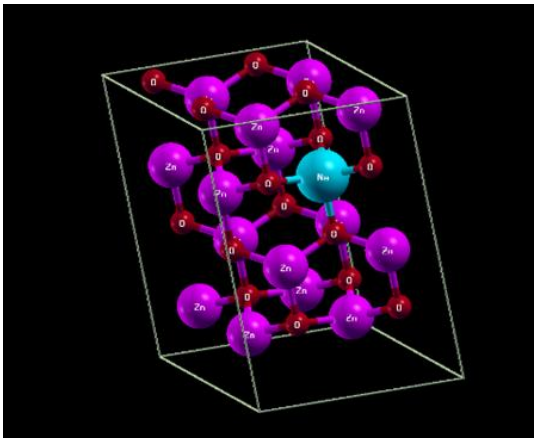


Fig. 2. Crystall structure of Na-doped ZnO

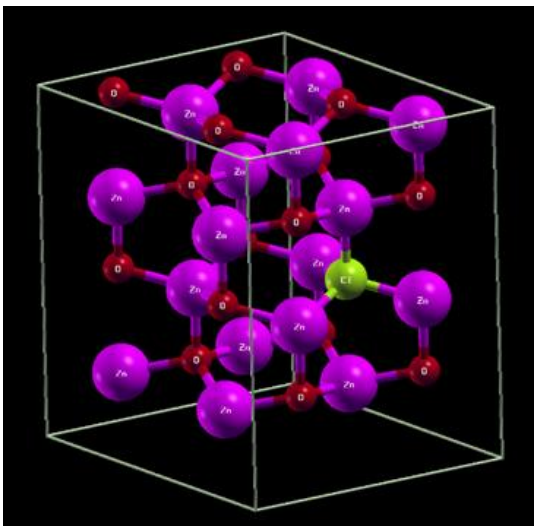


Fig. 3. Crystall structure of Cl-doped ZnO

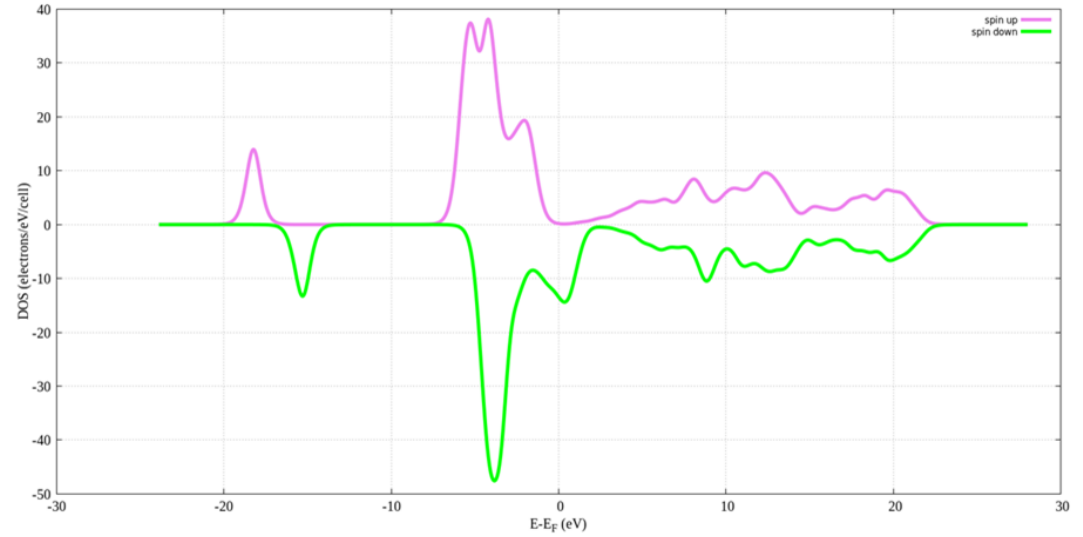
ZnO structure is wurzite consisting of 4 atoms including two Zn atoms and two O atoms which are determined using the wurzite crystal vector (see Figure 1). In cartesian coordinates, the basic atomic vectors are (0,0,0), (0,0, uc), a (1/2, √ 3 / 6, c / 2a) and a (1/2, √ 3 / 6 , [u + 1/2] c / a). Doping of atom Na is performed by substituting Zn atoms (Figure 2), the size of the Na atom is 1.86 Å which is not much different from the Zn atom which is 1.34 Å so that can be replaced by substitution. Figure 2 shows the supercell ZnO after doping the substitution of Na atoms with Zn atoms in position (0.66667, 0.33333, 0.69239). While doping of Cl atom is performed by substitution of oxygen atom as displayed by Figure 3.

Results and Discussion

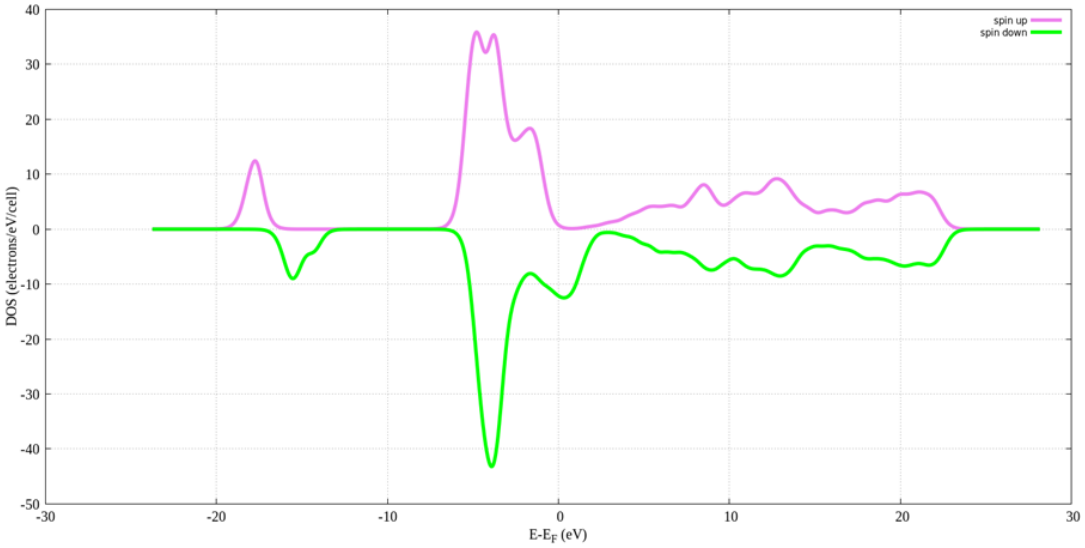
Magnetic property is the ability of a material to attract objects around it. This is caused by the spin and orbital motion of electrons, giving rise to a current and the current causes magnetization. In studies of three-dimensional structures such as ZnO, magnetic properties are analyzed by calculating polarized density of state (DOS). In the polarized density of state (DOS) there are density of state of spin ups and spin downs. If the two density of states are symmetrical, then the material that we study is nonmagnetic, in contrast, if the DOS of spin-up and spin-down plot shows asymmetrical results, then the material is ferromagnetic.

It was found that pure ZnO according to the results of this study has an asymmetrical DOS (Density of State) as seen in Figure 4 which also has a total magnification value of 0.9394 µB which indicates pure ZnO already has magnetic properties. Adding Na aton on Pure ZnO to the cell position (0.66667, 0.33333, 0.69239) produces a magnetic moment of 1.4802 µB and with a plot of density of state shown by Figure 4.b. This magnetic moment has increased up to 1.5756 times the magnetic moment produced by pure ZnO. When the ZnO supercell atom is doped with a Na atom, the Na atom will contribute to the spin-up electron orientation because the valence electron in Sodium is 1 different from the Zn orbital fully charged at 4s2. The plot results show that spin up and dpin down are asymmetrical.

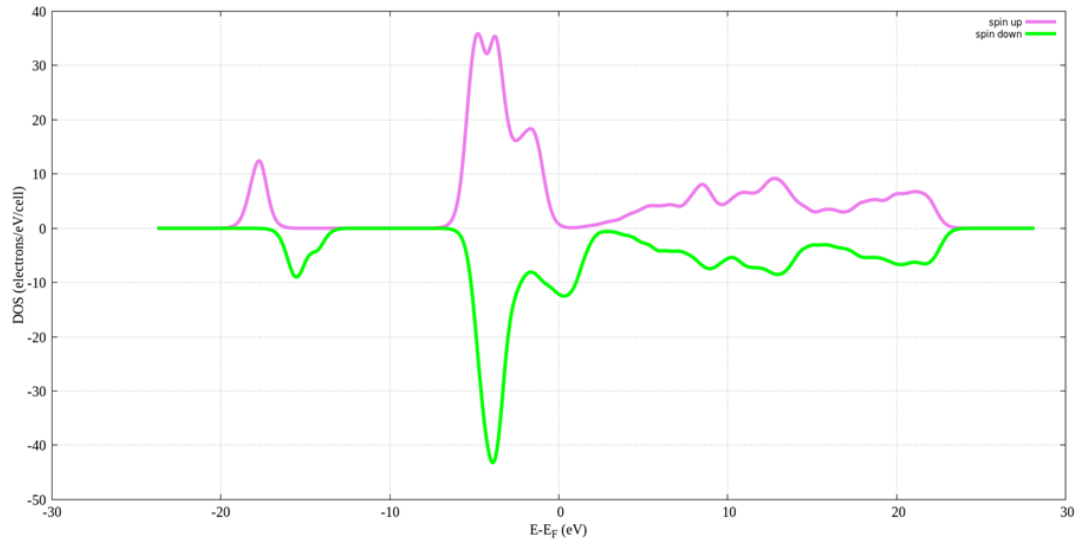
The DOS graph of ZnO doped with Cl atoms in the cell position (0.66667, 0.33333, 0.49035) shows that the spin up and down are asymmetrical so that ZnO doped with Cl still has magnetic properties as shown in Figure 4.3c, but has a magnetic moment of 0.8593 µB. This magnetic moment has decreased to 0.91473 times of the magnetic moment produced by pure ZnO. This is similar to what reported by Wang et al., (2012), that when ZnO doped with nonmagnetic elements oxygen vacancy will appear which leads to reducing its formation energy and ZnO system will be stable again after oxygen atom is substituted with Cl atom to a certain extent. That is agree well with the energy values obtained in this calculation, which are listed in Table 1, formation energy of Cl doped ZnO is lower than that of pure ZnO .



a)



b)



c)

Figure 4. Polarized Density of States of a. Pure ZnO , b. Na doped ZnO, c. Cl doped ZnO

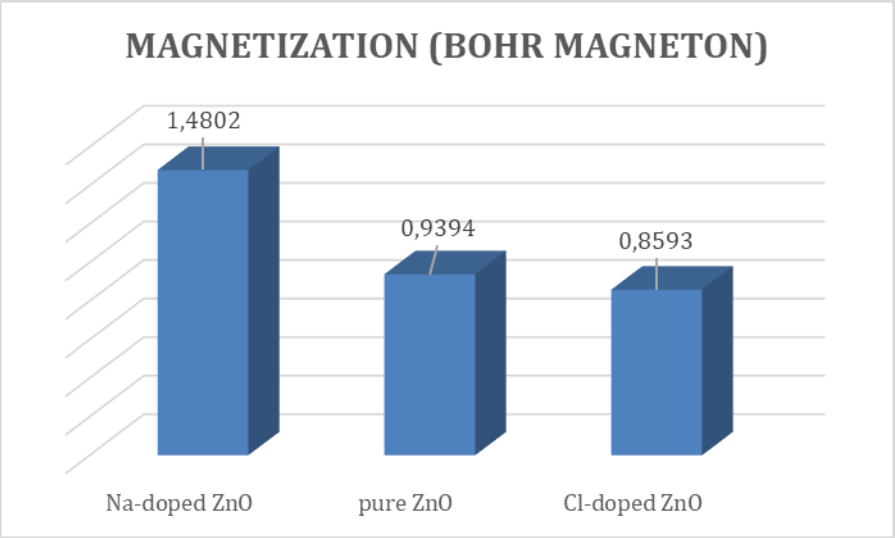


Table-I. Formation Energy of the three ZnO systems

No.	System	Formation Energy (eV)
1	Pure ZnO	-3.0897×10^{-4}
2	Na doped ZnO	-2.9413×10^{-4}
3	Cl doped ZnO	-3.0868×10^{-4}

III. CONCLUSION

A From the calculation of magnetic properties in pure ZnO, Na doped ZnO, and Cl doped ZnO, it is found that all systems are ferromagnetic due to the asymmetrical spin up-down state. The magnetization value of Na doped ZnO is 1.4802 μB greater than magnetization of pure ZnO, which is 0.9394 μB, while ZnO doping Cl is obtained magnetization value of 0.8593 μB smaller than that of pure ZnO.

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