



# DFT STUDY ON ELECTRONIC STRUCTURE AND BAND DECOMPOSED CHARGE DENSITY OF THE SMALL RINGS ZIGZAG BORON NITRIDE NANOTUBES

Riri Jonuarti, Triati Dewi Kencana Wungu, Freddy Haryanto and Suprijadi

Department of Physics, Institut Teknologi Bandung, Jalan Ganesha Bandung, Indonesia

E-Mail: [ririyo@cphys.fi.itb.ac.id](mailto:ririyo@cphys.fi.itb.ac.id)

## ABSTRACT

The small ring zigzag boron nitride nanotubes (BNNTs) which have a diameter less than 1 nm, possess the different characteristics from other BNNTs that make the small rings zigzag BNNTs are an interesting topic to be investigated. So that, in this study, we report the electronic structure of zigzag BNNTs consisted the stability and the band structure of zigzag forms under various chirality. We also verify the band decomposed charge density around the Fermi level to visualize the partially occupied valence bands and unoccupied conduction bands. The local density approximation (LDA) within the density functional theory (DFT) has been applied in our calculations. We find that the stability of nanotubes will increase as the diameter increases. We found that the increasing integer of  $n$  in chiral vectors for zigzag ( $n$ , 0) will increase the zigzag BNNTs band gap. The band decomposed charge density depicts that valence maximum band (VMB) is mainly located at the nitrogen atoms. While, conduction minimum band (CMB) is uniformly located at nitrogen and boron atoms. The band decomposed charge density also shows an overlapping occurred inside nanotube. The results confirm that a BNNT narrow band gap can be generated by the small rings zigzag form.

**Keywords:** Zigzag BNNTs, stability, band gap, band decomposed charge density.

## INTRODUCTION

Boron nitride nanotubes (BNNTs) have similar structures with carbon nanotubes (CNTs) but it has ionic character due to the differences in electronegativity between boron and nitrogen [1, 2]. The differences in electronegativity make BNNTs have structurally insensitive electronic property with the huge band gap (4 - 6 eV) [3, 4, 5]. Therefore, the applications of BNNTs can be applied in nanoelectronics [6], ceramics and polymeric composites [7], hydrogen storages [8-11], and bio-medicals [12]. Although BNNTs are good material for those applications, however, having a large band gap is unfavorable in a case of photocatalyst.

BNNTs are the promising materials for a photocatalysis application because of their effectiveness in separation of the photo-generated holes and electrons. While, the huge band gap of BNNTs limits the range of work of these materials in the ultraviolet wavelength. To improve the effectivity of BNNTs on photocatalysis application, the range work of BNNTs absorption should be increase until the visible light wavelength area by reducing the BNNTs band gap. To modified the band gap, several methods have been applied. One of the available methods was introduced by Khoo *et al* [13], wherein a transverse electric field was used for tuning the band gap of BNNTs. Furthermore, giving a defect is another method to obtain the narrow BNNTs band gap. However, it should be a simple effort to decrease the BNNTs band gap by investigating the pristine BNNTs characteristics further.

When the pristine BNNTs ring or diameter decrease to be less than 1 nm, the electronic properties of these materials become more different from the large one as predicted by Rubio [3] and Jian-Feng Jia [14]. These are mainly calculated using tight binding (TB), PBE-GGA

and GW calculation to describe the BNNTs electronic structure. However, it is known that TB method is less accurate to predict the small ring BNNTs because of the hybridization presence prediction [3]. Moreover, GGA always underestimates the interaction between nitrogen and boron atoms [15, 16] and GW takes a long time for calculations.

Another method is local density approximation (LDA) density functional theory (DFT). Although LDA tends to over bind atoms and underestimate the band gap in few percent [3], this value almost coincides with the experiments [17]. We anticipate an underestimation of the band gap values for the BNNTs using our calculation LDA band gap of hexagonal-BN is 4.6 eV while the experimental value is 5.8 eV as stated by Rubio [3]. In addition, we prefer to use LDA than others because this method is the simplest among the other methods that can save the calculation time.

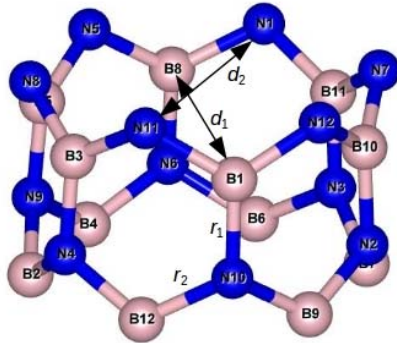
Therefore, to understand this phenomena, we need to investigate more detail about the electronic structure of the small ring zigzag BNNTs. In this study, we also calculate the band decomposed charge density around the Fermi level. The band decomposed charge density is needed to visualize the partially occupied valence bands and unoccupied conduction bands. Furthermore, it gives some important informations about charge distributions, bond types, hybridizations, and others. So that, the band decomposed charge density can be used to clarify the obtained band gap of zigzag BNNTs.

## COMPUTATIONAL METHODS

We carried out the first-principles calculations on the density functional theory (DFT) using Vienna *ab-initio* simulation package (VASP) [18-21]. The exchange-correlation energy and ion-electron interactions were



described by the local density approximation (LDA) [22] and the ultra-soft pseudopotentials [23, 24], respectively. A 450 eV cutoff energy and  $1 \times 1 \times 16$  k-point mesh were used during structural relaxation. The calculations will stop



**Figure-1.** Geometry and structural parameters of (6,0) BNNT. (Blue and pink are nitrogen and boron atoms, respectively).

until the energy differences and the Hellmann Feynman forces were converged to  $10^{-6}$  eV and  $-10^{-2}$  eV, respectively.

The BNNTs structure initially defined from conventional hexagonal BN (h-BN) sheet. After optimized h-BN obtained, the structure of BNNTs were constructed by rounding up the h-BN sheet. The orthogonal unit cell of BNNTs with  $a \times a \times c$  dimension size were then produced (where  $a$  corresponds to the unit cell in  $x$  and  $y$  directions while  $c$  corresponds to the unit cell in  $z$  direction).

We modelled the  $(n, 0)$  zigzag BNNTs. One of the nanotubes is the (6,0) zigzag form displayed in Figure-1. The (6, 0) zigzag BNNTs was chosen because it has a moderate system consisted by 12 nitrogen atoms and 12 boron atoms. In addition, the zigzag orientation is a preferred growth one [25]. The integer of  $n$  means a number of hexagon along circumference of the nanotubes. So that, we found 6 perfect hexagons in a unit cell of the zigzag (6,0) BNNT. The  $r_1$  and  $r_2$  were defined as bonds along the tube axis and bonds around the tube axis, respectively. Furthermore, the diameter of both boron ( $d_1$ ) and nitrogen rings ( $d_2$ ) are different,  $d_2 > d_1$ .

The relative stability of the zigzag BNNTs is defined by the average binding energy ( $E_b$ ) which is calculated by the following formulas:

$$E_{b-\text{zigzag}} = E_{h-\text{BN}} - E_n[BN(n, 0)/2n] \quad (1)$$

where,  $E_{b-\text{zigzag}}$ ,  $E_{h-\text{BN}}$ , and  $E_n[BN(n, 0)/2n]$ , corresponds to the average of energy binding of zigzag form, the total energy of h-BN per atom, and the total energy of zigzag BNNTs per atom, respectively. The electronic properties of BNNTs were analyzed from the electronic density of state (DOS) and the band structure calculations. In addition, the band decomposed charge density is obtained

after the electronic structure calculations by splitting charge per band.

## RESULTS AND DISCUSSIONS

The comparison of calculated lattice constant and B-N bond length ( $R_{B-N}$ ) between our work using LDA and other works using PBE and GGA are summarized in Table-1. The obtained lattice constant ( $a = 0.2490$  nm) and B-N bond length ( $R_{B-N} = 0.1438$  nm) for h-BN are relatively close to the references number 15 and 16. Hence, we confirmed that our calculations are acceptable.

**Table-1.** Structural parameters of h-BN.

	This work (LDA)	[14] PBE	[26] GGA
Lattice constant ( $a$ )	0.2490 nm	0.2489 nm	0.2504 nm
B-N bond length ( $R_{B-N}$ )	0.1438 nm	0.1437 nm	0.1446 nm
Band gap	4.6 eV	4.7 eV	-

The change in  $n$  integer produces various BNNTs structure which implicated to its stability. Therefore, we calculated varied zigzag BNNTs structures with  $n = 3-10$  to check their stability. We summarized our results and from other references in Table-2. We confirmed our calculated structural parameters are close to the available literatures [14, 27]. The listed data in Table-2 also informed that the increasing of the integer  $n$  in chirality induces the increasing of tube diameters and the increasing of the average binding energy.

The average binding energies provides stability of structures, the more negative binding energies the more stable of its structure. The negative sign of the binding energy signifies spontaneous reactions. It was found from our calculation that the (10,0) zigzag is the most stable structure among all calculated structures. As depicted in Figure-2, the increasing of nanotube diameter increases the stability of BNNTs structures.

In addition, beside the variety of the zigzag chirality influences the level of the structure's stability, it also produces the different electronic structures. We display the band structure of the zigzag BNNTs to verify that the band gap of the zigzag BNNTs is impressed by the chirality as shown in Figure-3. We also find that the band gap of the zigzag BNNTs will widely open with the increasing the nanotube chirality. The increasing of integer  $n$  in the zigzag forms shifts the valence maximum band (VMB) and the conduction minimum band (CMB) upward to the positive energy at  $\Gamma$  point as shown in Figure-3. The shifting of the valence maximum band (VMB) and the conduction minimum band (CMB) is clearly observed from (3, 0) to (5, 0) BNNTs. Whereas, from (5, 0) to (8, 0) BNNTs, the valence maximum band just very slightly moves to the positive energy compare to its conduction minimum band. Moreover, the valence maximum band (VMB) is stuck at -4 eV, but the conduction minimum band (CMB) slightly shifts upward from (8, 0) to (10, 0)



BNNTs. So that, we conclude that the increasing of the nanotube chirality will minimize the shifting of bands which refers to the band gap sensitivity.

We recognize that the smaller nanotube the more sensitive its electronic structures to its structural geometry. It means that the band gap of BNNTs will increase not only because of the increasing of nanotube chirality, but

also it caused by the enhancing of nanotube diameter. We clarify the widen of the nanotube band gap because of its raising diameter by defining the curvature effect of the BNNTs. When a nanotube is created by rolling up a 2D hexagonal-BN in a certain chiral angle, the curvature effect will appear after the structure optimization. To verify that the nanotube diameter relates to the curvature

**Table-2.** Structural parameters of BNNT.

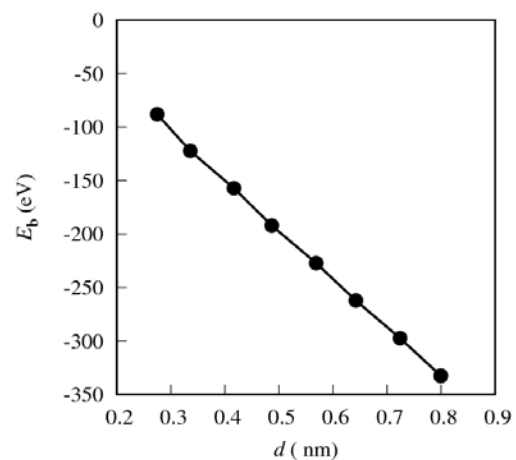
Tubes	$r_1$ (nm)	$r_2$ (nm)	$d_1$ (nm)	$d_2$ (nm)	$E_b$ (eV)
(3, 0)	0.1445 0.1416 <sup>a</sup>	0.1516 0.1508 <sup>a</sup>	0.2748 0.2493 <sup>a</sup>	0.2749 0.2869 <sup>a</sup>	-88.0581
(4, 0)	0.1439 0.1423 <sup>a</sup>	0.1479 0.1476 <sup>a</sup>	0.3220 0.3237 <sup>a</sup>	0.3504 0.3522 <sup>a</sup>	-122.3978
(5, 0)	0.1437 0.1429 <sup>a</sup>	0.1461 0.1460 <sup>a</sup>	0.4167 0.4000 <sup>a</sup>	0.4168 0.4226 <sup>a</sup>	-157.1547
(6, 0)	0.1436 0.1431 <sup>a</sup> 0.1437 <sup>b</sup>	0.1453 0.1452 <sup>a</sup> 0.1454 <sup>b</sup>	0.4777 0.4780 <sup>a</sup>	0.4960 0.4962 <sup>a</sup>	-192.0927
(7, 0)	0.1435 0.1433 <sup>a</sup>	0.1448 0.1448 <sup>a</sup>	0.5688 0.5571 <sup>a</sup>	0.5688 0.5723 <sup>a</sup>	-227.1143
(8, 0)	0.1435 0.1434 <sup>a</sup> 0.1438 <sup>b</sup>	0.1445 0.1445 <sup>a</sup> 0.1447 <sup>b</sup>	0.6357 0.6358 <sup>a</sup>	0.6489 0.6490 <sup>a</sup>	-262.1789
(9, 0)	0.1435 0.1434 <sup>a</sup> 0.1438 <sup>b</sup>	0.1443 0.1443 <sup>a</sup> 0.1446 <sup>b</sup>	0.7241 0.7144 <sup>a</sup>	0.7241 0.7258 <sup>a</sup>	-297.2686
(10, 0)	0.1435 0.1435 <sup>a</sup>	0.1443 0.1443 <sup>a</sup>	0.7942 0.7941 <sup>a</sup>	0.8046 0.8044 <sup>a</sup>	-332.3734

<sup>a</sup>From Ref. 14, <sup>b</sup>From Ref. 27 effect of nanotube, we had calculated the radius of the 'rolled-up' BNNTs using:

$$R = \sqrt[3]{(n_1^2 + n_1 n_2 + n_2^2) a_{(B-N)}^2} / 2\pi \quad (2)$$

Where  $n_1$  and  $n_2$  are the integer of chirality.  $n_2$  is 0 for the zigzag form and  $n_1 = n_2$  for the armchair form. In addition,  $a_{B-N}$  is the B–N bond length in hexagonal-BN.

We make a correlation between the radius of the 'rolled-up' BNNT with the radius differences of the nanotubes after the structure optimization as displayed in Figure-4. The rolled-up nanotube which has the smallest radius generates the largest difference of its radius after the optimization. It means the nanotube widens laterally after structure optimization and it corresponds to the decreasing in BNNT chirality. We conclude that the smaller of the nanotube size the stronger of the curvature effect possessed by that nanotube. So that, as a consequence of the increase of the BNNT curvature effect is the decrease of the nanotube band gap.



**Figure-2.** Binding energy vs. BNNT diameter.

For the further investigation, we display the band decomposed band charge density around the Fermi energy (-3.44 eV) of the (6, 0) BNNT. The band decomposed charge density refers to the valence maximum band (VMB) and the conduction minimum band (CMB) at the band structure as shown in Figure-5(a). Figure-5(b) shows the VMB is mainly located at the nitrogen atoms for the (6, 0) zigzag BNNT and refers to the free electron pairs at

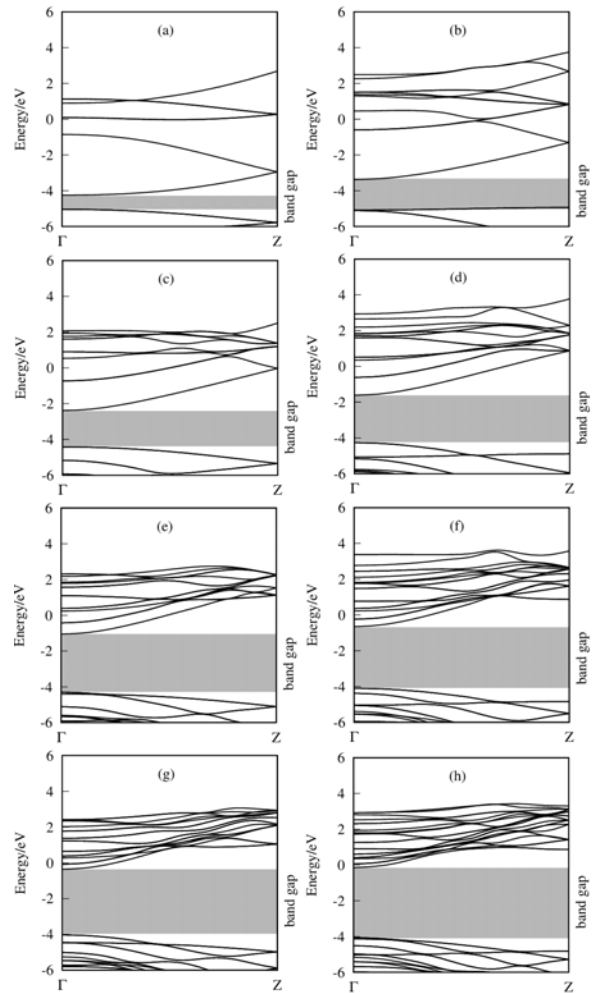


nitrogen atoms. While, boron atoms have a lack of electron in that valence band. Because nitrogen atoms are slightly negative and boron atoms are slightly positive, it will make nitrogen become more electronegative than boron atoms. Beside a electronegativity difference makes BNNT to possess both covalent and ionic bonds, it also generate the huge band gap of BNNT. However, we find the band gap of the (6, 0) zigzag form is around 2.3 eV. This is not really a huge band gap compare to 4.6 eV of the h-BN band gap.

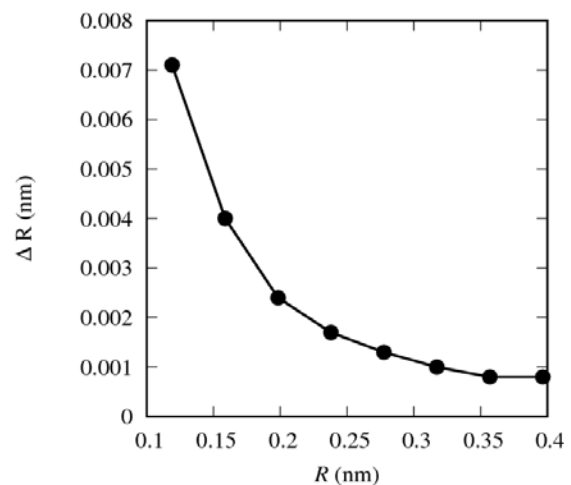
We clarify this fact with the Figure-5(c). In this figure, the conduction minimum band (CMB) is distributed by all nitrogen and boron atoms uniformly. As an implication, it causes an overlapping inside nanotube as shown in Figure-5(c) and Figure-6(b). This overlapping induces a strong hybridization between CMB called  $\pi^*$  state and another conduction band called the nearly free electron (NFE) state, so that it will generate a narrow band gap of the (6, 0) zigzag BNNT. That hybridization will be stronger with decreasing BNNT diameter and chirality as well. Another explanation can be obtained by comparing the charge density of (6, 0) zigzag nanotube with our another study of (5, 5) armchair nanotube as illustrated in Figure-6.

Four images in Figure-6 show the 2D charge density of the VMB-CMB of (6, 0) zigzag form and the 2D charge density of the VMB-CMB of (5, 5) armchair form, respectively. The VMB of (5, 5) armchair BNNT is like the VCM of (6, 0) zigzag BNNT which mainly distributed by nitrogen atoms. So that, their VMB's property is similar, although the 2D charge density between Figure-6(a) and Figure-6 (c) looks a little bit different. However, the CMB of (5, 5) armchair form is clearly different from the CMB of (6, 0) zigzag form. There is no overlapping appears in Figure-6(d). It means that there are no generated states inside nanotube caused by an overlapping.

In this case, we assume that the overlapping doesn't clearly appear in (5, 5) armchair BNNT because its shortest B-B distance (0.246 nm) is wider compare to the shortest B-B distance in (6, 0) zigzag BNNT (0.238 nm). A shorter B-B distance will be more convenient for an overlapping of the generate state inside the nanotube, then inducing the NFE- $\pi^*$  hybridization [16]. Furthermore, the increasing B-B distance declines the overlapping of charge density. Therefore, the band gap of the (6, 0) zigzag form is smaller than the band gap of the (5, 5) armchair form, although the integer  $n$  in chirality of the (6, 0) zigzag nanotube is higher than the integer  $n$  in chirality of the (5, 5) armchair nanotube. In addition, the zigzag forms always own the narrow band gap within BNNTs because of that explanation.

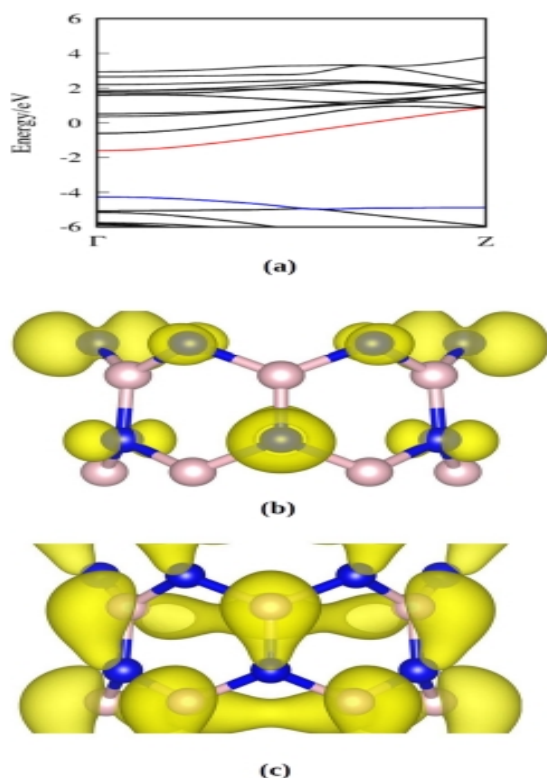


**Figure-3.** Band structure of zigzag BNNT. (a) (3,0) (b) (4,0) (c) (5,0) (d) (6,0) (e) (7,0) (f) (8,0) (g) (9,0) and (h) (10,0). The grey area indicates the band gap.



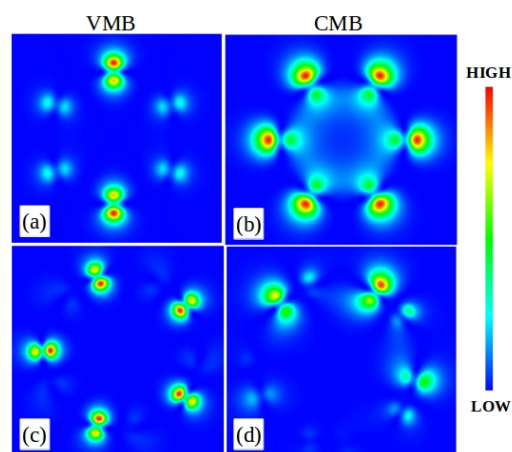
**Figure-4.** The rolled-up radius vs. the changes of radius after the nanotube optimization.





**Figure-5.** (a) Band structure, (b) Band decomposed charge density of VMB, (c) Band decomposed charge density of CMB of (6, 0) zigzag BNNT. Blue line, red line, pink balls, and blue balls represent VMB, CMB, boron atoms, and nitrogen atoms, respectively.

The narrow band gap of the small ring zigzag BNNTs will influence their optical properties. The smaller band gap the broader the absorption range of that materials until the visible light energy range. So that, it is favorable for the small ring zigzag BNNTs to be applied in photocatalysis application. A photocatalysis depends on the ability of the catalyst to produce a pair electron-holes in the valence band. These holes have a function as the oxidation places. The existence of electron-hole pairs will accelerate the transfer process electrons and redox-



**Figure-6.** (a) VMB 2D-charge density and (b) CMB 2D-charge density of (6, 0) BNNT, (c) VMB 2D-charge density and (d) CMB 2D-charge density of (5, 5) BNNT.

reactions. Semiconductors are chosen as photocatalysts because their small energy band gap makes the process much easier compare to the large band gap materials [28, 29]. This is a reason why the small ring zigzag BNNTs can be a new photocatalyst in the near future.

## CONCLUSIONS

In summary, we have studied electronic structure and band decomposed charge density of the small rings zigzag BNNTs using the DFT method. The average binding energies of BNNTs indicate that a nanotube with the largest diameter will be the most stable structure. The band gap of the zigzag forms is sensitive to the changing chiral vector. The band gap also increase with an increase of the nanotube diameter. A curvature effect and an overlapping induce the strong hybridization that makes the small rings zigzag nanotubes possess the narrow band gap. These results demonstrated that a small ring zigzag BNNT provides a good foundation for photocatalysis and other applications that need BNNTs with the narrow band gap. The simple calculation presented in this work may contribute to add the literatures of the BNNTs study and become a reference for calculating the optical properties of these materials.

## ACKNOWLEDGEMENT

This study is supported by JASSO and DIKTI Indonesia for the 2017 cooperation overseas program. The author thank to the quantum engineering design course (QEDC) for short-term research at Osaka University Japan in October 2016 - September 2017.

## REFERENCES

- [1] Tiano AL, Park C, Lee JW, Luong HH, Gibbons LJ, Chu SH, Applin S, Gnoffo P, Lowther S, Kim HJ, Danehy PM, Inman JA, Jones SB, Kang JH, Sauti G,



- Thibeault SA, Yamakov V, Wise KE, Su J, and Fay CC. 2014. SPIE Proceedings. 9060: 906006.
- [2] Cohen ML and Zettl Z. 2010. Phys. Today. 63(11): 34-38.
- [3] Rubio A, Corkill JL and Cohen ML. 1994. Phys. Rev. B. 49(7): 5081-5084.
- [4] Balse X, Rubio A, Louie SG, and Cohen ML. 1994. Europhys. Lett. 28(5): 335.
- [5] Lee CH, Xie M, Kayastha V, Wang J, and Yap YK. 2010. Chem. Mater. 22(5): 1782-1787.
- [6] Zhou Z, Zhao J, Chen Z and Schleyer PVR. 2006. J. Phys. Chem. B. 110: 25678-25685.
- [7] Bansal NP, Hurst JB and Choi SR. J. Am. Ceram. Soc. 2006. 89: 388-390.
- [8] Mohana Reddy AL, Tanur AE and Walker GG. 2010. Int. J. Hydrogen Energy. 35: 4138-4143.
- [9] Hu S, Kan EJ and Yang J. 2007. J. Chem. Phys. 127: 164718.
- [10] Shevlin S and Guo Z. 2007. Phys. Rev. B: Condens. Matter Mater. Phys. 76: 024104.
- [11] Durgun E, Jang YR and Ciraci S. 2007. Phys. Rev. B: Condens. Matter Mater. Phys. 76: 073413.
- [12] Ahmad P, Uddin Khandaker M, Raza Khan Z and Mohd Amin Y. 2015. RSC adv. 5: 35116.
- [13] Khoo K. H., *et al.* 2004. Phys. Rev. B. 69: 201401.
- [14] Feng Jia J, Wu HS and Jiao H. 2006. Physica B. 381
- [15] Marini A, Gonzalez PG, and Rubio A. 2006. Phys. Rev. Lett. 96: 136404.
- [16] Zhang Z, Guo W, and Dai Y. 2009. Journal of Applied Physics. 105: 084312.
- [17] Golberg D, Bando Y, Huang Y, Terao T, Mitome M, Tang C, and Zhi C. 2010. American Chemical Society. 4(6): 2979-2993.
- [18] Kresse G and Hafner J. 1993. Phys. Rev. B. 47: 558.
- [19] Kresse G and Hafner J. 1994. Phys. Rev. B. 49: 14251.
- [20] Kresse G and Furthmüller J. 1996. Comput. Mat. Sci. 6: 15.
- [21] Kresse G and Furthmüller J. 1996. Phys. Rev. B. 54: 1169.
- [22] Perdew JP and Zunger A. 1981. Phys. Rev. B. 23: 5048.
- [23] Vanderbilt D. 1990. Phys. Rev. B. 41: 7892.
- [24] Kresse G and Hafner J. 1994. J. Phys.: Condens. Matter. 6: 8245.
- [25] Arshadi S, Asghari A, and Zaghmarzi FA. 2013. Hindawi Publishing Corporation: Journal of Chemistry. 421091.
- [26] Lynch RW and Drickamer HG. 1966. J. Chem. Phys. 44: 181.
- [27] Akdim B, Pachter R, Duan XF, and Adams WW. 2003. Phys. Rev. B. 67: 345404.
- [28] Ibrahim SA and Teck KM. 2016. ARPJ Journal of Engineering and Applied Sciences. 11(14): 8704-8709.
- [29] Nyankson E, Agyei-Tuffour B, Asare J, Annan E, Rwenyagila ER, Konadu DS, Yaya A and Doodoo-Arhin D. 2013. ARPJ Journal of Engineering and Applied Sciences. 8(10): 871-886.