The Study of Band Structure of Graphite Intercalation Compound Containing Sodium Calculated Using Density Functional Theory

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Abstract. Sodium intercalation in graphite (GIC-Na) was investigated by the first principle calculation. The structure of GIC-Na was calculated using density functional theory (DFT) with the aid of CASTEP module of Material Studio. The exchange correlation functional has been treat by local density approximation (LDA) and generalized gradient approximation (GGA). It was shown that, unlike potassium GIC and lithium GIC, the band gap of GIC-Na was not induced and has same value of band gap with bulk graphite.

Keyword: density functional theory, graphite intercalation compound, Na.

1. Introduction

Since 1960s, graphite intercalation compounds were been developed by various method to achieve novel features in optical, structural, electronic and magnetic terms. Many atoms or molecules were introduced to fit important applications. Intercalation-induced doping altering the Fermi energy $E_F$, band structure, and density of states (DOS) at $E_F$ on graphite is of interest [1]. GICs, over graphite are well known due to the dramatic change of electrical conductivity. Their properties can be varied by choosing appropriate intercalants. Alkali metals had been capturing many attention toward GICs implementation because of the simplicity of their crystal structures. They obtained the simplest electronic configuration among other elements, therefore easily compared to the graphite band structure [2].

In bulk graphite, two dimensional carbon layers are held together via weak van der Waals forces. It is this feature which makes it possible to react chemically with various atoms or molecules [3]. Graphite behaves as a semiconductor with a vanishing energy gap, and in order to account for the magnetic and electrical properties, it is necessary to introduce impurities to it [4]. Carbon containing in the graphite...
would have four valence electrons. Three of them involves in $\sigma$ bonds, and the last one participates in $\pi$ bonding. This last electron contributes to most of transport properties in graphite. Upper and lower $\pi$ bands overlap by 30meV along the Brillouin zone boundaries, creating semi-metal signature.

Several attempts have been made to explain the electrical properties of graphite intercalation compound by a band structure. Alkali metals are able to intercalate graphite and modify its structure and properties [5]. Many researches have been done to study the graphite intercalation compound consisting alkali metals like potassium and lithium, but several only been investigated onto the structure of sodium-GIC. In contrast to lithium and potassium, the sodium intercalates are said to be difficult to be synthesized.

Sodium intercalated into GIC could be prepared only in the presence of impurities (such as oxygen, water, hydrogen or metal alloys) or with imperfectly graphitized carbon [6]. The liquid phase interaction of molten sodium with graphites provide only high stage compositions [7]. Metrot and co-workers have shown that intercalation from sodium vapour at high temperature yields the pure eight- stage NaC$_{64}$ compound and that lower stage compounds, seventh-stage (NaC$_{48}$) and sixth-stage (NaC$_{56}$) can be obtained from reactions performed at low temperature [2]. The problem of sodium intercalation into graphite is still one of the most interesting and extraordinary in the solid-state physics of intercalation compounds. The graphite intercalation compounds containing sodium are mostly present in high stages under high temperature and pressure [7]. The study of band structure of sodium-GIC is proposed to see the suitability of this material in semiconductor applications. Although graphite is said to be zero-bandgap semiconductor, its band widening is still an important art. Nevertheless, the absence of band gap in graphite limits its practical applications [8]. However, to date, no first principle study has been performed to address how electronic properties of graphite are modified by layered of sodium intercalants.

### 2. Calculation Method

In this research, CASTEP module of Materials Studio was used to develop the structure of graphite intercalation compound with sodium (GIC-Na). The plane wave basis set has been used. Two possible structures of GIC-Na were made up through parameters mentioned in Table 1 with space group hexagonal P63/mmc. The band structure has been calculated using Kohn-Sham equation with different approximation to treat exchange correlation potential. To identify the quantitative difference between bulk graphite and GIC-Na, graphite structure was also developed and set to the ground state so that comparison can be made between the bulk graphite and also the sodium GIC structures. Graphite acts as the reference structure along this study with same lattice parameter and carbon atoms positions. The lattice parameter, space group and basic coordinate of GIC intercalate with Li, K and Na has been discussed by Wang et al. [12].

| Type of structure | Lattice parameter (Å, deg) | Atomic coordinates (fractional) |
|-------------------|---------------------------|--------------------------------|
| 2 layer of graphene | | C$_1$: 0.000, 0.000, 0.250 C$_2$: 0.667, 0.333, 0.750 |
| GIC – Na (a type) | $a = 2.456$, $b = 2.456$, $c = 6.696$ | C$_1$: 0.000, 0.000, 0.250 C$_2$: 0.667, 0.333, 0.750 Na: 0.333, 0.667, 0.750 |
| GIC – Na (b type) | $\alpha = 90.000$, $\beta = 90.000$, $\gamma = 120.000$ | C$_1$: 0.000, 0.000, 0.250 C$_2$: 0.667, 0.333, 0.750 Na: 0.333, 0.667, 0.500 |
3. Band structure of GIC-Na

The intercalation of sodium atoms takes place into graphite structure with atomic coordinates such in Table 1. Two structures of GIC-Na were possible to be generated as the first stage intercalation compound. As stated before, low stages of GIC-Na are known to undergo difficulties to be synthesized experimentally compared to other alkali metal GICs. Figure 1 and figure 2 show the structure of sodium intercalation into graphite. After optimization with local density approximation (LDA) and general
gradient approximations (GGA), the lattice parameters inserted were optimized as indicated in Table 2. Lattice parameters inserted changed after optimized with LDA and GGA-PBE.

Table 2. The lattice parameters of GIC-Na (a type) and GIC-Na (b type) after optimized with LDA and GGA.

| Atomic Coordinates (fractional) | Approximation | Lattice parameter (Å, deg) |
|---------------------------------|--------------|-----------------------------|
| GIC-Na (a type)                 | LDA          | $a = 3.835349, b = 3.835349, c = 4.849585$ |
|                                 | GGA - PBE    | $a = 3.794112, b = 3.794112, c = 8.190601$ |
| GIC-Na (b type)                 | LDA          | $a = 3.492933, b = 3.492933, c = 8.253563$ |
|                                 | GGA - PBE    | $a = 2.682171, b = 2.682171, c = 15.455735$ |

The band structure was calculated along high symmetry k point in the Brillouin zone of the GIC-Na model. From the results in Figure 3, 4 and 5, the band structures of GIC-Na for both atomic arrangements show zero band gap after energy optimization using LDA and GGA-PBE approximations. These were indicated by the interception of valence band and conduction band near the Fermi level. Fermi level in graph is labelled with dashed line. The value of band gap for GIC-Na was proven had not induced from the graphite band gap. The intercalation of sodium seems did not alter the conductivity behaviour of graphite compound. Thus the electronic properties of graphite intercalation compound when intercalated with sodium does not change the electronic properties of graphite.

Figure 3. Band structure and DOS for GIC-Na (a type) optimized with LDA.
Density of states graph over energy revealed that carriers were probable to mostly occupy near Fermi level and it was clear that at energy equals to zero, no band gap appeared. The density of state near Fermi energy were enhanced in both cases. In the electronic transition view, for donor GIC, electrons transfer from donor to graphite atoms occupy anti-bonding $\pi^*$ band. While for acceptor GIC, charge transfer from graphite to acceptor empties the top of the $\pi$ bonding band. Charge transfer between graphite and intercalates increases number of electrons or holes around the Fermi energy and makes the GIC behaving metallic as in graphite.

Graphite structure optimization resulted band structure and density of state (DOS) are shown in Figure 6. Both approximations produced out almost same band structures and DOSs. High state density was shown in conduction band indicates that more states were available to be occupied by electron. This proved the metallic behavior of graphite, which is high electrical conductivity. Clear zero band gap is seen at the H point, indicating the position of corner point in Brillouin zone. In the band structure of graphite, the density of states near Fermi level (labeled dashed line in graphs) were entirely came from the p band around the Brillouin zone corner and there is no band near Fermi level around the zone center \[11\]. Our calculated band structure of two graphene layers shown similar result with the calculated band structure done by Noriza. A. Z. et al. \[9-10\]. We are using this layer as a base when we try to intercalate the sodium inside graphene layer.

Figure 4. Band structure and DOS for GIC-Na (a type) optimized with GGA - PBE.
4. Comparison with the Literature Review

Through reviewing the literatures, the value of bandgaps of graphite intercalation compound containing lithium (GIC-Li) and potassium (GIC-K) were known. GIC-Li and GIC-K possessed bandgaps of 0.6eV and 0.5eV respectively. It was estimated that GIC-Na must have band gap induced at certain value in between zero to 0.6eV since it should not differ too far from GIC-Li and GIC-K when they are in same group of periodic table, having same valence electron. Despite of that, intercalation of sodium seemed does not behave the same way as these two alkali metal intercalants.
5. Conclusion

Bandgaps are supposedly very important in the way that they allow control of electrical conduction and energy storage. This study proved that graphite intercalation compound containing sodium (GIC-Na) is

![Graph showing energy levels and density of states](image)

**Figure 6.** Graphite undergo (a) LDA and (B) GGA approximations.
not capable of these applications and does not behave such that of lithium GIC and potassium GIC. Although sodium ions are smaller than potassium ions, they cannot be easily intercalated into graphite and always form unstable compounds at low stages.

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References

[1] Oelhafen P, Pfluger P, Hauser E and Guntherodt J 1980. Evidence for an alkali-like conduction band in alkali graphite intercalation compounds Solid State Communications 33 241-244
[2] Metrot A, Guerard D, Billaud D and Herold A 1979 New results about the sodium-graphite system. Journal of Synthetic Metals 1 363-369
[3] Weller T E, Ellerby M, Saxena S S, Smith R P and Skipper N T 2005. Superconductivity in the intercalated graphite compounds Cd2Yb and Cd2Ca. Journal of Nature Physics 1 39-41
[4] Slonczewskit J C and Weiss P R 1957 Band structure of graphite Journal of Physical Review. 109 (2) 272-279
[5] Akuzawa N, Yoshioka J, Ozaki C, Tokuda M, Ohkura K and Soneda Y 2002 Preparation and characterization of sodium- graphite intercalation compounds Journal of Mol. Cryst. Liq. Cryst. 388 415-421
[6] Pascal GE and Fouletier M 1988 Electrochemical intercalation of sodium in graphite Journal of Solid State Ionics 28-30 1172-1175
[7] Udod I A 1997 Sodium-graphite intercalation compound of the first stage: two-dimensional structure and stability Journal of Synthetic Metals 88 127-131
[8] Guo X and Zhou Y G 2013 Band gaps of graphene on layered ZnO substrate: a first principle study Journal of Applied Physics 113 054307
[9] Zabidi N A, Kassim H A and Shrivastava K N 2010 Dft calculation of band structure of carbon chain pulled from graphene AIP Conf. Proc. 1250 (1) 241-244
[10] Zabidi N A, Kassim H A and Shrivastava K N 2008 Energy band crossing points in multilayers of graphene AIP Conf. Proc. 1017 326
[11] Kamakura N, Kubote M and Uno K 2008 Band dispersion and bonding character of potassium on graphite Surface Science 602 95-101
[12] Wang Z, Selbach S M and Grande T 2014 Van der Waals density functional study of the energetics of alkali metal intercalation in graphite RSC Adv. 4 4069