

A Density Functional Theory Study of a Calcium-Montmorillonite: A First Investigation for Medicine Application

Triati Dewi Kencana Wungu^{1,2}, Muhammad Rifqi Al Fauzan³, Widayani¹, Suprijadi^{1,2}

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10 Bandung 40132, Indonesia

²Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10 Bandung 40132, Indonesia

³Master Program in Computational Science, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10 Bandung 40132, Indonesia

Email : triati@fi.itb.ac.id

Abstract. In this study, we performed structural geometry and electronic properties calculations of calcium – based clay mineral for medicine application using first principles calculation by means of Density Functional Theory. Here, a kind of clay mineral used was Ca-montmorillonite and it is applied as an absorber of dangerous metal contained in a human body, such as Pb, which causes osteoporosis. Osteoporosis is a disease associated with bone mass decreases. Since montmorillonite has ability to exchange its cation (Ca^{+2}), therefore, it plays an important role in preventing or/and cure human bone from osteoporosis. In order to understand how Ca-montmorillonite can do detoxification in the human body, we firstly investigated the mechanism of Pb adsorption on the surface of Ca-montmorillonite in an atomic level point of view. We found that the repulsive interactions between H of OH groups with Ca and Pb yielding the rotation of the H of OH groups of montmorillonite. A relatively small movement of Ca was observed when Pb is adsorbed and the band gap of Ca-montmorillonite becomes 1.87 eV narrow.

1. Introduction

Osteoporosis is a disease where the bone mass of human body decreases. The bone mass decreases can be caused by exposure to a toxic substance such as heavy metals and pesticides. One toxic heavy metal of great concern is lead. The lead toxicity might affects the functions of every organ system in a human body. It is because lead has ability to mimic the actions of calcium in various body processes. When lead mimics calcium, it can interfere or even inhibit the process in which calcium is involved within the body.

Calcium is the most abundant mineral in the body and plays many vital roles. The deficiency of calcium may lead the body to take calcium from bones to ensure normal cell function. In that case additional calcium needed to replace the calcium that is “borrowed” from the bones otherwise it can lead to weakened bones or osteoporosis. Since calcium is not made in the body, so additional calcium must be absorbed from the food we eat into the blood circulation as macro-molecules. However, in the



exposure lead toxicity, if we suffer from calcium and other nutrients in the body, ingested lead can be easily absorbed into the body and become incorporated into the body's tissues. Therefore, we need enough calcium-rich food consumption and remove lead from our body to maintain healthy bone tissue.

To prevent the body from lack of calcium, many supplements contain calcium are produced. One of material that good for dietary is a calcium-montmorillonite (Ca-montmorillonite). Ca-montmorillonite is an excellent edible clay-based mineral used to detoxify and to supply a calcium dose internally. Detoxification can work because montmorillonite has a large surface area and negative charge, therefore it can adsorb heavy metals within body [1,2]. The cation such as calcium in montmorillonite may exchangeable, released, and transported within the body. Hence, calcium of montmorillonite can be functioned as a supplement for bone healing.

In order to understand how calcium-montmorillonite can be useful for the application of osteoporosis, investigation of the adsorption of Pb on the Ca-montmorillonite from atomic scale is important. Therefore, in this study, we investigated the structure and electronic properties of Pb/calcium-montmorillonite adsorption as a first investigation for osteoporosis application.

2. Model and Computational Method

Montmorillonite is formed as a result of alteration of volcanic rocks. The structure of montmorillonite has been defined from our previous works [3,4] and more less similar to our model showed here except that the atomic substitution consist on it are different, therefore, it will not be explained in more detail here. In this study, we theoretically performed simulation of calcium-montmorillonite using the Density Functional Theory (DFT) within Kohn-Sham formula implemented in Vienna Ab initio Simulation Packages (VASP) [5,6] at an absolute zero temperature. The generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) functional was employed for the exchange-correlation energy [7]. The Brillouin zone was sampled using $5 \times 5 \times 1$ Monkhorst-Pack k-point grid and the cut-off energy was set to 410 eV. The total energies were converged to 0.01 meV.

The montmorillonite is configured by layers of alumina octahedral and silica tetrahedral. The isomorphic substitution was taken into account within those layers so that the chemical formula of a unit cell of montmorillonite change from $\text{Si}_8\text{Al}_4\text{O}_{20}(\text{OH})_4$ into $(\text{Si}_7\text{Al})(\text{Al}_3\text{Mg})\text{O}_{20}(\text{OH})_4$. The isomorphic substitution generates a net negative charge which is usually balanced by additional cation atom, in this case is divalent ions such as Ca^{+2} . Hence, the chemical formula of montmorillonite after neutralized by Ca^{+2} is $\text{Ca}(\text{Si}_7\text{Al})(\text{Al}_3\text{Mg})\text{O}_{20}(\text{OH})_4$, called Ca-montmorillonite. According to chemical formula, one of Magnesium atom replaced one of Aluminum atom in the alumina octahedral layer while one of Aluminum atom replaced one of Silicon atom in the silica tetrahedral layer. In this calculation, a number of atoms per unit cell of montmorillonite are 40 atoms and was repeated periodically. Addition of Ca and Pb atoms to a unit cell of montmorillonite produces 42 of total atoms per unit cell of Pb/Ca-montmorillonite system.

3. Results and Discussion

In this section we present the results of the optimized geometry and the parameters related to the electronic structure of Pb adsorbed on the Ca-montmorillonite. Before understanding the mechanism of Pb adsorption on montmorillonite, we firstly observed the geometry structure and the electronic properties of the Ca-montmorillonite. The effect of the Pb adsorption on Ca-montmorillonite is further discussed. The optimized structures of Ca-montmorillonite and Pb/Ca-montmorillonite obtained from the DFT calculations are shown in Figure 1.

As depicted in Figures 1a and 1b, where the optimized structure of Ca-montmorillonite viewed from YZ and YX planes are presented, Ca atom is located at the montmorillonite surface particularly at the ditrigonal cavity of montmorillonite surface. It is observed that there are three coordination numbers between Ca and three O atoms. Also, there is one coordination number of Ca and Al. These

coordination numbers correspond to the number of Ca-O and Ca-Al bonds. The occurrence of these ionic bonds prevents the Ca atom to infiltrate into the lower layer of montmorillonite which are the alumina octahedral layer and the bottom of silica tetrahedral layer. The Ca atom has the tendency to fill an area that isomorphic substitution occurred and distribute its electron charge density to its neighbor atoms, O and Al atoms, which results in formation of Ca-O and Ca-Al bonds. The strong bond between Ca and montmorillonite surface, indicated by Ca-O and Ca-Al bonds, implies a completion reaction or we may say that Ca and montmorillonite are both neutralized each other.

As compared with our previous calculation of Li-montmorillonite, it was reported that Li atom can be infiltrate into the alumina octahedral layer by surpassing energy barrier of around 6 eV [3]. However in this calculation, Ca could not infiltrate due to some factors such as ionic radius of the Ca which is relatively larger than Li, the force of repulsion between Ca and H of OH is far greater than the force of attraction, and strong Ca-O and Ca-Al bonds.

Figure 1c corresponds to the optimized structure of Pb adsorption on the Ca-montmorillonite (Pb/Ca-montmorillonite). The Pb/Ca-montmorillonite is modelled to determine the possibility of montmorillonite to adsorb toxic such as Pb within the human body. Despite the fact that in the real body, water is an essential and should be considered in the calculation to mimic the real environment of body. However, as a first investigation we only consider in a dry and vacuum environment for efficient DFT calculation.

As it is mentioned earlier that Ca is needed as a supplement to maintain healthy bone tissue, then Ca from montmorillonite is predicted to detach from the surface of montmorillonite and entering the bone tissue. As a consequence, Pb allows attaching and adsorbs on montmorillonite surface and then through the chemical reactions Pb will flow out with urin from the body. Hence, in this calculation, Pb is predicted to be absorbed on montmorillonite surface.

As shown in Figure 1c, Ca is a little bit protruding out from the ditrigonal cavity of montmorillonite surface as Pb inserted on top of the Ca-montmorillonite. This implies that our prediction that Ca can move from montmorillonite is confirmed by the DFT calculation and to some medicine application can be beneficial as an osteoporosis drug. Although the Ca atom is not fully detach from montmorillonite surface due to Ca-O or Ca-Al bonds formation and the need energy is high to break the Ca-O and Ca-Al bonds, however, if the system of Pb/Ca-montmorillonite involve water molecules then both Ca-O and Ca-Al bonds might weak and Ca could be exchanged and move from montmorillonite to bone tissue.

Addition of Pb to the Ca-montmorillonite affects not only to the Ca but also to the orientation of the hydroxyl (OH) groups of montmorillonite. In a view of the YZ plane (Figures 1a and 1b), the H of OH which is closest to the Ca rotating in counterclockwise direction causing OH groups becomes parallel with the Y-axis (see Figure 1c). The charges distributed by Pb and Ca are responsible for the H of OH rotation since it induces repulsive coulomb interaction between H of OH with Ca and Pb. The Pb interaction with Ca-montmorillonite has much 0.14 eV/atom higher in total energy than the total energy of only Ca-montmorillonite. This is related to PbCaO compound resulted from the Pb interaction with Ca-montmorillonite.

Figure 2 corresponds to the total density of states (DOS) of montmorillonite, Ca-montmorillonite, and Pb/Ca-montmorillonite structures. Each DOS shows different energy gap that is 5.693 eV, 4.185 eV, and 2.320 eV for montmorillonite, Ca-montmorillonite, and Pb/Ca-montmorillonite, respectively. It shows that the montmorillonite and the Ca-montmorillonite are an insulator with a wide band gap while the Pb/Ca-montmorillonite is a metallic because there is density of states that crossing the Fermi level. The energy gap of montmorillonite is large since in nature, montmorillonite mainly composed by silicate layers which has an insulator characteristic. While Ca-montmorillonite has an energy gap lesser than montmorillonite by 1.508 eV because of p-orbital contribution of Ca. And finally after Pb adsorption on the montmorillonite surface, the system becomes metallic because of contribution of d-orbital of Pb.

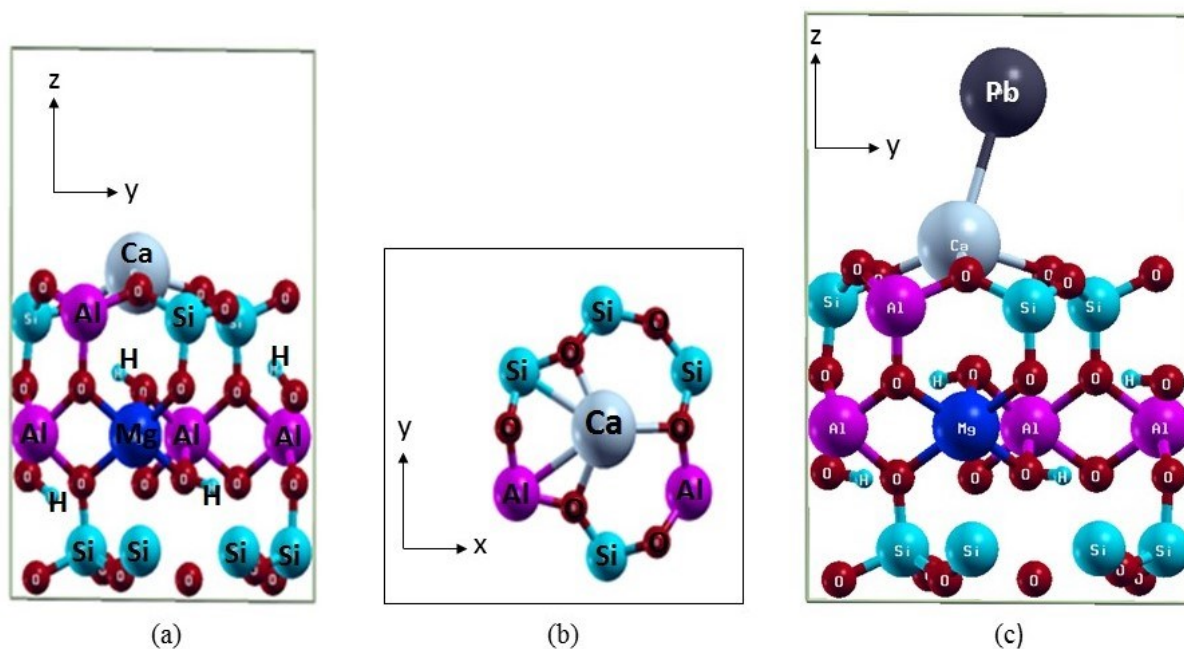


Figure 1. The optimized structure of a unit cell of Ca-montmorillonite viewed from (a) the YZ-plane and (b) the YX-plane; (b) The optimized structure of a unit cell of Pb/Ca-montmorillonite viewed from YZ-plane.

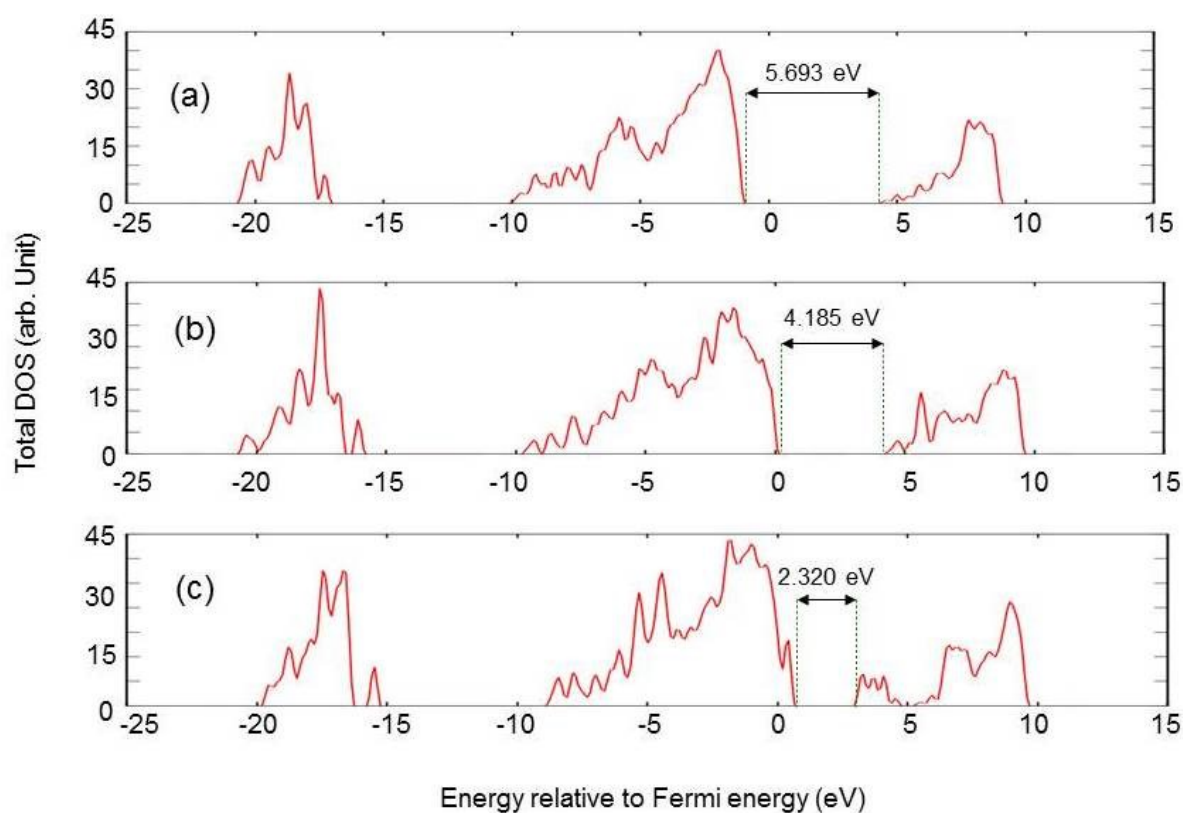


Figure 2. The total density of states (DOS) of the optimized structure of (a) montmorillonite; (b) Ca-montmorillonite; and (c) Pb/Ca-montmorillonite. The energy is shifted to Fermi level.

4. Conclusion

The calculation of Pb interactions with Ca-montmorillonite using the density functional theory (DFT) was done to study the structure and electronic properties of Pb/Ca-montmorillonite for osteoporosis application. The Pb with surface of Ca-montmorillonite yields the rotation of the H atoms of OH groups due to the occurrence of repulsive interaction between H of OH with Ca and Pb. In this study, the change electrical property of Ca-montmorillonite was observed through the density of state analysis. From the DOS, addition of Pb to the Ca-montmorillonite changes electronic properties from insulator to metallic. A relatively small movement of Ca was observed when Pb is adsorbed which implies that Ca-montmorillonite can be used as a supplement for body and can prevent osteoporosis since Pb can adsorbed strongly to montmorillonite.

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