

DENSITY FUNCTIONAL THEORY CALCULATION OF BAND STRUCTURE OF PEROVSKITE-TYPE MATERIAL BARIUM TITANATE (BaTiO₃)

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ABSTRACT

Perovskite-type structure, barium titanate (BaTiO₃) has a great potential in microelectronic industry especially, in capacitors and energy storage devices due to the high dielectric constant and wide band gaps around 3.2 eV. Many theoretical investigations on the band structure of BaTiO₃ by using density functional theory (DFT) calculation has been done with the different approximations but the accuracy of the calculation was questionable. The most fundamental local density approximation (LDA) methods were reported to be heavily underestimated the band gap of BaTiO₃ by 50% between the experimental values. In this study, the hybrid functional B3LYP was used in order to overcome the “band gap problem” in DFT calculation. The first-principle calculations based on DFT method were performed using Material Studio, CASTEP then the results were compared with the previous experiment data.

Keywords: Barium titanate; band structure; density functional theory; band gap;

INTRODUCTION

Since year 1945, the ferroelectric properties have been discovered in a unique structure so-called ABO₃ perovskites crystal by researchers and the first ever material which exhibits ferroelectric properties is barium titanate (BaTiO₃) at tetragonal phase around 120°C [1,2,3]. Barium titanate becomes one of the promising materials in the microelectronics industry due to their excellent ferroelectric and piezoelectric properties, high dielectric constant, high band gap and low current loss [4]. Barium titanate exists in three main phases which are influenced by the increasing of the temperatures. It undergoes transition from cubic (Pm3m) to tetragonal (P4mm) at 120 °C, from tetragonal to orthorhombic (Amm2) at 5 °C and from orthorhombic to rhombohedral (R3m) at -90 °C [5,6]. All these phases need to be optimized as there are some internal degrees of freedom of the atoms distributed in perovskites structure [7]. Some studies stated that BaTiO₃ perovskite structure has the ferroelectric properties

which exhibits spontaneous polarization without any external electric field applied at tetragonal phase, while at cubic phase it become paraelectric materials [8]. The numerous properties of the ferroelectric materials of the BaTiO_3 type perovskite crystal structure give abundant potential applications in industry especially in multilayer ceramic capacitors due to its high dielectric constant and permittivity, infrared detectors and energy storage devices [3,9]. Besides that, pure barium titanate (BaTiO_3) has a potential to become a semiconductor ceramic by doping a pure BaTiO_3 lattice structure with the transition metals [10]. It has great chance to be used as a semiconductor with the positive temperature coefficient of resistivity (PTCR) by substitution at Ti site with the dopants [11]. Barium titanate (BaTiO_3) has been reported to have a wide band gap around 3.00 eV from previous experimental studies compared to the theoretical studies calculation with the different approximation such as local density approximation (LDA) and generalized gradient approximation (GGA) [7,12]. This structure will continuously give high charge carrier flexibility and long diffusion length to the solar cell to prevent energy loss during the atoms transmission. The lattice constant of the perovskite-type structure BaTiO_3 in theoretical readings (using LDA) are normally around 3.958 Å and 3.954 Å for cubic and tetragonal phase respectively which is considered as underestimating the experimental results that reported around 3.996 Å - 4.006 Å [4]. In this paper, we present the band structure of BaTiO_3 simple cubic calculated using GGA and B3LYP. The calculated result will compare with the experimental data and also other calculations of BaTiO_3 . We have done a calculation on Kesterite structure and graphite intercalation compound with Na. The calculation result show a good agreement with the experimental result [13, 14].

METHOD

Density functional theory method has been performed using CASTEP in Material Studio to find the structure of simple cubic BaTiO_3 at the ground state energy. The structure has been developed from data in table 1. Density functional theory (DFT) calculation with hybrid functional B3LYP and general gradient approximation (GGA) have been used to treat the exchange-correlation potential in Kohn-Sham equation. Then BaTiO_3 been optimized to the ground state energy using CASTEP software. The test calculations are done with cut off energy 351.0 eV. Therefore, all lattice vectors and atomic positions are fully relaxed by minimizing the quantum mechanical stresses and forces. The relative deviation (%) for lattice constant of the compound for hybrid functional B3LYP was 0.726 respectively. Then, the electronic band structure and density of state for BaTiO_3 structures have been calculated from the optimized structure.

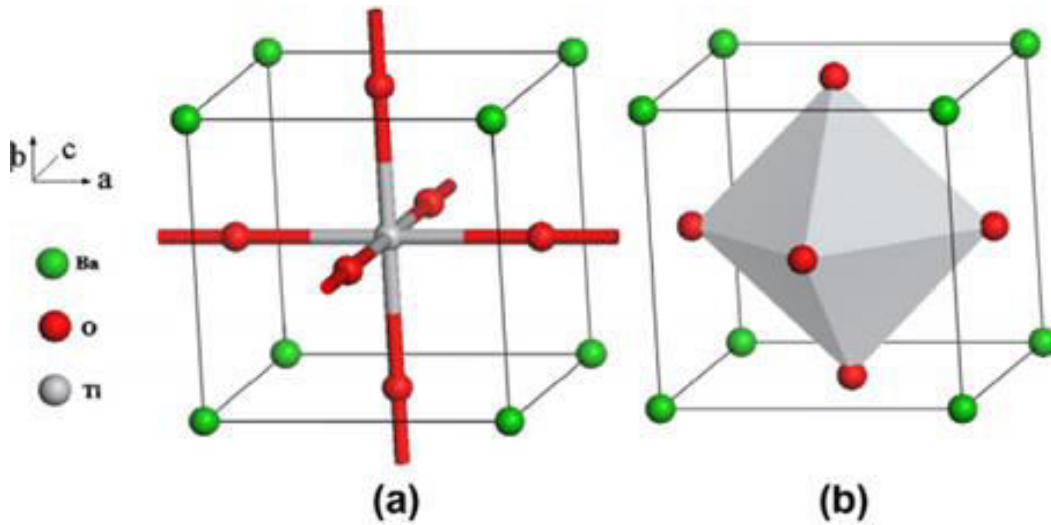


Figure 1: (a) Cubic barium titanate (BaTiO₃) unit cell. (b) Polyhedral view for cubic barium titanate (BaTiO₃)

Table 1: Basic parameters needed for the development of BaTiO₃ structure: Space group, lattice constant and atomic coordinates

Space Group	Lattice Constant (Å)	Atomic Coordinates (fractions)
221-Pm $\bar{3}$ m	a=b=c= 3.996 $\alpha=\beta=\gamma= 90^\circ$	Ba (0.00,0.00,0.00)
		Ti (0.50,0.50,0.50)
		O ₁ (0.50,0.50,0.00)
		O ₂ (0.50,0.00,0.50)
		O ₃ (0.00,0.50,0.50)

RESULT AND DISCUSSION

The calculations have been done in measuring the band structure of the perovskite-type material, barium titanate (BaTiO₃) using hybrid exchange-correlation B3LYP functional and different type of approximation for GGA. The band gap of the optimized barium titanate (BaTiO₃) structure by using hybrid functional B3LYP showed a high band gap around 3.223 eV, thus it was in accordance with the experimental value which is reported as 3.2 eV [12]. As predicted, a calculation using GGA shows an underestimated value when compared with the experimental energy gap. Table 2 shows our calculation using several type of GGA and also B3LYP.

Table 2: The comparison of band gap calculated by DFT using GGA (PBE, PBEsol, WC, PW91) and hybrid functional B3LYP of BaTiO₃ with the experimental value

	GGA				HYBRID FUNCTIONAL B3LYP	Experimental [11]
	PBE	PBEsol	PW91	WC		
Band gap (eV)	1.749	1.769	1.743	1.781	3.223	3.2 eV

Figure 2 shows the band structure calculated with B3LYP with a direct gap at Gamma point with value of 3.223 eV. Figure 3 shows the total density of state (DOS) of cubic BaTiO₃ using hybrid exchange-correlation (B3LYP) functional against the energy (eV). The dotted line on the 0 eV refer to the Fermi energy level which described as highest energy level for single particle at temperature of 0 K that has 50% probability to be filled. The energy difference between the conduction and valence band was approximately 3.223 eV where the gap was located above the Fermi level at the conduction band region. At -35 eV, there was a highest peak of DOS by 11.6 eV.

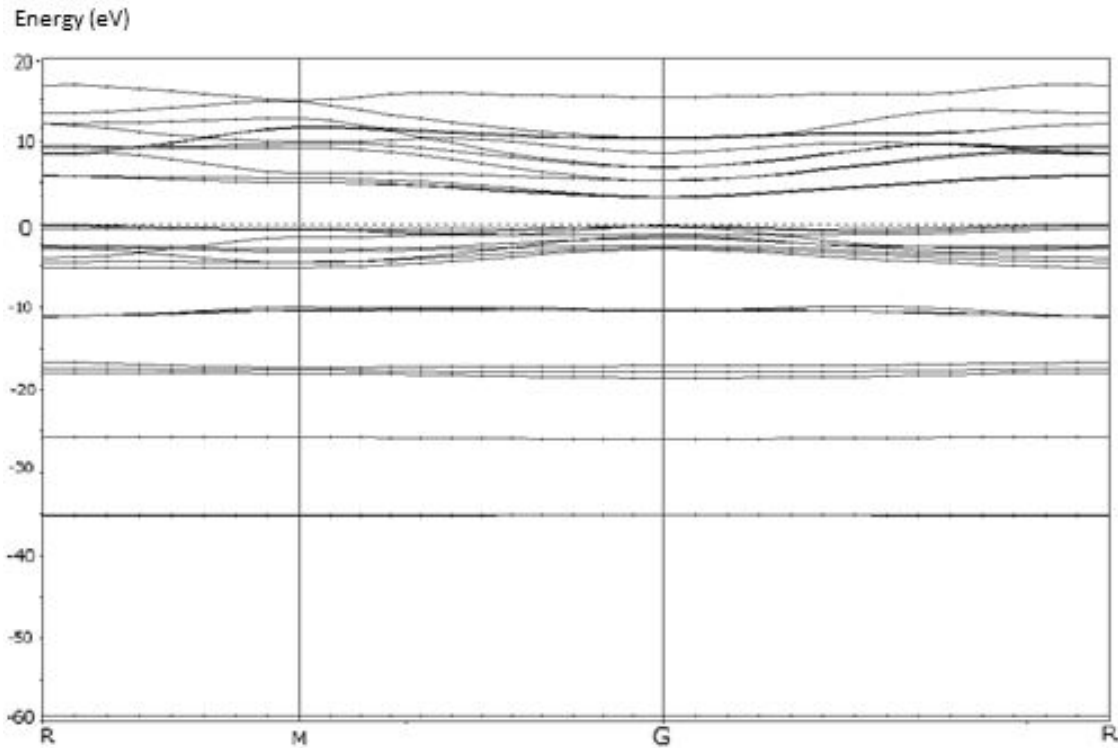


Figure 2: Band structure of cubic BaTiO₃ using hybrid B3LYP exchange-correlation has a direct band gap of 3.223 eV along the high symmetry of Brillouin zone at point R-G.

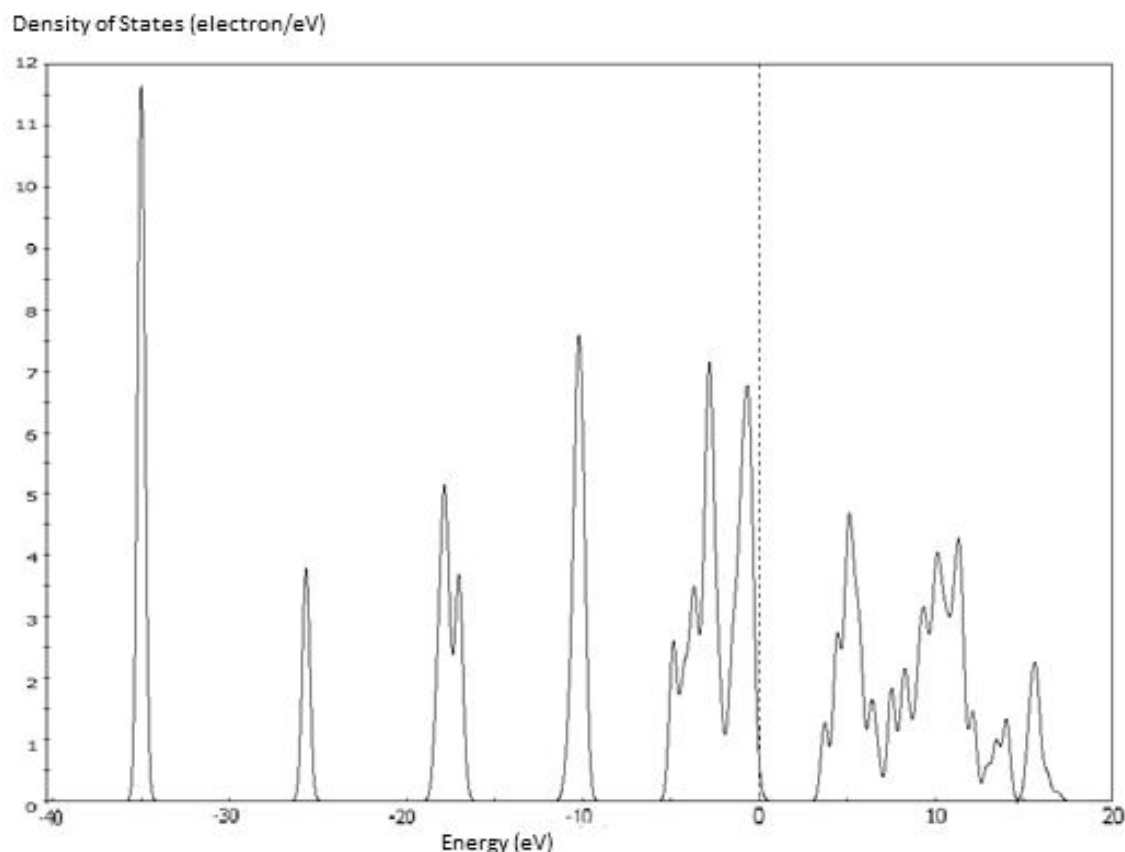


Figure 3: Density of state (DOS) of cubic BaTiO₃ using hybrid B3LYP exchange-correlation

CONCLUSION

The optimized crystal structure of perovskite-type material, barium titanate (BaTiO₃) was successfully built using CASTEP module of Materials Studio software by considering the lattice parameter, space group and atomic coordinates. The calculated result shows a good agreement with the experimental result when B3LYP is used. However, a calculation using GGA shows a big difference compared with the experimental result. It agreed with the other calculational results that use GGA. We can conclude that the hybrid function B3LYP is a better approximation compared to the GGA for measuring an energy band gap of the perovskite-type material [1, 15].

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