Modeling and simulation of mechanical and physical properties of Barium orthotitanate (Ba$_2$TiO$_4$) composite by Materials Studio (MS)

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Abstract

This research including a study of mechanical, physical properties (band structure, density of states) and the elasticity constants of the Barium orthotitanate by using Materials studio software. The calculations were based on the generalized gradient approximation (GGA) by linear method. The calculated equilibrium lattice constants of monoclinic barium orthotitanate were: a = 0.612nm, b = 0.77nm, c = 1.05nm, calculated bulk modulus = \(42.3021\) GPa, young modulus = \(40.29\) GPa, shear modulus = \(15.97\) GPa, lame constant \((\lambda) = 142.56\) GPa, and energy band gap = 3.435eV which is indirect band gap and the composite is insulator and the electronic properties where be calculated in first Brillion zone. According the mechanical stability conditions the composite is stable mechanically. These results were calculated by Materials studio software.

Key words: Molecular dynamic, Geometry optimization, Modeling, simulation.

1. Introduction

As our requirements for materials have increased recently, we focus our attention on how to improve materials properties and make them suitable in all aspects of life and in many applications and approaches of mechanical and electronic properties of ceramics to improve its advantages as it received a lot of attention from researchers. Simulation of molecular dynamics is a very important process and an important means of predicting the crystal structure, mechanical properties of ceramic materials. Rooksby study crystal structure in 1947, In 2001, Shackelford studied mechanical properties and mechanical behavior of ceramic and glass materials when exposed to external forces, including ceramics Ba$_2$TiO$_4$ and Ding Ying et al study mechanical properties in 2012 and The Materials Simulation Program in Materials Science named Materials Studio, developed by the American Accelrays Foundation is being used extensively in the pharmaceutical, petrochemical, automotive and industries as well as being used by researchers in materials science$^1$. Barium ortho titanate Ba$_2$TiO$_4$ is a good material for some applications and plays an important role in the scientific researches of composites, Ba$_2$TiO$_4$ was first examined crystallographically by Rooksby (1947) who showed that its X-ray powder pattern resembles that of Ba$_2$SiO$_4$ which has ß-K2SiO$_4$ structure and have perovskite crystal structure in two modifications as Rooksby et al and Net rer et al discovered$^2$.

2. Computational Methods

The commercial software package Material Studio, including the Cambridge Serial Total Energy Package CASTEP module was used to conduct these simulations the calculations were performed on a parallel computer cluster consisting of 14 AMD Opteron 64-bit processors utilizing a LINUX based operating system. Starting with the base structure, a geometric optimization was performed to determine the initial lattice parameters and density$^3$. In our calculations, we used the generalized theory of grading(GGA) along with ultra-soft pseudo potentials to represent the atoms. Specifically, for this geometric optimization, the Perdew-Burke-Ernzerhof potential for solids (PBEsol) was used. To obtain accurate band structures, calculations using the GGA PBEsol, as well as the hybrid functional Becke, three parameter, Lee Yang-Parr (B3LYP) potentials, were used. The finite element displacement method applied to a super cell of the geometrically optimized primitive lattice using norm-conserving potentials to calculate the phonon dispersion curves was used. The real space cutoff radius was set to 5 Å which resulted in a super cell volume 493.08 Å$^3$ for Ba$_2$TiO$_4$$^4$.

3. Results

3.1. The crystal structure

Ba$_2$TiO$_4$ is found in nature in two forms of monoclinic and orthorhombic crystalline structure$^2$, the orthorhombic shape cannot be found in stable state except at high temperatures while the other type is stable at normal temperature and room temperatures. The orthorhombic type of Ba$_2$TiO$_4$ is troubled compound especially if we are exposure it to air. As Rooksby (1947) found the monoclinic of Ba$_2$TiO$_4$ has a ß-Ca$_2$SiO$_4$ structures type and has lattice parameters: \(a = 0.612\)nm, \(b = 0.77\)nm, \(c = 1.05\)nm, \(\alpha = \gamma = 90^\circ\), \(\beta = 92.99^\circ\), and the orthorhombic of Ba$_2$TiO$_4$ has a ß-K2SiO$_4$ structure and the following lattice parameters: \(a = 0.765\)nm, \(b = 1.055\)nm, \(c = 0.61\)nm. (space group is \(Pna\)). These results are in agreement with researches$^{12,15}$. Orthorhombic consists of cations of the same compound with quadruple equivalents in a tetrahedral format that is unprecedented from other compounds. The crystal structure is shown in Figure (1), present calculations of lattice constants and experimental values are shown in the tables shown below$^5$. 

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Figure 1 shows the crystal structure of Ba$_2$TiO$_4$ indifferent forms where (a) is the unit cell and (b) is the primitive cell.

Table 1 shows Comparison of the theoretical results obtained from the MS program with experimental results for previous studies demonstrating a good agreement in the results obtained with previous studies.

| Parameters | Present Study (theory) | Experimental [7] |
|------------|------------------------|------------------|
| a (Å)      | 6.096                  | 6.098            |
| b (Å)      | 7.681                  | 7.682            |
| c (Å)      | 10.545                 | 10.544           |
| α (degrees)| 90                     | 90               |
| β (degrees)| 92.990                 | 92.990           |
| Volume (Å$^3$) | 493.08              | 493.1            |
| Density (g/cm$^3$) | 5.207               | 5.206            |

3.2. Simulation steps of mechanical and electronic properties

1. To determine the composite select: File: Import: Structures: Ceramics, and choose the compound Ba$_2$TiO$_4$.
2. To build the primitive unit cell choose: Build, Symmetry, Primitive cell, from the menu bar.
3. Geometry optimization, select: Modulus, Forcite, Calculation, and select, geometry optimization from the task dropdown.
4. To calculate mechanical properties select, Modulus, Forcite, Calculation and choose, Mechanical properties from the calculation menu.

$$C_p = \begin{bmatrix}
53.2241 & 29.1140 & 23.7314 \\
29.1140 & 92.5526 & 38.8026 \\
23.7314 & 38.8026 & 51.6460 \\
0.0000 & 0.0000 & 0.0000 \\
0.0800 & -1.7226 & -0.4849 \\
0.0000 & 0.0000 & 0.0000
\end{bmatrix}$$

The mechanical stability conditions of the monoclinic Ba$_2$TiO$_4$ can be written as:

$$C11, C22, C33, C44, C55, C55 > 0 \ldots (6)$$

5. To calculate electronic properties (density of states and band structure $E_g$), select: Castep bottom from modulus tool bar and select, Analysis, Density of states or choose, Band structure, and click Import.

3.3. Mechanical properties

The mechanical properties of Ba$_2$TiO$_4$ include the elastic constants of the crystal line and these constants are the result of the response to external forces. There are six components of tensile strength, as well as six other stress-related compounds in the three dimensions 3D of the crystal. Hook's law of elasticity can be expressed on the expression formula:

$$\sigma_{ij} = C_{ij} \varepsilon_{ij} \ldots \ldots \ldots (1)$$

$$\varepsilon_{ij} = S_{ij} \sigma_{ij} \ldots \ldots \ldots \ldots (2)$$

Where $C$ = elasticity constant, $S$ = mutant, $\sigma$ = stress and $\varepsilon$ = strain. Hook's low for elasticity that possesses (6x6) compounds on the surface of the material, it can be expressed as in the following formula:

$$\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{bmatrix} \begin{bmatrix}
e_1 \\
e_2 \\
e_3 \\
e_4 \\
e_5 \\
e_6
\end{bmatrix} \ldots \ldots \ldots (3)$$

And the elastic matrix $C_p$ can be written as:

$$\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{bmatrix} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{bmatrix} \begin{bmatrix}
e_1 \\
e_2 \\
e_3 \\
e_4 \\
e_5 \\
e_6
\end{bmatrix} \ldots \ldots \ldots (4)$$

Where the elastic matrix of monoclinic Ba$_2$TiO$_4$ obtained by Materials studio program and having the values as shown below.

$$C_p = \begin{bmatrix}
0.0000 & 0.0800 & 0.0000 \\
0.0000 & -1.7226 & 0.0000 \\
0.0000 & -0.4849 & 0.0000 \\
11.9197 & 0.0000 & 74.5826 \\
0.0000 & 16.3627 & -143.4170 \\
74.5826 & 0.0000 & -143.4170
\end{bmatrix} \ldots \ldots (5)$$

And the condition

$$(C22+C33–2C23) > 0 \ldots (7)$$
According to the mechanical stability conditions the composite is stable mechanically, and this agreed with research\(^{[10]}\). The elastic modulus for Ba\(_2\)TiO\(_4\) are obtained by Materials studio program using (Reuss model) shown in table 2.

**Table 2.** The computed elastic modulus for Ba\(_2\)TiO\(_4\) by materials studio MS.

| Elastic constant       | Symbol | Magnitude | Model |
|------------------------|--------|-----------|-------|
| Young modulus          | Y      | 40.29 GPa | Reuss |
| Shear modulus          | G      | 15.97 GPa | Reuss |
| Lame coefficient       | \(A\)  | 142.56 GPa| Reuss |
| Bulk modulus           | \(B\)  | 42.3021 GPa| Reuss |
| Poisson's ratio        | \(Y\)  | 0.3256 GPa| Reuss |

The ratio between stress change and corresponding change in strain is called elasticity, provided that the stress is within the limits of elasticity. This ratio is a fixed amount for each material, so it represents the behavior of these materials in relation to the influence of forces on them. The coefficient of elasticity is defined by the young coefficient, which is denoted \((Y)\)\(^{[10]}\). There is a clearly decrease of the slope (Young modulus) for the aged sample. The increase in failure strain was also observed for the aged sample, as shown in figure 2 the stress-strain curve representation \(^{[11]}\).

**Figure 2** shows the stress–strain curve (young modulus) of the composite \(^{[12]}\).

### 4. Discussion

Some properties were investigated by theoretical methods using 'the first principles calculations'. The calculated elastic constants as in table 1 and lattice parameters are accessible and comparable values to experimental studies and we have get the convergence of distances between atoms versus optimization step curves from (MS) when we do geometry optimization for the composite as shown in figure 3.

**Figure 3.** Convergence versus geometry optimization

The energy change versus optimization step had been obtained by MS as shown in figure 4 as we see the energy Greatly decreased after optimizing process on the crystalline structure.
Density of states is the number of patterns to the frequency unit, calculated by MS is increase as the energy increases shown in figure 5, where the peaks (which represents the energy via density of states) increase as energy increase. The physical meaning of figure 5 is that the density of states is increasing versus the energy increase as we can see below in figure 5. Density of states at high level meaning that level is ready for occupation by electrons and density of states at zero level meaning that the level can’t be occupied at that level, as we can see the density of states at high level at Fermi level which means that level is can be occupied by electrons [13].

The band structure of barium orthotitanate having forbidden band gap found equal to $E_g = 3.435\, eV$ along high symmetry $k$-points. These values were obtained directly from Materials studio program by applying the simulation steps of the band gap structure, as shown in figure 6 where this value is accessible compared with the other studies and the composite fall in the dielectric range of materials.
نمذجة ومحاكاة الخواص الميكانيكية والفيزيائية لمركب أوثرتتانات الباريوم

باستخدام برنامج (Ba₂Ti₄O₉)

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الملخص

تتضمن هذه البحث دراسة الخواص الميكانيكية والفيزيائية لمركب أوثرتتانات الباريوم (Ba₂Ti₄O₉) باستخدام برنامج Materials studio . تم قياس القيم المحسوبة لمعدّلات المرونة للمركب باستخدام (GGA) .



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