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RESEARCH ARTICLE

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Calculations of $Ba_{(1-x)}Sr_xTio_3$ structure and band gap properties by using density functional theory

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Abstract

The aim of this study is to simulate features using molecular modeling methods. The point is to show that it will accelerate research in material development studies by directing us, researchers, in terms of gaining time, material and workforce. In this study, the structural and electronic properties of undoped $BaTiO_3$ and Sr-doped $BaTiO_3$ were calculated by molecular modeling. In the study, energy calculations were made with the PBE and GGA (Generalized Gradient Approximation approach) developed by Perdew, Burke and Ernzerhof (PBE) using the density functional theory (DFT) calculation method, the CASTEP module of the Materials Studio program. First, the structural and electronic properties of the $BaTiO_3$ crystal phase were calculated. Then, the lattice constants, band gap values and electron state densities of the Sr doped structure to $BaTiO_3$ structure were calculated. The values in the literature were compared with the calculations made using the(DFT) density functional theory and it was determined that the calculations were in agreement with the values in the literature. It has been revealed that it will accelerate research in material development studies by giving direction to us researchers in terms of gaining from materials and workforce. As a result of geometric optimization of the non-stoichiometric $Ba_{(1-x)}Sr_XTiO_3$ structure and DFT calculations, it was determined that the electronic band gap shifted after %1 and %3Sr addition towards the conduction band and the band gap respectively decreased to 1,911 eV and 1.989eV.

Keywords: BaTiO3; DFT; Molecular Modeling

1. Introduction

Barium titanate ($BaTiO_3$) has been of great interest for decades as a perovskite ferroelectric material and due to its superior physical properties, such as high dielectric constant, ferroelectricity, high voltage tunability, positive temperature resistivity coefficient, pyroelectricity and piezoelectricity, it is used in multilayer ceramic capacitors, piezoelectric ceramic transducers, It is widely used in memories, infrared sensors and temperature controllers [1][2].

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$BaTiO_3$ capacitors used in many applications such as piezoelectric sensors, transducers, thermistors, energy carriers, etc. $BaTiO_3$ is used as dielectric material in multilayer capacitors, because of its high capacitance [3]. Many studies have been carried out with the addition of dopant to further improve the dielectric and ferroelectric properties of $BaTiO_3$ [4].

Today, many disciplines contain many complex problems that need to be solved. The fact that these complex problems cannot be solved analytically in many areas or that their solution is very difficult has led to the simulation technique with new searches in parallel with the development of technology. Molecular modeling is generally used to evaluate the current performance of a business process or to predict the future. It is designed to help practitioners discover new ways to achieve optimal results using mathematical, statistical and other analytical methods.

Molecular modeling methods have developed rapidly with the developments in computer technology. As a result of the developments in Molecular modeling methods, physical events that are very difficult to perform experimentally have been created in the computer environment and resolved within acceptable error limits [5].

$BaTiO_3$ has a high dielectric constant of 5000 at room temperature, with a Curie temperature of 120 °C, and an optical band gap of 3.3 eV, indicating its insulating nature. Its optical absorption in the UV range occurs below 400 nm. Additionally, $BaTiO_3$ possesses a perovskite structure of ABO_3 type and experiences three structural phase transitions from cubic to tetragonal, then orthorhombic, and finally rhombic phases as temperature decreases. [13]

The aim of this study is to simulate features using molecular modeling methods. The study is based on the effect of dopants on BaTiO3 structure. The aim of this study is to show that it will accelerate research in material development studies by directing us, researchers, in terms of gaining time, material and workforce.

Nomenclature

DFT	Densıty Functıonal Theory
DOS	Density of States
pDOS	Partial Density of States

2. DFT studies

2.1. Molecular modeling with densıty functıonal theory

This study calculations were made using the simulation package CASTEP (Materials Studio CASTEP Package ID:11795). Materials Studio is a simulation program that models materials at the atomic scale with electronic structure calculations or quantum mechanical molecular dynamics (QMD) using DFT-based ab-initio computation techniques[15]. The Materials Studio Castep program aims to obtain approximate solutions of Schrodinger equations representing multibody systems by solving DFT and Kohn-Sham equations or HF and Roothaan equations. Hybrid functionals in the program are a mixture of HF approach and DFT. Moreover, Green's function methods and many-body perturbation theory are also embedded in the program [6]. The interactions of plane wave basis sets with electronic charge density, local potential and single electron orbital are considered. Interactions between electrons and ions are described using the norm-concerning or ultrasoft pseudopotential or projective extended wave method. By using the density functional theory (DFT) calculation method CASTEP module, energy and band gap calculations were made with the PBE and GGA (Generalized Gradient Approximation approach) developed by Perdew, Burke and Ernzerhof (PBE) [6].

Perdew-Burke-Ernzerhof (GGA-PBE) function and the soft pseudopotential proposed by used . Also the generalized gradient approximation (GGA) have been performed and electron displacement coaction, as well as electron-ion interaction[16]. The cut off energy of the calculation used as 500 eV. Electronic Configuration for Ba is $5s^2\ 5p^6\ 6s^2$, for O $2s^2\ 2p^4$, Ti electronic configuration is Ti $3s^2\ 3p^6\ 3d^2\ 4s^2$ where Sr configuration is Sr $4s^2\ 4p^6\ 5s^2$.

By establishing the convergence criteria at 1.0 × 10−5 electronvolts per atom for energy, 0.03 eV per angstrom for the highest force exerted on atoms, 0.05 gigapascals for the maximum stress, and 1.0 × 10−3 angstroms for the maximum atomic displacement as detailed in the publication authored by M. Hassan and collaborators [12].

3. Results

3.1. Geometry optimization of stoichiometric $BaTiO_3$ and non-stoichiometric $Ba_{(1-x)}SrxO_3$ structures

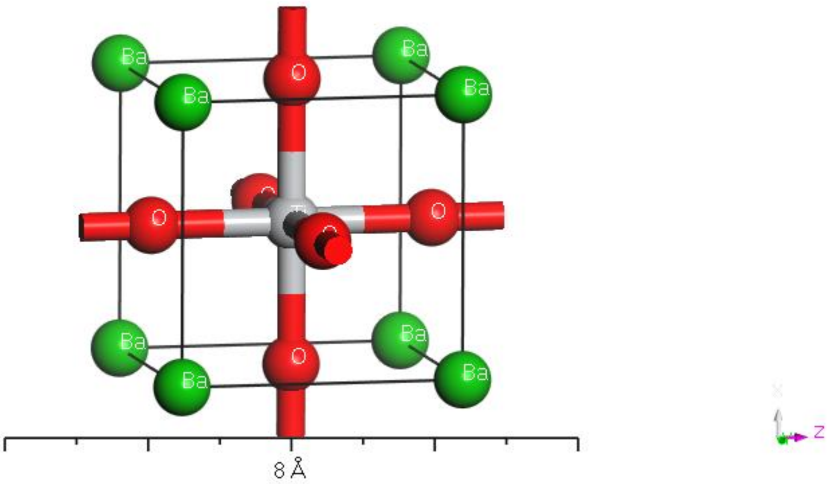
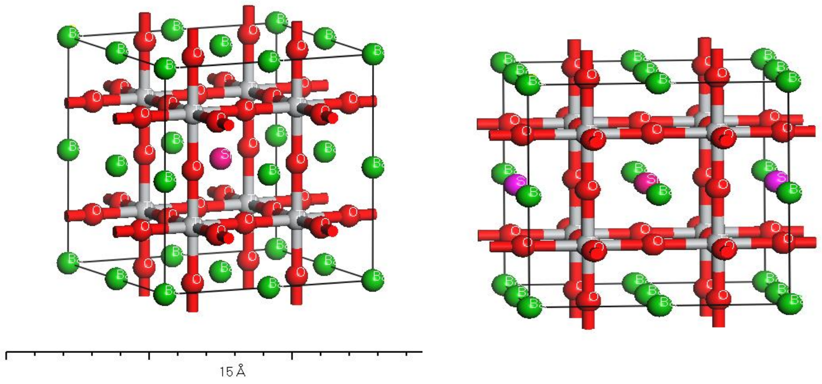


Fig. 1. Stoichiometric $BaTiO_3$ Structure

Calculations are completed using DFT, which includes the plane wave pseudopotentials. This approach allows us to make quick calculations with better efficiency. The soft pseudopotential proposed by Perdew-Burke-Ernzerhof (GGA-PBE) used to compare (GGA) generalized gradient approximation and electron displacement coaction, as well as electron-ion interaction. The cut off energy of the calculation used as 600 eV. Configuration of electronic for Ba is $5s^2$ $5p^6$ $6s^2$, for O $2s^2$ $2p^4$, Ti electronic configuration is Ti $3s^2$ $3p^6$ $3d^2$ $4s^2$ where Sr configuration is Sr $4s^2$ $4p^6$ $5s^2$. After the geometric optimization of Ba $5s^2$ $5p^6$ $6s^2$ was completed, a single point energy calculation was made. After Sr doping, the lattice constants of the structure were calculated as a=b=c= 8.001085 Å and the unit cell volume was calculated as 512.208 A3. The unit cell is slightly reduced by the Sr dopant. The unit cell volume of the pure material was calculated as 64,481 A^3. (Figure 1)



(a) (b)

Fig. 2. (a) Non-Stoichiometric $Ba_{0,99}Sr_{0,01}TiO_3$ Structure (b)Non-Stoichiometric $Ba_{0,97}Sr_{0,03}TiO_3$ Structure

Table 1. Optimized Lattice Constants of unit cell volume and Sr-doped $BaTiO_3$

	Lattice Parameters (Å)			Volume (Å3)
	A	b	C	
Literature (BaTiO3)	4.034	4.034	4.034	64.481 [6]
Experimental Value	4.000	4.000	4.000	64.000 [6]
Literature (BaTiO3)	4,03	4,03	4,03	65,67 [11]
BSTO (Ba0.875Sr0.125TiO3)	4,03	4,03	4,03	65,28 [11]
Stoichiometric BaTiO3 -This study	4.010	4.010	4.010	65.6459
Ba(1-x) SrxTiO3 This study	4.005	4.005	4.005	64.240

$BaTiO_3$ exists in cubic form with PM3M space group at 120 °C [7]. Quantum mechanics has been used to calculate the structural properties and electronic properties of Ba(1-x)SrXTiO3. In this structure, Ba is located at the corners. The lattice parameters of $Ba_{(1-x)}Sr_xTiO_3$ are optimized. The lattice constants have calculated as a = 4.010 Å; b =4.010 Å; c = 4.010 Å in our study. This lattice constant value has calculated approximately close in value with the experimentally reported 4.000 Å [8]. The differences between the value we have calculated and the experimental value is only 0.010 Å and is close to 99.75%. This shows the closeness of this study to reality. A supercell was formed by shifting the stoichiometric structure 2x2x2. For the supercell a=b=c=8.020 Å and the volume is calculated as 515.849 A^3.

3.2. Electronic properties of stoichiometric $BaTiO_3$ and non- stoichiometric $BaTiO_3$

The density of states (DOS), band structure, electron density . such electronic properties provide important information about the bonding nature of the material and its physical properties. The specific study of the binding properties of stoichiometric $BaTiO_3$ and Non-Stoichiometric $Ba_{(0,97)}Sr_{(0,03)}TiO_3$ is very important. [12] However, the impact of Sr doping on the electronic properties remains significant, as the band structure is altered by Sr being added to the Ba-site, which in turn affects the Ti-O binding.[14] We used GGA to calculate the electronic propertiesand k-points are used for these calculations. In order to understand the binding nature of these compounds well, for (TDOS) the total density of states and for (PDOS) partial density of states were calculated. The first Brillouin region and doped electron density and Brillouin zone regions has shown in Figure3 (a) and Fig 3(b).

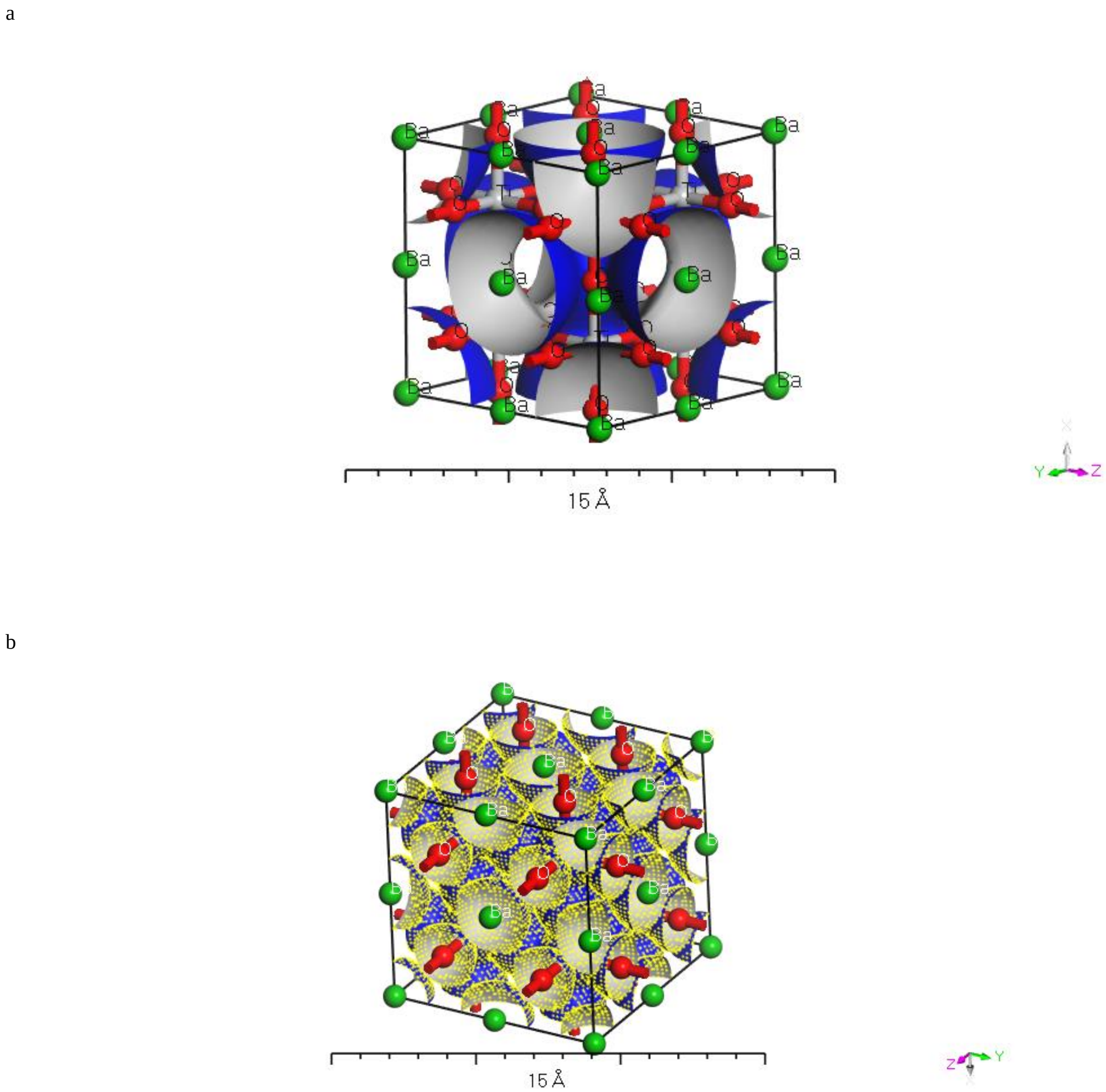


Fig. 3. (a) electron density of $BaTiO_3$ (b) electron density of $BaTi_{(1-x)}Sr_xO_3$

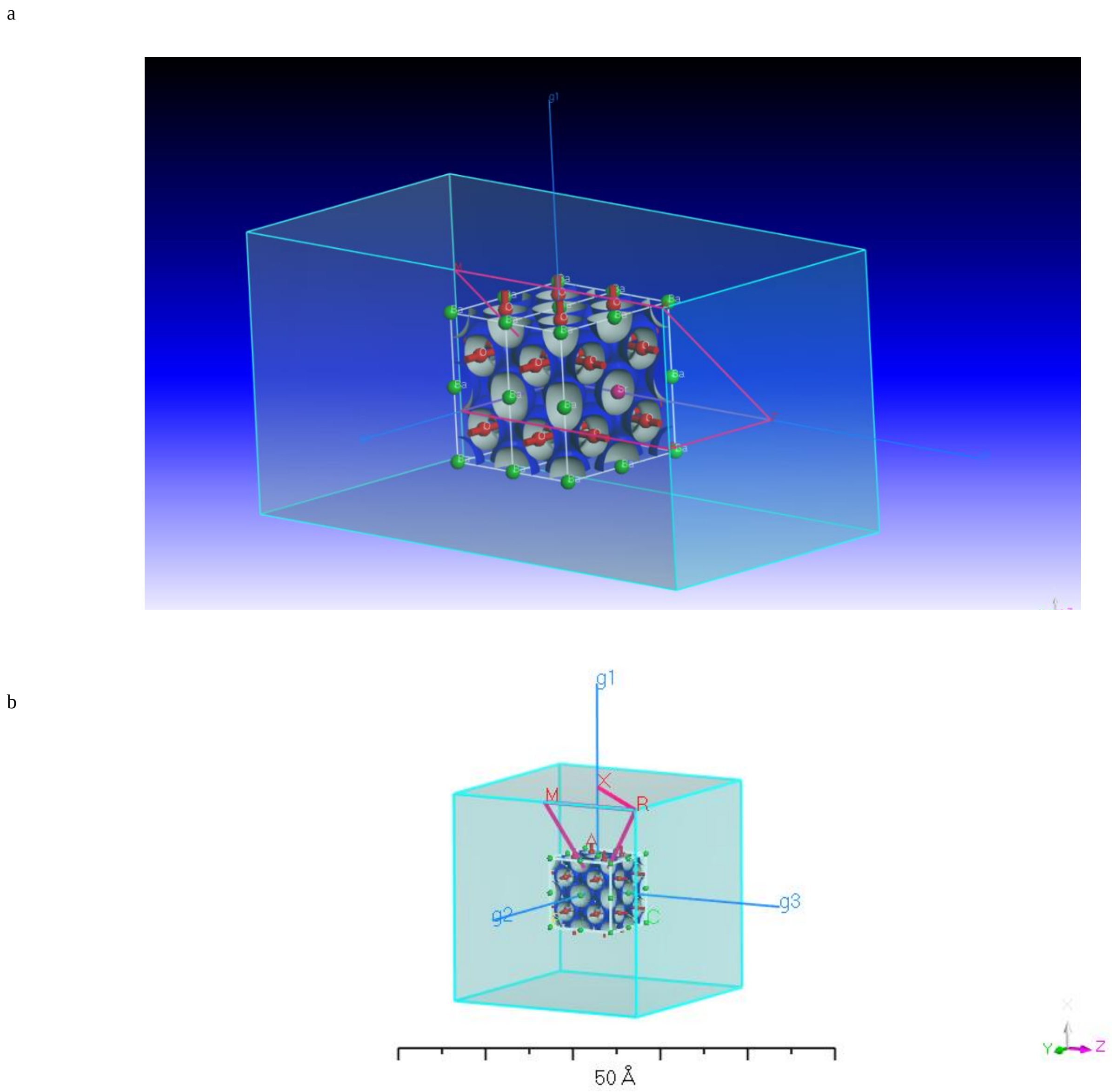
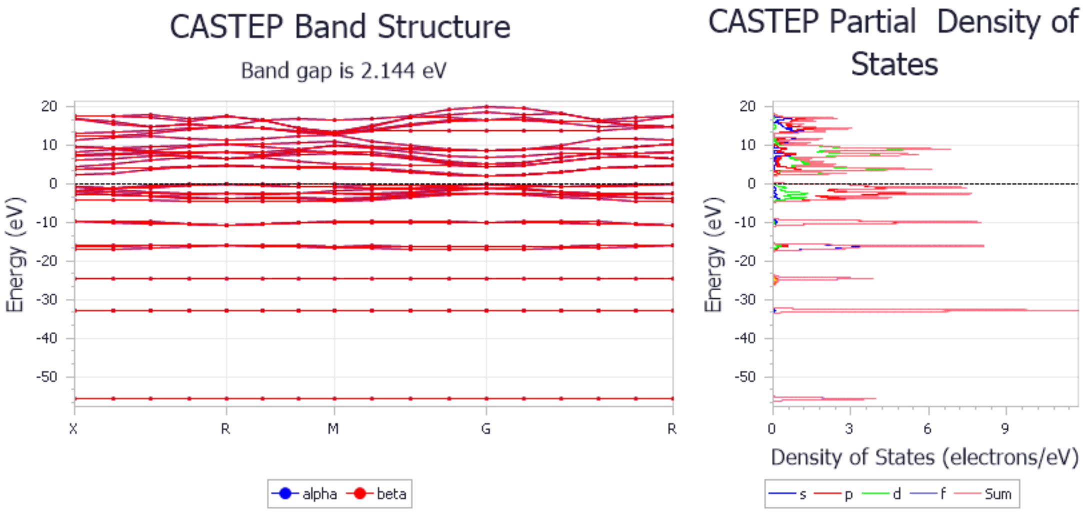


Fig. 4. (a) Brillouin zone path of BaTiO$_3$; (b) Brillouin zone path of BaTi$_{(1-x)}$SrO$_{3\ C)}$

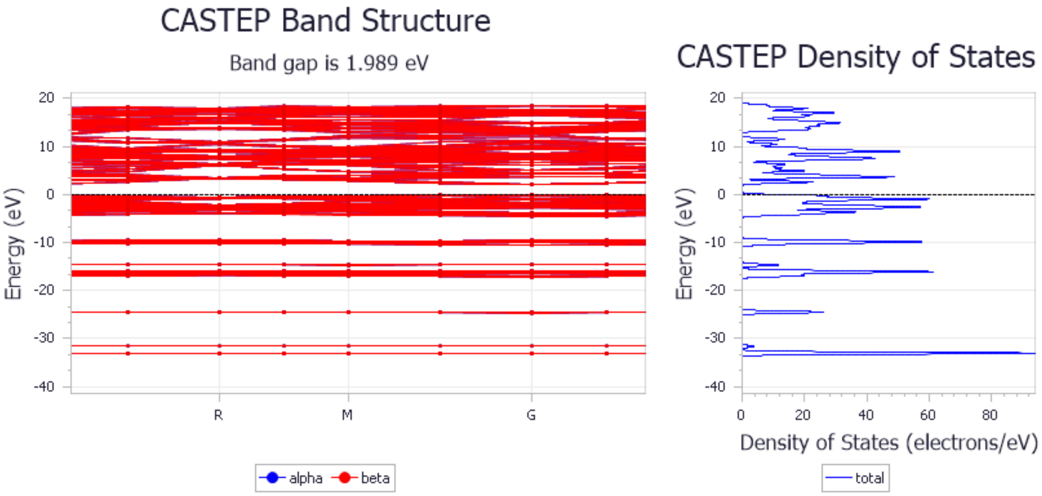
3.3. Band gap results

Materials band structure is examined as it provides useful information for understanding the nature of pyroelectricity and ferroelectricity.[6] The band structure of $BaTiO_3$ and doped $Ba_{(1-x)}Sr_xTiO_3$ is shown in Figures 3a and b. The electronic band gap diagram calculations in the direction of the highly symmetric Brillouin zone of cubic $BaTiO_3$ are shown in Figure 4 . The band gap of pure $BaTiO_3$ is found 2,144 eV, 1,989 eV for $Ba_{0,99}Sr_{0,01}TiO_3$ semiconducting and 1,911 eV for $Ba_{0,97}Sr_{0,03}TiO_3$ nature that had been shown in figure. The band gap of $Ba_{(1-x)}Sr_xTiO_3$ is lower than the band gap of pure $BaTiO_3$ They told that band gap reduces by doping. [12]

a



b



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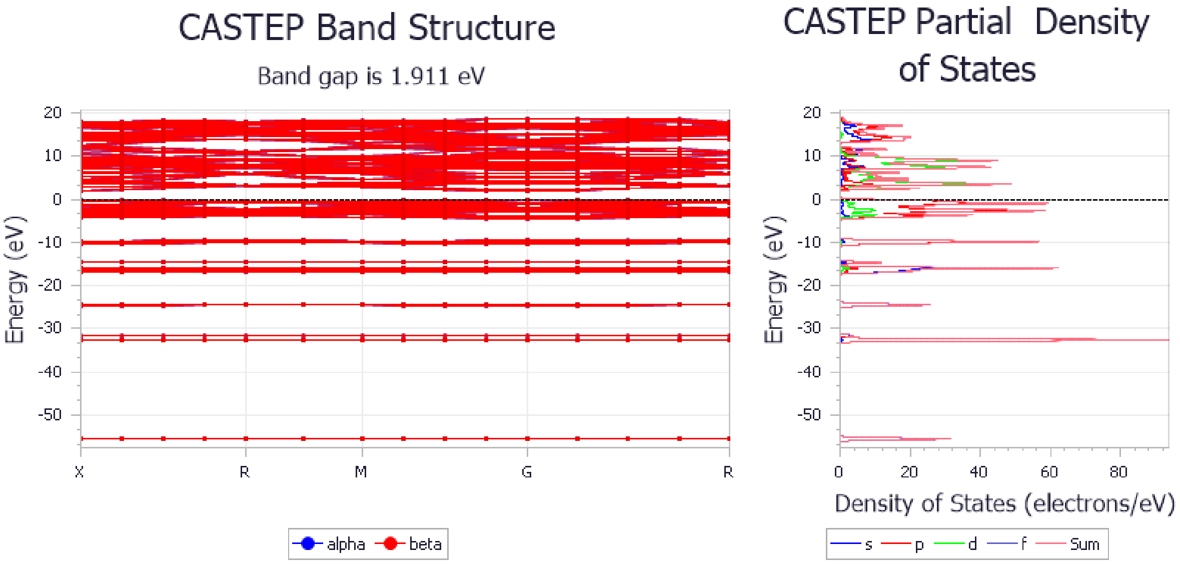


Fig. 5.(a) band gap of $BaTiO_3$ (b) band gap of %1 Sr doped $Ba_{(1-x)}Sr_XTiO_3$ (c) band gap of %3 Sr doped $Ba_{(1-x)}Sr_xTiO_3$

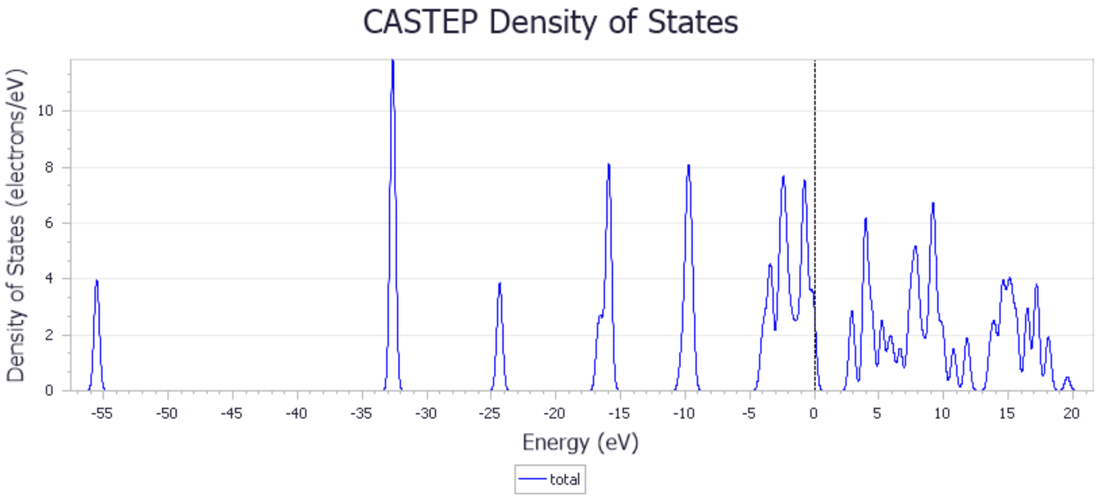
The minimums of the Conduction Band which have been controlled and pushed by the Titanium (Ti) 3d-states are located at the G point. The Valence Band maximum occurring is driven by the O-2p states of Oxygen. Figure 3 (a) shows the electronic band for stoichiometric $Ba_{(1-x)}Sr_xTiO_3$ and (b) non-stoichiometric $Ba_{(1-x)}Sr_xTiO_3$. In this study, the band gap at the R-G points is 2.144 eV and is indirect. This value is closer to the theoretical ~3.2 eV [10] Experimental band gap value compared to the band gap value of 1.723 eV reported in the previous study [8]. In DFT calculations, the value that we have calculated is smaller due to the pd pushing of the cation and the anion of the Generalized Gradient Approach application.

Calculations show that after doping $BaTiO_3$ with Sr in the Barium zones in Figure 4b, the electronic band structure shifts to the conduction band and the band gap value is 1,911 eV for %1 Sr dopped eV as seen in Figure 5a and Figure 5b we can see from figure 5(c)the band gap value is 1,989 eV %3 Sr doped. As a result of our calculations, it was determined that the nature of the Sr-doped $BaTiO_3$ band structure changed directly from the indirect structure. The minimum energy required to excite the electron is determined by the band gap in semiconductors and insulators. However, it cannot fully explain whether the phonon will be absorbed by the material. It has been noticed that due to finite momentum the indirect band gap shows weak optical transmission. [9] The shift of the band gap after Sr doping in $BaTiO_3$ defines that the conductivity of the material is increased directly due to the easy recombination of electron hole in the band gap.

3.4. DOS-pDOS results

Electronic configuration for Ba is $5s^2$ $5p^6$ $6s^2$, for O $2s^2$ $2p^4$, Ti electronic configuration is Ti $3s^2$ $3p^6$ $3d^2$ $4s^2$ where Sr configuration is Sr $4s^2$ $4p^6$ $5s^2$. Figure 6(a) shows the total density of states for stoichiometric $BaTiO_3$, figure 6(b) shows the total density of states for $Ba_{(1-x)}Sr_XTiO_3$ and figure 6(c) shows the partial density of states for stoichiometric and Sr doped $BaTiO_3$ systems.

a



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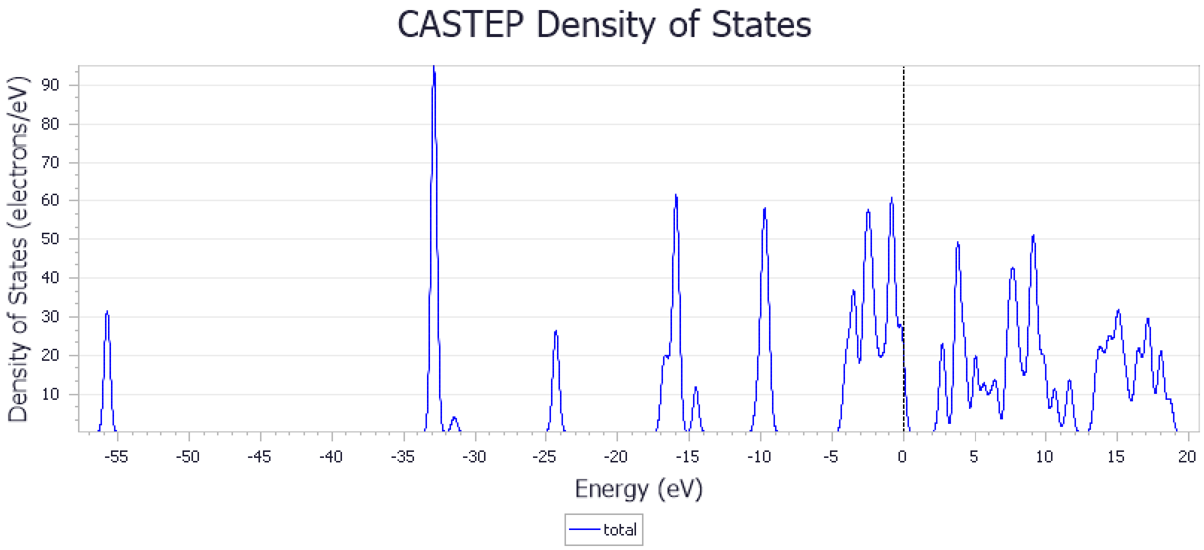

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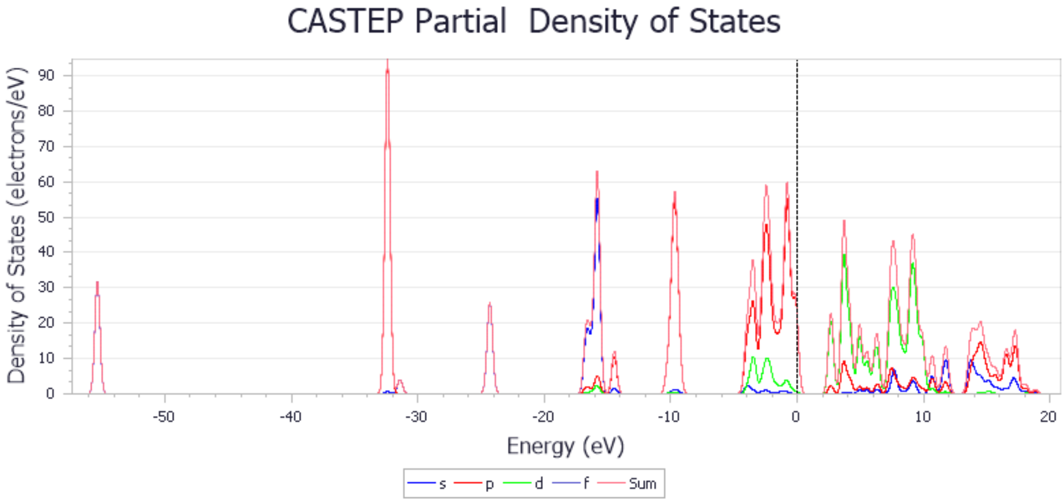

Fig. 6. (a) DOS Graph of $BaTiO_3$;(b) DOS Graph of %1 Sr doped $Ba_{(1-x)}Sr_xTiO_3$; (c) DOS Graph of %3 Sr doped $Ba_{(1-x)}Sr_xTiO_3$

In the examination, the primary importance of BaTiO3 resides in the 6p states present within the valence band (VB), undergoing modifications upon the incorporation of Sr doping into the structure. We can say that the top of VB indicates the main contribution by the p-density of the states and the d-density of the states. In Figure 6, the density of states was increased after the addition of Sr. In Figure 6, p-DOS and d-DOS were considered to be the dominant contributors.

4. Discussion

In the study, our DFT calculation results in experimental and consistent with other studies. After Sr doping, the lattice constants of the structure were calculated as a=b=c= 8.001085 Å and the unit cell volume was calculated as 512,208 A3. The unit cell is slightly reduced by the Sr dopant. In this study, the band gap at stoichiometric $BaTiO_3$ R-G points is 2.144 eV and is indirect. As a result of geometric optimization of the non-stoichiometric $Ba_{(1-x)}Sr_xTiO_3$ structure and DFT calculations, it was determined that the band structure switch towards the conduction band. The band gap decreased to 1,911 eV for %1 Sr dopant to the $BaTiO_3$ system and for %3 dopant to the $BaTiO_3$ system the band gap decreased to 1.989 eV while the band gap is 2,144 eV for stoichiometric $BaTiO_3$

First, the band gap decreased with $BaTiO_3$ Sr doping. Secondly, the band gap has also changed directly to the band gap. In that case, $BaTiO_3$ produced by Sr doping is suitable for electronic devices.

We think that this study will contribute to, at the beginning of experimental studies to be carried out for future optoelectronic device applications, thus benefiting from saving time and materials.

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References

[1] M. Vijatović, J. Bobić, & B. Stojanović,, History and challenges of barium titanate: part I, *Science of Sintering*, 40(2), 155-165,

doi:10.2298/SOS0802155V, 2008

[2] S. Dahbi, N. Tahiri, O. El Bounagui,H. & Ez-Zahraouy, Electronic, optical, and thermoelectric properties of perovskite $BaTiO_3$ compound under the effect of compressive strain, *Chem. Phys*., doi:10.1016/j.chemphys.2021.111105, 2021

[3] F.D. Morrison, D.C. Sinclair, & A.R. West,, Doping mechanisms and electrical properties of La-doped $BaTiO_3$ ceramics, *Int. J. Inorg. Mater*., 3(8),1205-1210, 2001

[4] F.,Yang,, First-principles investigation of metal-doped cubic BaTiO3, *Mater. Res. Bull*., 96(4), 372-378, doi.org/10.1016/j.materresbull.2017.03.023

[5] C. Soykan, *Yeni manyetik şekil hafizalı alaşımların yoğunluk fonksiyonel teorisine dayalı ab-initio metodu ile tasarlanması: ni-fe-ga*., Doktora Tezi, Pamukkale Üniversitesi Fen Bilimleri Enstitüsü, Denizli, 130s., 2014

[6] L. Hedin, New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem. *Physical Review*, 139, 796-823, doi.org/10.1103/PhysRev.139.A796, 1965

[7] C. Soykan, H.Gocmez, The physical properties of bismuth replacement in lead halogen perovskite solar cells: CH3NH3Pb1−xBixI3 compounds by ab-initio calculations, *Results in Physics*, 13,102278, doi.org/10.1016/j.rinp.2019.102278, 2019

[8] R. King-Smith, D. Vanderbilt, A first-principles pseudopotential investigation of ferroelectricity in barium titanate, *Ferroelectrics*, 136 (1) 85–94., 1992

[9] M.Rizwana,, H. Zebab, M.Shakila, S.S.A. Gillanic, & Z.Usmand, Electronic, structural and optical properties of $BaTiO_3$ doped with lanthanum (La): Insight from DFT calculation, *Optic - International Journal for Light and Electron Optics*, 211,164611

[10] H.Shen, K.Xia, P.Wang, & R.Tan,, "The electronic, structural, ferroelectric and optical properties of strontium and zirconium co-doped $BaTiO_3$": First-principles calculations, *Solid State Communications*, 355, 114930, 2022

[11] A.Boubaia, A. Assali , S. Berrah , H. Bennacer, I. Zerifi ,& A. Boukortt,Band gap and emission wavelength tuning of Sr-doped $BaTiO_3$ (BST) perovskites for high-efficiency visible-light emitters and solar cells, *Materials Science in Semiconductor Processing*, 130 ,105837, 2021

[12] M.Hasan, A.K.M.,& A.Hossain, Structural, electronic and optical properties of strontium and nickel co-doped BaTiO3: A DFT based study, *Computational Condensed Matter*, 28, 578, 2021

[13] A. Rehman , A. Muhammad Iqbal , A. I. Channa , S. U. Awan , & M. T. Khan, Structural, electronic and optical properties of BaTiO3-CoFe2O4 nanocomposites for optoelectronic devices, *Materials Science and Engineering: B*, 296, 116626, 2023

[14] C. Sidar, M.N. Tripathi, & P.K. Bajpai, Effect of Sr-doping on the band structure of BaTiO3 through density functional theoretical calculations, *Computational Condensed Matter*, 11, 27-32, 2017

[15] S. Aksan, Determination of Structural and Electronic Properties of Sr Doped BaTiO3 Using Density Functional Theory, *XI. Ceramics Congress with International Participation*, the proceedings summary book, 2022

[16] Aksan, S.,Hussaini, A.A., Erdal, M.O. et al. Investigation of photosensitive properties of novel TiO2:Cu2O mixed complex interlayered heterojunction: showcasing experimental and DFT calculations. *Opt Quant Electron*, 56, 578, doi.org/10.1007/s11082-023-06266-7, 2024