THE ELECTRONIC, STRUCTURAL AND OPTICAL PROPERTIES OF BARIUM PEROVSKITE COMPOUNDS

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Abstract: In this research, first-principle density functional theory calculation was used to determine the structural, electronic and optical properties of ternary and quaternary chalcogenide perovskite compounds ($BaTiS_3$, $BaTiSSe_2$ and $BaTiS_2Se$). Bandgaps of 1.61 eV, 0.54 eV and 1.39 eV were obtained for the three compounds respectively. These band gap values show that $BaTiS_3$ and $BaTiS_2Se$ are ideal for photovoltaic applications. The high absorptance of 7 x 10^8 m^{-1}, 7 x 10^8 m^{-1} and 6.8 x 10^8 m^{-1}, low reflectivity of 0.7, 0.72 and 0.68, refractive index of 8.2, 8.8 and 8.2, and dielectric function of 78, 87 and 69 values respectively show that these compounds are good light absorbers.

Keywords: Chalcogenide perovskites, density functional theory, photovoltaic, absorptance and dielectric function.

Introduction

Due to the increasing demand in energy consumption, non-sustainability of fossil fuels and environmental pollution, the need for a sustainable and clean alternative source arises. Solar energy which is provided by nature, is renewable, sustainable, and abundant. However, its high production costs as compared to fossil fuel energy sources is its major drawback [1,2]. Research have led to the discovery of a thin-film photovoltaic technology, which has a promising photoelectric property.

Perovskites were first discovered by Gustav Rose in the Ural mountains of Russia in 1839 and renamed by L.A. Perovski. In 2012, Kim et al obtained a power conversion efficiency of about 24% [3]. Perovskites have gained attention by researchers due to its low production cost and high-conversion efficiency [4]. Perovskite solar cell is a type of solar cell which has a perovskite structured material as its absorber [5]. They have a general formula of ABX_3, where A is an organic or inorganic cation, B is a cation and X is a halide, oxide or S or Se for a chalcogenide perovskite [6,7]. The favorable properties of these perovskites are high charge carrier mobilities, a balanced electron and hole transport, high absorption coefficients, and tunable bandgaps [14,16].

Methylammonium lead iodide ($MAPbI_3$) is the most researched perovskite solar cells and have shown and improved efficiency and stability. However, the presence of lead hinders its commercialization due to its poisonous nature [8,14] and also degrades when in contact with moisture and oxygen [9]. In order to overcome the shortcomings of lead-based perovskites, compositional tuning is adopted, which is the substitution of the Pb2+ cation and/or inorganic cation with non-toxic cations [12,13]. Tin-based perovskite is not a good substitute, given that it is toxic and oxidizes from 2+ to 4+ when exposed to moisture. Cesium lead iodide perovskite is also a good alternative, because of the stability of its black perovskite phase $_\beta$-$CsPbI_3$[21].

Metal chalcogenide perovskites semiconductors proffer solution to the limitations of lead-based perovskites due to its bandgap tunable properties [5]. These perovskites are better alternative to hybrid organic-inorganic halide perovskites due to its high absorption coefficient, stable and non-toxic and environmentally friendly [17,18]. Theoretically, about 30% of solar cell efficiencies of some chalcogenide perovskites were obtained and Zr-chalcogenides are the most studied family of chalcogenide perovskites [9]. Chalcogenide perovskites have a general formula ABX_3 where X = S or Se while A and B are 2+ and 4+ cations respectively [6,7]. Sun et al investigated the band gap of $CaTiS_3$, $BaZrS_3$, $CaZrSe_3$ and $CaHfSe_3$ and obtained the values of 1.0eV, 1.75eV, 1.3eV and 1.2eV respectively [6,16].

In this work, barium compound perovskites ($BaTiS_3$, $BaTiS_2Se$ and $BaTiSSe_2$) are studied to obtain their structural, electronic and optical properties and determine if they are potential solar cell absorber material.

COMPUTATIONAL METHOD

The first principles density functional theory (DFT) calculations have been performed by the plane wave pseudopotential method with the Quantum Espresso software package [23]. The crystal structure of each perovskites was first optimized by performing the vc-relax calculations using Projected Augmented Wave ultrasoft pseudopotentials from the standard Quantum Espresso library and PBEsol exchange correlation functional [24]. The relaxed atomic positions were then used to optimize both the plane wave energy cut off and the k-point grid. The Monkhorst-pack k-point of 3 x 3 x 3 and plane wave cut off energy of 40Ry was used for the structural optimization. The third-order Birch-Murnaghan isothermal equation of state is given by:

$$P(V) = \frac{3B_o}{2}\left[\left(\frac{V_o}{V}\right)^{\frac{7}{3}} - \left(\frac{V_o}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(B_o' - 4)\left[\left(\frac{V_o}{V}\right)^{\frac{2}{3}} - 1\right]\right\} \quad \text{..... (1)}$$

The internal energy, E(v) is found by integration of the pressure.

$$E(V) = E_o + \frac{9V_oB_o}{16}\left\{\left[\left(\frac{V_o}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_o' + \left[\left(\frac{V_o}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left[6 - 4\left(\frac{V_o}{V}\right)^{\frac{2}{3}}\right]\right\} \quad \text{..... (2)}$$

Where P is the pressure, V_o is the reference volume, V is the deformed volume, B_o is the bulk modulus, B_o is the derivative of the bulk modulus with respect to pressure. The lattice equilibrium constant B, bulk modulus B_o and ground state energy, E_o were obtained [25,26]. Goldschmidt tolerance factor, t = $\frac{r_A+r_B}{\sqrt{2}(r_B+r_X)}$was used to evaluate the stability of these perovskites [22]. Crystal structures were visualized using the Xcrysden program suite.

For electronic calculation, the self-consistent field, non-self-consistent field, band, and DOS input files were used for simulations and the band structure, density of state graphs were plotted using gnuplot.

For the optical properties, non-conserving pseudopotentials were used for its input file. Fortran compiler was used to calculate the output files of scf.out and nscf.out, from which the optical properties are calculated and plotted using gnuplot.

Kramers-Kronig (KK) relations relate the real and imaginary parts of dielectric function using the mathematical tool [19,20].

$$\varepsilon_r = \varepsilon_1 + i\varepsilon_2 \quad \text{..... (3)}$$

This equation is the sum of the real and imaginary part of the dielectric function, where ε_r is the dielectric function, ε_1 is the real part of the dielectric function and ε_2 is the imaginary part of the dielectric function and ω is the angular velocity.

The real part of the dielectric function is solved using equation:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega^1\varepsilon_2(\omega)\delta\omega^1}{\omega^{1^2}-\omega^2} \quad \text{..... (4)}$$

The imaginary part is also determined using the equation:

$$\varepsilon_2(\omega) = \frac{-2}{\pi}\int_0^\infty \frac{\omega^1\varepsilon_2(\omega)\delta\omega^1}{\omega^{1^2}-\omega^2} \quad \text{.....(5)}$$

Other optical properties such as absorption coefficient (α), refractive index $(n(\omega))$, extinction coefficient $(k(\omega))$ and reflectivity $(R(\omega))$.

$$\alpha(\omega) = \sqrt{2}\omega\left(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)\right)^{\frac{1}{2}} \text{.... (6)}$$

$$n(\omega) = \frac{1}{\sqrt{2}} + \varepsilon_1(\omega \text{ ..... (7)}$$

$$\boldsymbol{k}\,(\omega) = \frac{1}{\sqrt{2}}\left(\sqrt{\varepsilon_1(\omega^2) + \varepsilon_2(\omega)^2} - \varepsilon_1\right) \text{) .....(8)}$$

$$R(\omega) = \left|\frac{\sqrt{\varepsilon(\omega)}-1}{\sqrt{\varepsilon(\omega)}+1}\right|^2 \quad \text{.....}$$

(9)

Results and Discussion

These barium perovskite compounds ($BaTiS_3$, $BaTiS_2Se$ and $BaTiSSe_2$) have a perovskite structure ABX_3 (A= Ba, B=Ti, X=S,Se) which are shown in fig. 1. The materials are orthorhombic crystal structure.

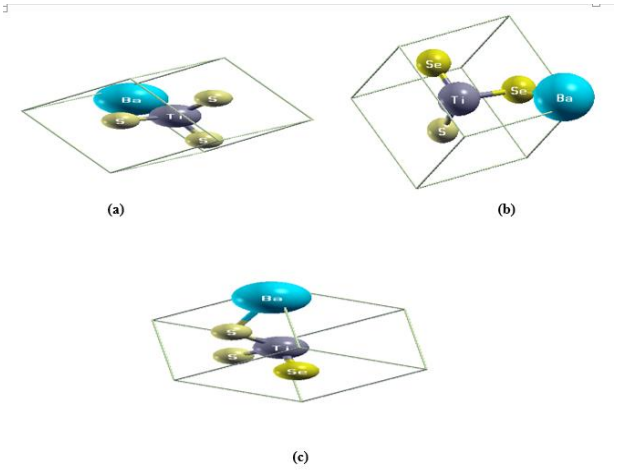

Fig 1. Cyrstal structure of (a) $BaTiS_3$ (b) $BaTiSSe_2$ (c) $BaTiS_2Se$ perovskite

The lattice constant, bulk modulus, bulk modulus derivative, minimum energy and volume obtained from the Birch-Murnaghan equation of state is shown in Table 1.

Using Goldschimdit tolerance factor, the value obtained was 0.9976 for the three compounds, which indicates its stability.

Table 1: Table showing the lattice constant, bulk modulus, minimum energy volume and band gaps of $BaTiS_2Se$, $BaTiSSe_2$ and $BaTiS_3$.

Compound	Lattice constant(a.u.)	Bulk modulus (B_o) (GPa)	Bulk modulus derivative (B_o')	Minimum Energy (eV)	Volume(a.u.)^3	Band gap
$BaTiS_2Se$	9.4668	53.3	52	-928.72831	849.2333	1.39eV
$BaTiSSe_2$	9.4668	48.3	15.0	-1048.90170	849.233	0.54eV
$BaTiS_3$	8.5219	70.7	11.02	-806.99046	764.4727	1.62eV

Analysis of the electronic band structures of $BaTiSSe_2$, $BaTiS_2Se$ and $BaTiS_3$ perovskites as shown in fig.2, shows it is an indirect band gap of 0.54eV, 1.39eV and 1.61eV respectively along $\Gamma - U$ and $\Gamma - R$ brillouin zone for $BaTiSSe_2$. Doping of $BaTiS_3$ with Selenium (Se), reduced the band gap from 1.62eV to 0.54eV, which is in close agreement to Zitouni et al reduced the band gap value by applying different percentage of doping using Se atom $BaZrS_{3-x}Se_x$.

The density of states (DOS) of a system describes the number of states per interval of energy at each energy level for electrons to occupy. A DOS of zero shows that no states are available for electrons to be occupy, the plots in fig 3 show that the materials are semiconductors as the region around zero has no states.

Optical properties of these chalcogenide compounds give details about the internal structure of the material, and its interaction with light [10]. The absorption spectra, reflectivity, refractive index, dielectric coefficient, and extinction coefficient of these properties are shown in the graph.

Absorption spectra of these materials show the light harvesting ability, describing the exponential decay of light intensity as it penetrates the material [11]. The high absorption peak value of these materials in the order of $10^8 m^{-1}$ in the visible and infrared as shown in fig 5, fig 6 & fig 7, is needed

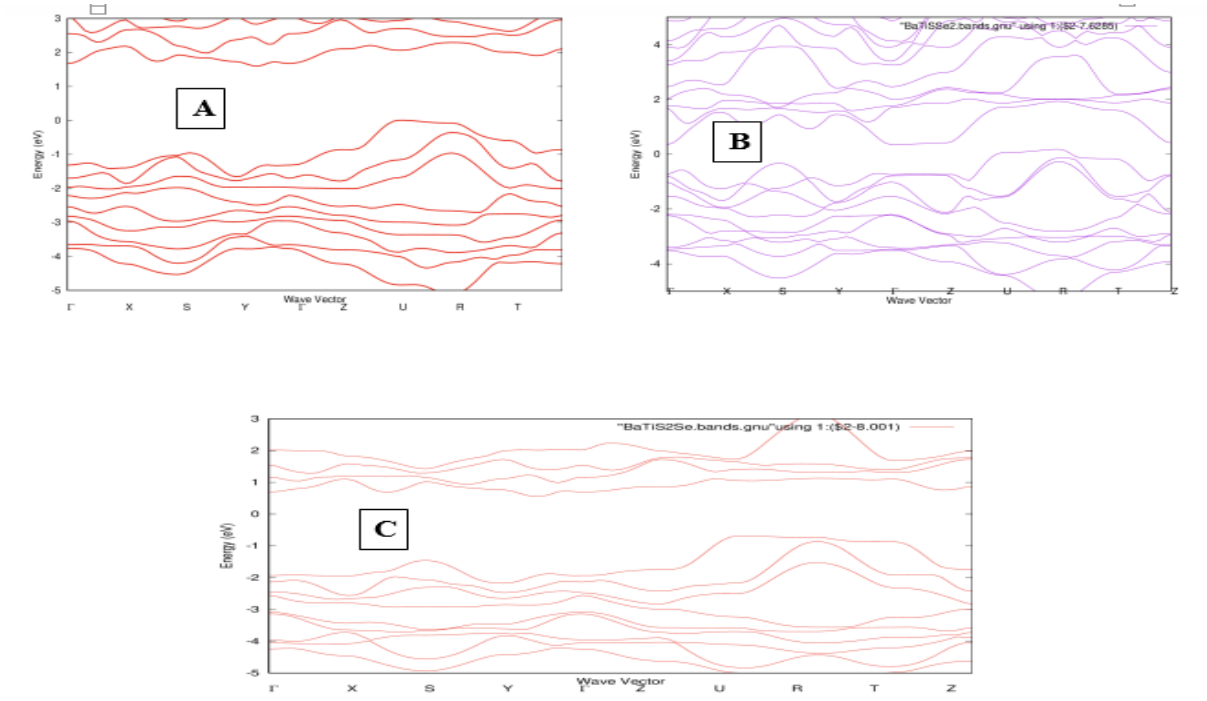

Fig 2.0: Band structures of (a) $BaTiS_3$ (b) $BaTiSSe_2$ and (c) $BaTiS_2Se$

Reflectivity of a material shows its ability to reflect light incidents on it. The low values obtained from these materials indicate that less sun rays are reflected, as a result more energy can be generated [16]. The reflectivity peak values of $BaTiS_3$, $BaTiSSe_2$ and $BaTiS_2Se$ are at 0.7 at 1.9ev, 0.72 at 1.8ev and 0.68 at 1.9ev with a corresponding wavelength of 654nm, 691nm and 654nm respectively. Their peaks lie in the visible region of the electromagnetic radiation.

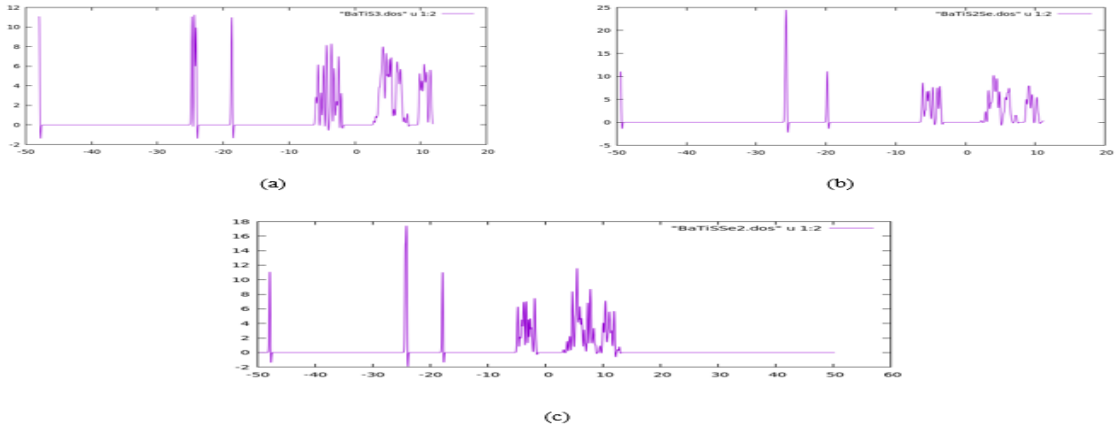

Fig 3.0: The graph of density of states of (a) $BaTiS_3$ (b) $BaTiS_2Se$ (c) $BaTiSSe_2$

Figures 5, 6 and 7 show the refractive index as a function of photon energy in 0.5 eV to 3 eV energy range increasing from 0.7eV to 1.8eV and decreases afterwards. $BaTiS_3$, $BaTiSSe_2$ and $BaTiS_2Se$ have the highest refractive index of 8.2, 8.8, and 8.2 at a photon energy of 1.7 eV, 1.8 eV and 1.8 eV respectively. The dielectric function describes how the material optical properties respond to an electromagnetic field. The peak values show that they are promising candidates for photovoltaic applications. For $BaTiS_3$, $BaTiSSe_2$ and $BaTiS_2Se$, the real and imaginary peak is ~ 60 at 1.7 eV and ~ 78 at 1.9 eV, ~ 68 at 1.7 eV and ~ 87 at 1.8 eV, and ~ 58 at 1.9 eV and ~ 69 at 1.7 eV respectively. The high value of dielectric function shows that it is a promising candidate for photovoltaic applications [16]. Extinction coefficient shows the extent to which the intensity of light is reduced as it passes through a material. The extinction coefficient of the three compounds increases with increase in photon energy, the maximum extinction coefficient value of $BaTiS_3$, $BaTiS_2Se$ and $BaTiSSe_2$ are 5.5 at 1.8 eV, 5.7 at 1.8 eV and 5 at 2eV respectively and decreases at 4.0 at 2.7eV, 3.0 at 2.7eV and 3.0 at 2.8eV respectively

Table 2: Table showing the comparison of the optical properties and band gaps of the three chalcogenide perovskites and other solar cell materials.

Compound	Absorption coefficient	Refractive index	Reflectivity	Extinction coefficient	Dielectric function	Band gap
$BaTiS_3$	7×10^8 m^{-1}	8.2	0.7	5.5	R = 60, I = 78	1.62eV
$BaTiS_2Se$	6.8×10^8 m^{-1}	8.2	0.68	5.7	R = 58, I = 69	1.39eV
$BaTiSSe_2$	7×10^8 m^{-1}	8.8	0.72	5.0	R = 68, I = 87	0.54eV
GaAs	$0.22 \times 10^8 m^{-1}$ [13]	5.0	0.82	4.2	R = 24, I = 26	1.519 [17]
Si	10^8 m^{-1}					1.12eV
$MaPbI_3$	$2.5 \times 10^6 m^{-1} - 8.7 \times 10^6$ m^{-1} [14]					1.6eV
$CsPbI_3$	10^6-10^7 m^{-1} [15]					1.7eV [15]
$BaZrS_3$	5.93×10^7 m^{-1} [7]		0.35			1.62eV

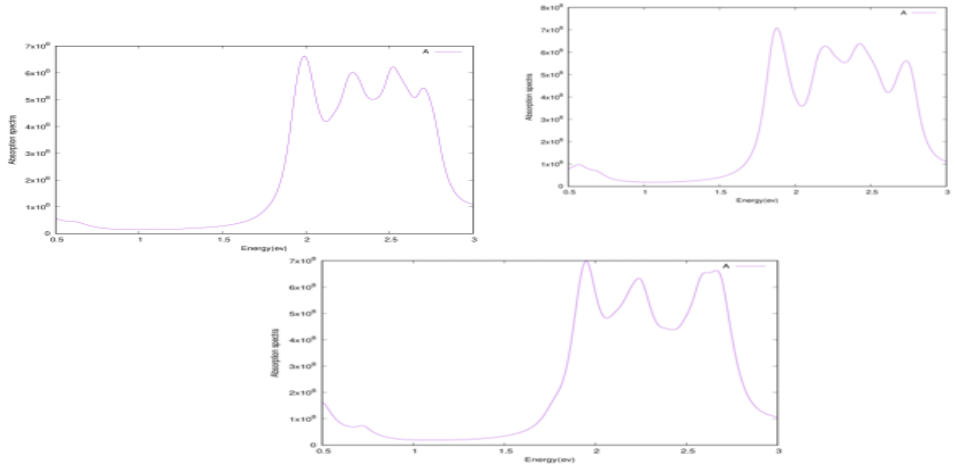

Fig 4.0: Absorptance of (a) BaTiS3 (b) $BaTiSSe_2$ (c) $BaTiS_2Se$

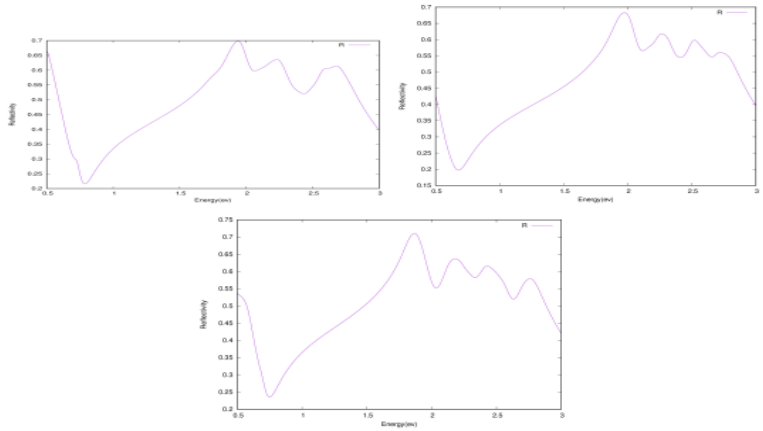

Fig 5.0 : Reflectivity of (a) $BaTiS_3$ (b) $BaTiSSe_2$ (c) $BaTiS_2Se$

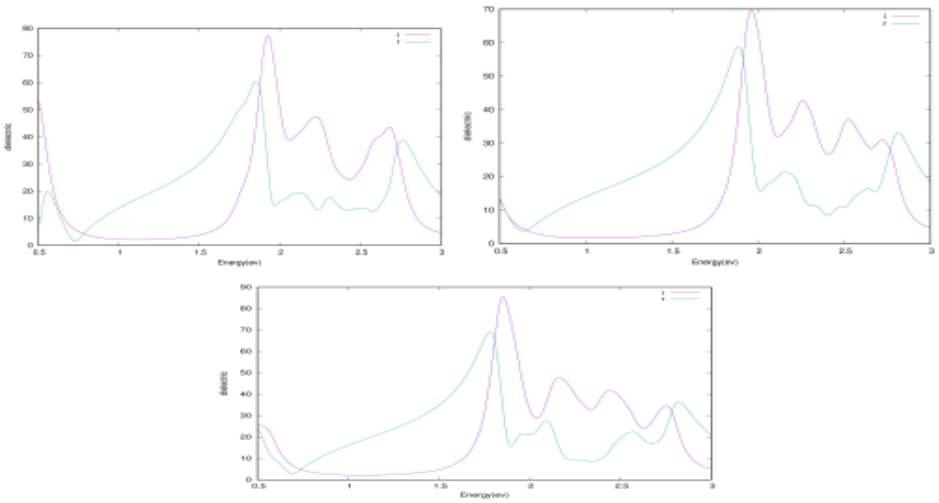

Fig 6.0: The Dielectric constant of (a) $BaTiS_3$ (b) $BaTiSSe_2$ (c) $BaTiSe_2S$

Conclusion

The structural, electronic and optical properties of three chalcogenide perovskites ($BaTiS_3$, $BaTiSSe_2$ and $BaTiS_2Se$) were studied using first-principle density functional theory calculations. The three compounds ($BaTiS_3$, $BaTiSSe_2$ and $BaTiS_2Se$) have a stable orthorhombic crystal structure and an indirect band gap of 1.62eV, 0.54eV and 1.39eV respectively. They have high absorption coefficient of 10^8 m^{-1}, within the range of 460nm – 777nm, showing that it is a strong absorbing material for visible light and near infrared. In comparison to other solar cell materials such as Silicon, Methylammonium lead iodide, these three chalcogenide perovskites are suggestive of good materials for solar cells given its high absorption coefficient and low reflectivity as well. It was also discovered that doping $BaTiS_3$ with Selenium (Se) tuned the bandgap by lowering its values.

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