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Structural and Electronic Analysis of Ternary Alkali Chalcogenide Compound $CsBiS_2$

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Abstract

Startup ventures in terms of highly efficient and flexible photovoltaic devices carry a very successful idea of mainstream electricity generation. This technology with getting into a more commercialized startup platform can help in providing a better opportunity for the young and dedicated researchers/scientists to invest their innovation and develop a more efficient photovoltaic device. The ternary alkali Chalcogenide materials are replacing the lead-based halide perovskites due to their toxicity and chemical instability. The structural and electronic analysis of a ternary alkali Chalcogenide compound $CsBiS_2$ has been performed in our research work. We have tried to represent a novel work based on this compound as it has not yet been explored theoretically to explore its optoelectronic aspect. The use of this compound can introduce an inexpensive and environment-friendly solution to it. The sample undertaken for the theoretical analysis is computed in a Quantum Espresso mathematical tool named BURAI. The electronic analysis of the compound is performed based on two features one is density of states which helps in defining contributing orbitals in formation of densities of different states and the other is band structure which helps in defining energy bands at a particular K point. The bandgap calculated for the compound is 1.53 eV analyzed through Perdew Burke Ernzerhof (PBE) exchange correlation which falls in the solar cell band gap range. This resultant turns out to be a favourable range for the compound to be utilized in optoelectronic applications.

Keywords: *Bandstructure, Chalcogenide compounds, Density of states, Dielectric tensor, Electronic property*

1.0 Introduction

Solar cell is a technology that has currently taken over the electricity generation market. Solar cells follow the principle of photoelectric effect, thus the conversion of solar radiation into electric power is done on the basis of semiconducting compounds[1]. At present, there is a considerable research being carried out for an efficient utilization of the material in photovoltaic devices. The development of third generation solar cells has been done to enhance the quality and efficiency of solar cell in terms of built and working. The adequate generation from solar photovoltaic devices basically depends upon the properties of material used for the fabrication of solar cells. Solar materials should have some features such as optimum band gap, good absorption of sun light and economic nature. The metal chalcogenide compounds are inorganic in nature with one part as a chalcogen anion and another as electropositive metal element. Basically their name metal chalcogenides[2-3] originates from its base element known as chalcogens which comprises

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sulphides, selenides etc[4]. Amongst the second generation advancement as thin film technology, chalcogenide compounds are considered and applied as highly efficient photovoltaic devices absorbers. Thus, these chalcogenide compounds are formed by the group 16 elements majorly. Metal chalcogenides facilitates the features like absorption of light and photodetector, thus this class of compounds offer a large variety of applications.

The metal chalcogenides are classified into two categories: one is transition metal chalcogenides (TMCs) and the other one is main group metal chalcogenides (MMCs). These compounds also showcase the semi-metal nature in compounds. The TMCs present a band gap of the range 1.0 to 2.1eV and some types of the MMC group also provides the scope of these compounds being utilized as optoelectronic devices[5]. This compound is used as solar light photocatalysts because they usually have their conduction band at a high position[6]. Initially when these materials came to be known, there were very few compounds discovered in the category of metal chalcogenide which exists in structural phase namely $CsBi_3S_5$, $RbBi_3S_5$, $Cs_3Bi_7Se_{12}$ and $Sr_4Bi_6Se_{13}$[7]. The compound utilized for our research work is $CsBiS_2$, which is discovered in the ternary alkali metal chalcogenide compound phase.

McCarthy et al. in one of their research work carried out an experimental work with many structural phases of metal chalcogenides out of which β & γ-phase of $CsBiS_2$ were studied. The α phase of $CsBiS_2$ was discovered as a red Coloured substance which was reported to have crystallised as a monoclinic primitive compound. The γ-phase of $CsBiS_2$ reported as an n-type semiconducting compound along with another compound i.e. $K_2Bi_8Se_{13}$ and β phase is reported as an insulator based on the experimental study. In one of the research work by Yang et al., the Bismuth based alkali metal chalcogenide nanocrystals have been explored and the introduction of Bi element in it has reported to have a non-toxic, highly effective in quality and abundant impact in the discovery of it[8]. The ternary halide based perovskites of the structure base - ABZ_3 are believed to be toxic and so with introduction of Bi, the toxicity and chemical instability has been filtered. Due to this the alkali metal-based chalcogenide compound has been the centre of attraction for the research which is focused on providing inexpensive semiconducting nature of compound. In a work by Huang et al., the base compound i.e. $CsBiS_2$ has been utilized by extending the ternary structure into quaternary structure through the insertion of another element X=Zn, Cd or Mn providing the tetrahedral coordination[9]. The compounds transformed were $Cs_2Bi_2ZnS_5$, $Cs_2Bi_2CdS_5$, and $Cs_2Bi_2MnS_5$ and studied based on electronic band structure, synthesis etc. Similar compounds like $CsBiS_2$ (namely $NaBiS_2$[10-13] and $KBiS_2$) have also been researched and worked upon. In a work by Syam et al. the XYZ_2 type of compound where X stands for Na and K; X stands for Bi and Z stands for S or O has been theoretically studied. The compound has found to be thermodynamically active and has attained mechanical stability along with the semiconductive energy gap[14]. In a potentially unique study by He and other authors, the dielectric screening was used in order to explore new compounds amongst the metal pnictide ternary sulfosalts including Bi and Sb elements. The dielectric properties were used as a screen to recognize the potential electronic compounds[15]. The introduction of Cs element in a compound provides a promising improvement scope in the perovskite layer and interface[16].

With advancement in this technology the commercial market is also rapidly moving towards renewable energy. In recent times, several solar energy and related renewable energy startup ventures have come up in order to lessen the usage of natural resources which cannot be replenished. These startups not only aim at reducing the dependency on natural resources but also aim at providing scope of improvement in terms of efficiency and flexible and compact design. Startup ventures like these help in providing a sustainable and cost efficient solution to the renewable energy market in India, which can prove to be a boon for Indian economy once the ideology reached out to the global market.

The framework of this research paper further is as follows: Section I describes the computational parameters, section II describes the structural property analysis, section III describes the electronic property analysis, and the last section is the conclusion part based on the results of the research.

2.0 Computational Parameters

The computational material science and engineering makes use of features like modelling of a material, its simulation on a specifically design tool, analyzing its theoretical aspects and informatics to understand the material in depth. The main goal of the computational study is to discover new materials, determine the behaviour of material and its mechanisms, explain the experiments and explore material theories. Following the analysis of the $CsBiS_2$ compound[17], the computational tool opted for our research work is BURAI which is a mathematical GUI for Quantum Espresso, which adopts a DFT-based approach in its functioning. Quantum Espresso is defined as a first principles-based electronic and structural material modelling tool. It utilizes the electronic and structural calculation-based computer codes which are open source. The tool also supports material modelling at the nano-scale level. In a more generalized manner, we can quote that the Quantum Espresso tool utilizes DFT based approach along with pseudo-potentials and plane waves. In our work, we have taken up P21/c spacegroup numbered 14 which is a monoclinic primitive structure having a≠b≠&± $\alpha=\gamma=90$ and

β=103.28 degrees. The exchange correlation that has been utilized in our work is Perdew Burkhe Ernzerhof (PBE) which is considered to be the most basic form of functional. This exchange correlation functional is suitable and reliable for bulk calculations predominantly[18]. This functional is most commonly used for the case where molecules are interacting with the surfaces of metal. These exchange correlations are used as they incorporate the GGA functionality as well, here GGA stands for Generalized Gradient Approximations[19]. The pseudopotential type utilized in our work are ultrasoft pseudo potentials (USPP) and norm-conserving pseudo potentials (NCPP). The norm conserving pseudo potentials describes the electron-ionic interactions, this PP is a soft potential used for valence electrons and core electrons are not considered. In most cases, the accurate calculations are done considering the modified size. The ultrasoft pseudo potentials in comparison with the NCPP are more relaxed and they make use of lesser plane waves to explain their pseudopotential wave functions[20-21]. The cutoff energy for work function used in the calculation is 80 Ry and the cutoff charge is 360 Ry meant as a true electronic output.

3.0 Structural Analysis

The structural property analysis of material involves significant components of a material that helps in the characterization of a solid material. Structural analysis is the one that decides the properties of a material including the structure type, crystal structure, spacegroup, atomic arrangement, the position of functional group etc. The material with structural capabilities are known for bearing load. Materials' key properties with respect to bearing load are: hardness, ductility, elastic modulus, yield strength, fracture toughness, fatigue, ultimate tensile strength and creep resistance. With corrosion of a material or its wear-tear, their ability to bear a load degrades. The properties are known to be attributed to system structure defining the type of structure. Based on the cautious investigation of mineral specimen the crystal is divided into family of 6 crystals namely: monoclinic, anorthic, orthorhombic, tetragonal, hexagonal and isometric. The spacegroup of our structure is monoclinic primitive P21/c [#14] and as per the atomic arrangement the structure consists of BiS_3 trigonal pyramids which are bonded at the two vertices in order to form $(BiS_2)_n$ chains. This is built along the α-axis with the presence of Cs ions in the middle of the chains. The crystal structure of $CsBiS_2$ is shown in the Figure 1 with single bonds present in between the elements. Cs atoms and Bi atoms are 4 in number respectively and as per the multiplicity in unit cell S atoms are 8 in number. Amongst the three, Bismuth (Bi) has the highest atomic mass and sulphur (S) has the least atomic mass.

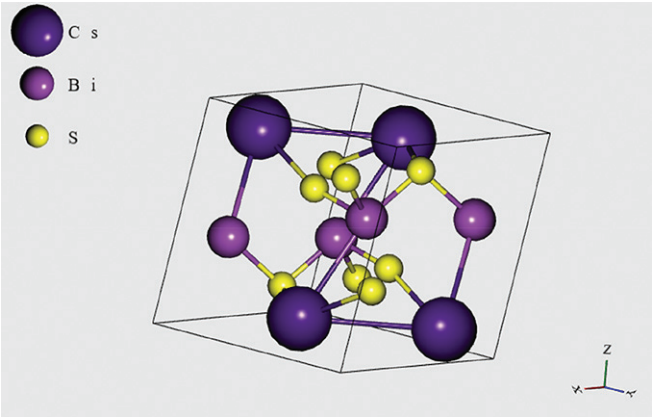

Figure 1: Crystal structure of the compound $CsBiS_2$ along with directions

4.0 Electronic Property Analysis

The electronic property analysis of the compound includes band structure and density of states investigation. The band structure analysis is defined by the eigenvalues energy that are obtained as a k-vector function in the end of the KS calculation[22]. Values of electronic band structure for solids are believed to be very sensitive to the apt correlation potential's determination. When this determination is proved to be accurate than the lesser accurate $E_{exchange}$ (exchange energy) this justifies that the calculations for band structure in solids is appropriate. In the band structure plot, we can see the k points along which the bands have been plotted [namely Γ, Y, D, Z, X, A] vs the energy range [-5 to 6] in eV. The band structure plot is given in Figure 2. The band structure plot helps in identifying a bandgap calculated of about 1.53 eV. The nature of band gap is seen to be indirect lying between D and Z points. Density of states give a clear picture of the materials and their band gap and can be easily correlated with the band structure plot in terms of energy range axis. The density of states (DOS) plot describes the

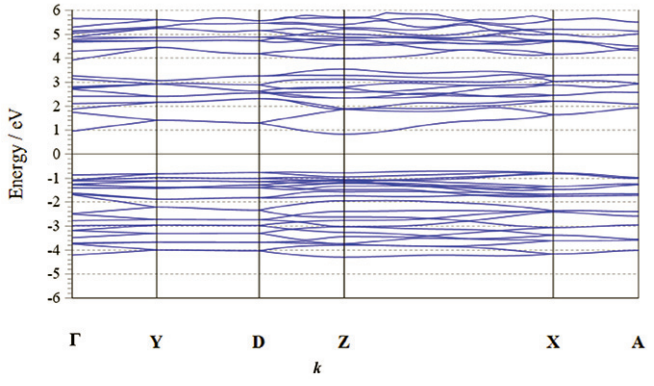

Figure 2: Bandstructure plot representation for $CsBiS_2$

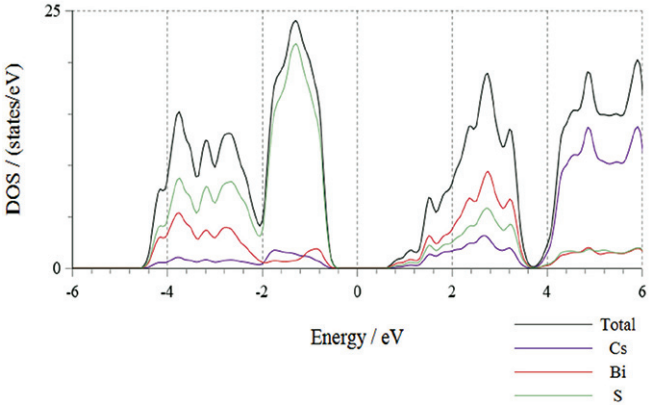

Figure 3: Density of state representation for $CsBiS_2$

Table 1: Comparative Analysis of Bandgap of Ternary chalcogenide compounds

	Compound	Bandgap value (eV)
1.	$CuInSe_2$	1.0 eV [22]
2.	$CuInS_2$	1.5 eV [22]
3.	$CuaGaSe_2$	1.7 eV [22]
4.	$CsBiS_2$	1.53 eV [Present work]
5.	$SrSnS_3$	1.56 eV [23]
6.	$SrSnSe_3$	1.00 eV [23]
7.	$CaSnS_3$	1.58 eV [23]
8.	$CaGeO_3$	1.15 eV [23]

total density of states for the entire compound and each element in the compound is explained through the partial density of states in Figure 3.

The electronic configuration of each element depicts that Cs has s orbital dominant in the 6th shell, Bi has s & p orbitals in the 6th shell and S has s and p orbitals in the 3rd shell. As per the Figure 3, the black line depicts Total DOS, purple line depicts Cs, red line depicts Bi and green line depicts S.

The Table depicts a comparative analysis of the energy gap values for different chalcogenide compounds.

The Table shown above depicts a comparative analysis of the compounds which are observed to lie in the band gap range of 1.0 eV and 1.58 eV.

5.0 Conclusions

Summarizing our work, we would like to state that the exchange correlation utilized here i.e. Perdew Burkhe Ernzerhof embodied in the GUI of Quantum Espresso code. The compound $CsBiS_2$ is believed to be a promising material in the field of optoelectronics due to its accurate bandgap lying in the solar spectrum range. The bandgap calculated is 1.53 eV in value which is lying in the 1.0 eV to 1.9 eV energy range. The studied structural and electronic aspects of these compounds show their proper coordination in terms of energy range and energy gap which is showcased through bands at different k points and different states of density. The structural aspect of the study is carried out in terms of spacegroup, phase, bonds, atomic arrangements and the electronic study of the compound is carried out in terms of band structure and density of states. In the future aspect of this compound, we can present the structural stability of the compound in order to prove its usefulness. We can dope the Cs element site and this can yield an enhanced optoelectronic properties of the perovskite photoactive layer. Hence we can conclude that solar cell technology and its development holds an important place in the future commercial market for energy generation. This can be beneficial for the Indian economy and for creating a sustainable solution for growing energy demands.

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