

Original Article

First-principles Study of Electronic Properties of Dimethyl-Ammonium Tin Triiodostanate (II) Perovskite for Photo-voltaic Application in Solar Cell

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Abstract - Metal-halide perovskites have emerged as a novel and promising photovoltaic materials for use in solar cells. In the current research, they are the potential light-harvesting mediums. The electronic properties of Dimethylammoniumtriiodostanate (II) hybrid halide perovskites are of much importance and need to be studied because it can be a good light absorber material due to the wide bandgap exhibited. We employed the PBE-GGA exchange-correlation implemented in Quantum Espresso based on DFT to study the electronic properties. From the study, the band structure and energy bandgap of 2.7 eV a direct bandgap were obtained. The density of states (DOS) and the partial density of states (PDOS) were also determined. It was found that the VBM major contributions are from I-5p and Sn-5s and little hybridization by Sn-5p. On the other hand, the CBM is significantly contributed from Sn-5p and I-5p and is little hybridized by I-5s. The band structure and the density of states (DOS) are important in analyzing the electronic properties of materials which are key in the use of DASNI3 as a solar cell material in photovoltaics.

Keywords — Density, functional, theory, first, principle

I. INTRODUCTION

Perovskite materials are potential organic-inorganic materials to be used as photo-absorbers in perovskite-based solar cells. The interesting characteristics of the inorganic components in the hybrid perovskite materials include good thermal stability and a high degree of structural order, according to Fan *et al.* (2014). The organic components are also important due to their functional versatility, their low process-ability cost and mechanical flexibility (Giannelis, 1996). Hence, the possibility of merging the properties of an inorganic crystal and the molecular organic solids has stimulated recent research into the versatile properties of hybrid perovskites, which are organic-inorganic in nature.

The use of Methyl ammonium(MA) as the A site does not

only reduce the formation of defects but incorporating the dipolar MA cation with mixed cation mixed halide will widen the bandgap of the perovskites and also heal deep trap defects resulting in a defect-tolerant material (Tan *et al.*, 2018). An ideal cubic halide perovskite, the B-site, which is the divalent metal, is located at the body-centred position of the cube, and the anions occupy the six face-centred locations forming an octahedral surrounding for the divalent metal, the monovalent cations are situated at the vertices of the cube.

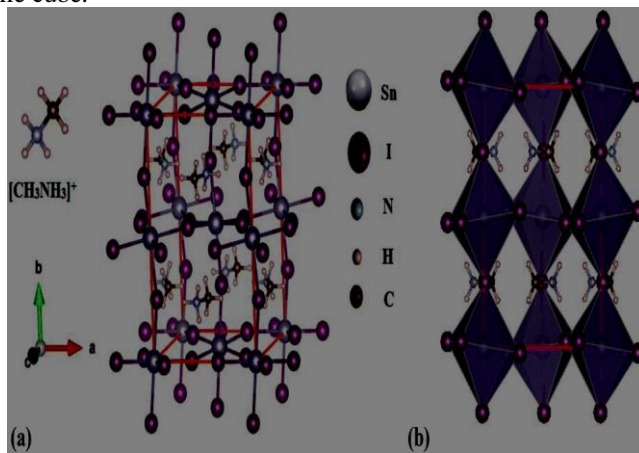


Fig 1: The orthorhombic phase of CH₃NH₃SnI₃ represented as balls and sticks in (a) and polyhedral style (b) adapted from Paschal *et al.* (2020)

A new choice of A-site cation, for instance, Dimethyl Ammonium (DA) which is larger in size than methylammonium (MA), results in an increase in the bandgap (Hautzinger *et al.*, 2020). This is due to the modification of the lattice constant. The extent of the metal-halide orbital overlap is influenced by the A-site cation. Philippe *et al.* (2017) state that this change of the bonding of the metal halide has a direct impact on band positions, the



valence band and the conduction band. For instance, when DA is used as the A-site cation, the bandgap of the perovskite increases as compared with MA perovskite. This fact can be exploited to achieve the most recent advances in photovoltaic performances. This shows that DA produces more thermally stable materials and are also promising materials in reaching higher efficiencies in photovoltaics (Goetzberger et al., 2003). The 3D perovskites exhibits have been proven to exhibit a sharp optical absorption onset, according to De Wolf *et al.* (2014). The physical and chemical properties of any system are affected mainly by the interaction of the electrons with the atomic cores. These are electron-electron interaction, nuclear-electron interaction and nuclear-nuclear interaction. The major source of difficulty in these interactions is the treatment of electron-electron interaction while interpreting their properties since the interactions are inseparable and are only treated with approximation. There are many forms of modelling approaches that are mainly *ab-initio* in nature for the approximation (Giannozzi *et al.*, 2001). Here a well solved Schrödinger equation for a specific system can be differentiable from one to another. The solution of the Schrödinger equation remains a difficult task. The introduction of approximations that are used to reduce the equations to a form that can be solved reduces the degree of accuracy and the predictive power. Using computer simulation and applying the density functional theory (DFT) methods involved in various solving of the Schrödinger equations has had remarkable success in calculations involving electronic and other material properties applicable to several other systems (Mattsson *et al.* 2004). The solution of the single-particle equations for electrons in solids results in energy eigenvalues the band structure. The corresponding eigenfunctions provide insight into the arrangement of the electrons from an energetic and spatial perspective and produce the cohesion between atoms in the solid. (May, V., & Kühn, O. 2008). These results can be useful in several applications. For instance, the band structure of the solid can elucidate the way in which the electrons responds to external perturbations such as the absorption or to the emission of light. The response to light is directly related to the optical and electrical properties of the solid. (Ahmed *et al.*, 2019). In a study of the band structure, for example, one can determine the possible optical excitations that determine the colour, reflectivity, and dielectric response of a solid Gong *et al.* (2018). Other effects include the creation of excitons, that is, the bound pairs of electrons and holes, which are important in determining the optical and electrical properties. Finally, the band structure can also be used in calculating the total energy of the solid, which helps in determining a variety of properties which includes thermodynamic and as well as mechanical properties.

II. METHODOLOGY

All density functional theory (DFT) calculations were performed using Perdew-Burke-Ernzerhof (PBE) Norm conserving pseudopotentials. The PBE pseudopotentials of Tin, Hydrogen, Carbon, Nitrogen and Iodine ('Sn', 'H', 'C', 'N' and 'I') distributed within the QUANTUM ESPRESSO pseudo library were used for all calculations. The Crystal Information Files were obtained from the Materials Project. The cell shape and atomic positions were relaxed in DFT using the standard PBE version of the GGA electron exchange-correlation functionals were the convergence of the plane wave cut-off (ecutwfc), lattice parameters, as well as the charge density cut-off (ecutrho) with the total energy, was achieved. The density of states function $g(E)$, which defines the number of electronic states per unit volume, per unit energy, for electron energies, was determined as stated by Mejia-Rodriguez *et al.* (2021). The density of state function is important for calculations of effects based on band theory.

III. RESULTS AND DISCUSSION

An orthorhombic phase of $C_2H_8I_3Sn_1N_1$ with 60 atoms per cell space group Pna21 was considered. The lattice parameter obtained was $a = 15.999 \text{ \AA}$, $b = 17.3669 \text{ \AA}$ and $c = 28.2926 \text{ \AA}$. Murnaghan's equation of state was used according to Madsen *et al.* (2016) for volume optimization.

A. The Band Structure

The calculated band structure of the orthorhombic phase $C_2H_8I_3N_1Sn_1$ crystal along the high-symmetry lines in the first Brillouin zone is presented in Figs. 2 below. The orthorhombic crystal has a direct band-gap at gamma symmetry points of 2.7eV calculated band gap energy from PBE, GGA exchange-correlation functionals. The Fermi level is located between the valence band maxima and the conduction band minima of the material with the Fermi energy of 2.4eV. The diagram below shows the band structure of the dimethyl ammonium trio do stanate (II), where it is observed that $DASnI_3$ is a wide-band-gap semiconductor with a direct bandgap.

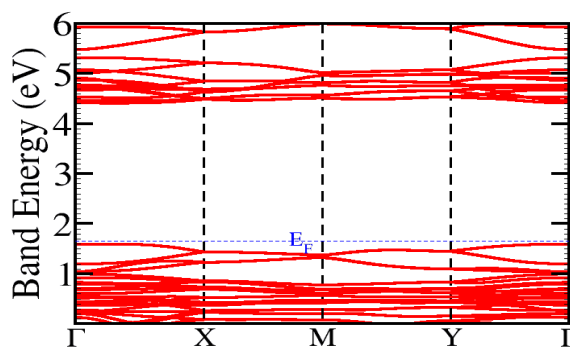


Fig. 2 The band structure of dimethyl ammonium triiodostanate (II)

B. The Band Structure

To understand the electronic structure of a material, a study of the DOS and the PDOS is necessary. The DOS and PDOS for DA compounds are given in Figs. 3 and fig 4 below, respectively. The Fermi level separates the valence and conduction bands. From the total DOS of $C_2H_8Sn_1N_1I_3$, the position and height of spectral peaks infer that the electronic states of Sn, I, N, C and H are hybridized in both valence and conduction bands in some specific regions. The nature of DOS and PDOS spectra reveal $DASnI_3$ is a semiconductor.

From the PDO's diagram below, the VBM has major contributions from I-5p and Sn-5s and little hybridization by Sn-5p. On the other hand, the CBM is significantly contributed from Sn-5p and I-5p and is little hybridized by I-5s. Therefore the prediction across the bandgap is majorly contributed by iodine and tin s and p orbitals, which suggest strong hybridization.

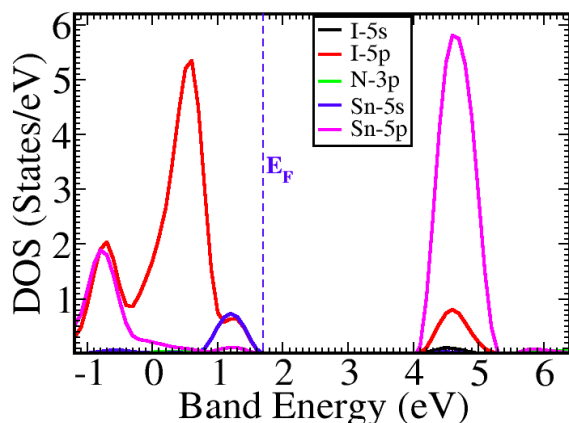


Fig 3. The density of states of Dimethylammoniumtriiodostanate (II)

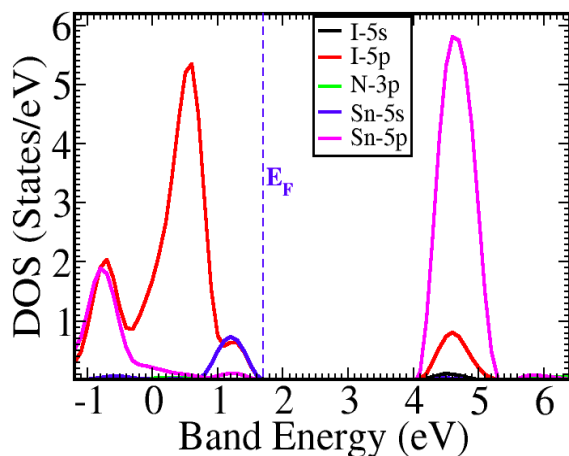


Fig 4. Partial density of states of Dimethylammoniumtriiodostanate (II)

C. Electronic properties

In order to examine whether a material is an insulator, conductor, or semiconductor, the study of electronic nature through the band structure and density of states (DOS) is important. According to Khan *et al.* (2012), a direct bandgap material is more efficient for optoelectronic applications when compared with an indirect bandgap material because of phonon involvement, which makes indirect bandgap semiconductors a bad emitter of light, as stated by Khan *et al.* (2013)

DOS is mostly used in the study of the physical properties of materials such as the dielectric and the photoemission spectra, and also the transport properties. DOS shows the role and location of different energy orbitals, specifically in the band structure formation. From the total DOS and partial DOS of $DASnI_3$, it is inferred that the high energy in Sn 5s states which occupy the VBM is mainly responsible for the promising photovoltaic properties, according to Xiao *et al.*, 2017. The high energy states observed at the top of the valence band are stable with respect to decomposition. The study of the efficiency of solar cells and other optical materials can be done through observation of the band dispersion and the effective carrier masses. The Valence Band Maxima and the Conduction Band Minima of $DASnI_3$ are located at Γ symmetry of the Brillouin zone and have large band dispersion. This large band dispersion results in the small carrier effective masses.

IV. CONCLUSION

The $DASnI_3$ structure is a wide direct band gap of 2.7 eV material. The Fermi energy is 2.4eV, and it is located between the conduction band and the valence band. The study shows that this material is highly hybridized by the I-5p and Sn-5s. The $DASnI_3$ displayed the properties of a semiconductor as deduced from the band structure. Therefore $DASnI_3$ is a good material to be used in solar cells since it shows that the bandgap was well-modulated and more stable as compared to the traditional $MASnI_3$ material. It is therefore recommended that an investigation into the cause of the wide bandgap will be insightful.

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