

# Ab-initio Investigation of Chlorine-Doped Molybdenum Di-Telluride Single-layer for Low-Cost Solar Cell Applications

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## Abstract

*The development of low-cost semiconducting materials is highly essential for realizing economically feasible solar conversion at global scale, further it enables facile, scalable and economical technical process. Monolayer semiconductor Transition metal di-chalcogenides have great potential for use as light-weight, flexible, transparent, ultra-thin, inexpensive and wearable photovoltaic modules due to their appealing optical and electronic properties. Here, specifically we investigate the structural, band structure and optical properties of 8.3% chlorine doped and pristine 2H-phase molybdenum di-telluride monolayer to predict its application in photovoltaic by using First-principles density functional theory calculation. The investigated electronic band structure suggests that the pure is direct band gap with electronic band gap value of 1.13eV and while the cl-doped is 1.45eV. The optical properties investigation result reveals high dielectric constant and good optical absorption in the visible regions. Our result suggests that cl-doped 2H-phase molybdenum di-telluride monolayer is very promising in photovoltaic and other optoelectronic device applications.*

**Keywords:** Photovoltaic modules, Density Functional Theory, 2H-phase, Molybdenum di-telluride

## 1. Introduction

The need for more electrical energy increases as the global population increases. The photovoltaic (PV) effect is an energy conversion process, from which utilizes solar energy in conjunction with solar cell and thereby meet the global energy demand (Hao et al., 2020). Hence the development of new renewable and reliable energy source such as PV is a current global challenge. Research in solar cell is nowadays focussing on third generation (thin film) photovoltaics with the aim of producing higher and higher efficiencies, at relatively low-cost with higher stable device and with eco-friendly materials.

The discovery of graphene by Novoselov et al., 2004 opens up a new research area in two-dimensional (2D) or monolayer material compounds. Though graphene is zero band gap and cannot be used for solar cell but their excellent outstanding optoelectronic properties inspired researchers to explore transition metal dichalcogenides (TMDC) compounds. These 2D-TMDCs materials are generally represented with the structural formula  $MX_2$  where M stands for transition metals and X is group vi elements of the periodic table (e.g., S, Se and Te). These materials are characterized by having high transparency, large thermal conductivities, small diffusion length, reduced charge recombination rates, large charge carrier mobility and appreciable tunable band gap (Letizia, 2019).

A two-dimensional monolayer of  $MoTe_2$  material is three atoms thick, a sheet Mo atom sandwiched between two sheets of Te atoms, giving a monolayer  $\approx 0.7$ nm in thickness (Yu-Chuan et al., 2021). Their unique structural and optoelectronic properties, which makes them different from their bulk counterpart makes them appealing for many applications such as optoelectronics, sensors, and Photovoltaic. Moreover, their ultrathin structure makes this material inherently flexible, almost transparent which all these are desired for the new generation nanoelectronics where light weight, flexibility and transparency are needed, and these are some of their

advantages over the traditional silicon (Si) and gallium arsenide (GaAs). At room temperature MoTe<sub>2</sub> shows either 2H, 1T<sub>0</sub> or T<sub>d</sub> phase. These three stable phases each have different electronic and optical properties. 2H-MoTe<sub>2</sub> is relatively stable in ambient conditions, but, due to the very small energy barrier with 1T<sub>0</sub>-MoTe<sub>2</sub>, under excess Te deficiency or strain it will quickly change into the 1T<sub>0</sub> (Guo and Liu, 2022)

Doping is the intentional addition or substitution of atoms of different types into a given crystal structure. This has significant impact on the band structure, band gap energy and the Fermi level of the material. 2D MoTe<sub>2</sub> is naturally p-type semiconductor. Its metal site (Mo) can be doped with element from group IV of the periodic table for n-doping and group for p-doping. Similarly, the chalcogen site (Te) can be doped with elements in group XVII of periodic tables to give n-type or group XV to obtain p-type material (Yu-Chuan et al, 2021)

The 2D TMDCs are ambipolar in their nature, when doped they can be used both as electron transport or hole transport material in perovskite solar cell. These materials are promising for their improved optoelectronic properties (Akrajas et al, 2020)

Herein, we want to investigate the structural, electronic band structure and optical properties of chlorine doped 2H-phase molybdenum di-telluride monolayer to predict its application in photovoltaic by using First-principles density functional theory calculation.

## 2. Computational Method

A 2x2 super cell of Molybdenum Di-telluride (MoTe<sub>2</sub>) monolayer, with space group P-6m2 has been built as pristine structure with total number of 12 atoms, 4 Mo and 8 Te atoms. It was then doped at the 8.3% concentration of chlorine by substituting Te atoms. A vacuum of 15 Å slab is placed in vertical direction, which is meant to prevent the gas interaction between adjacent layers during periodic calculations.

The studies were carried out by using Kohn-Sham equation within the framework of density functional theory (DFT) as implemented in Quantum ESPRESSO code (Giannozzi et al, 2017). The electronic exchange and correlation energy are represented by generalized gradient approximation compiled by Perdew-Burke-Ernzerhof (GGA-PBE) for solids (Perdew., 1976). A plane wave basis sets with cut off energy of 40Ry and augmented density of 160Ry was considered for all calculations. Brillouin zone sampling was done over optimized 12x12x1 k-points sampled by Monkhorst-Pack scheme (Monkhorst, 1996). Geometry optimization was conducted by the minimization method as proposed by Broyden-Fletcher-Goldfarb-Shannon (BFGS) to optimize the material structures and ground state energies, considering a density mixing scheme (Wei, 2021).

For a semiconductor material, structural and electronic properties determine the optical one. Recent studies on monolayer semiconductors have shown that though there is absorption along z-direction but significant absorption is along xy plane of the monolayer (Lalmuan et al., 2021). Therefore, only results in the xy plane were utilized in this work.

The linear optical properties of the pure and chlorine doped 2D-MoTe<sub>2</sub> are computed using yambo program as implemented in Quantum ESPRESSO. It is very important to consider electron-hole interactions, more importantly the convergence of k-point sampling. Here we used 12x12x1 k-point sampling to calculate the linear optical properties using random phase approximation (RPA) method.

### 2.1 Theoretical Review

#### 2.1.1 Structural properties

After substituting the tellurium (Te) atom with chlorine one in the super cell we run optimization of the structure, since there is atomic radii difference between Te and Cl the chemical bond around the dopant (Cl) shortened which results in a tensile strain around the dopant atom.

The optimized structure of chlorine doped and pure monolayer 2H-MoTe<sub>2</sub> are presented in figure 1 and the optimized lattice constants and the corresponding bond length between Mo and Te are given in table 1.

### 2.1.2 Electronic properties

The band structure of the considered materials was calculated towards the highly symmetric direction of the Brillouin zone with path  $\Gamma$ -M-K- $\Gamma$ . The valence band maximum (VBM) and conduction band minimum (CBM) are both observed at the K-point of the Brillouin zone. This indicates that the materials are direct band gap semiconductors and the energy band gaps were found to be 1.13eV and 1.45eV for the pure and the doped material respectively. The Fermi level of the doped structure is closer to the CBM than VBM this indicates also that the doped material is n-type. There was, inadequate literature from experimental and theoretical for the doped material. However, from the results obtained (table 1 and figure 2), it shows that there is modification in the band structure of the pristine compound which may be associated with the lattice strain generated in the process of doping with chlorine which has smaller atomic radius compared to tellurium atom that is substituted.

### 2.1.3 Optical properties

It is essential for a photovoltaic material to have high absorption in the visible region of the solar spectrum which occupies 45% of the whole spectrum range (Deobrat and Ahuja., 2022). The calculated dielectric function as a function of photon energy is plotted up to 30eV (figure 3 and 4). The absorption profile shows that our material has high optical absorption in the photon energy range 1.2 to 5.1eV which is above the direct transition band gap energy of the compound. Dielectric constant which is the dielectric function at zero photon energy (Roknuzzaman et al, 2021) is 5.70 for chlorine doped 1.76 for pure 2H phase MoTe<sub>2</sub> monolayer (figure 3 and 4).

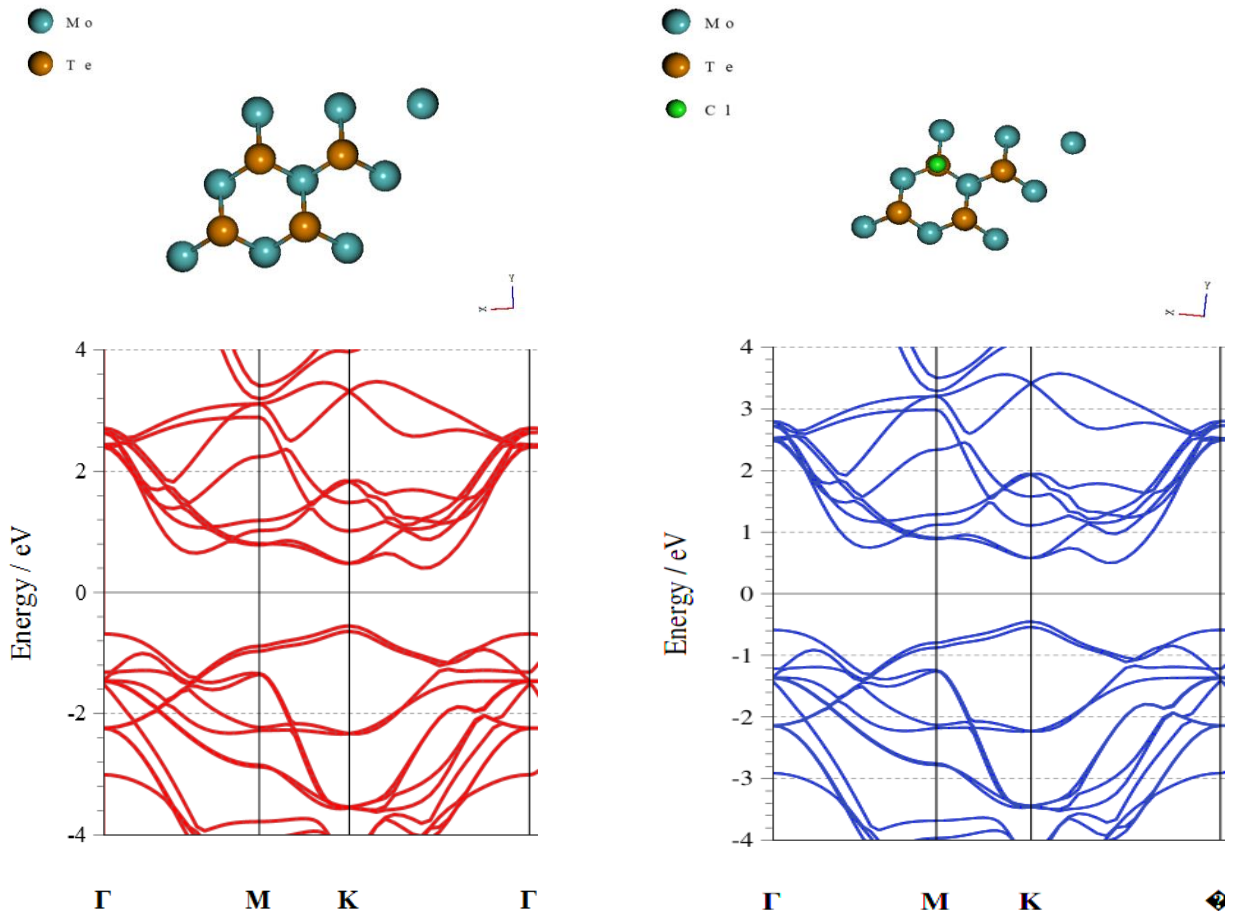


Figure 2. Band structure of Chlorine doped MoTe<sub>2</sub> left and pure on right monolayer

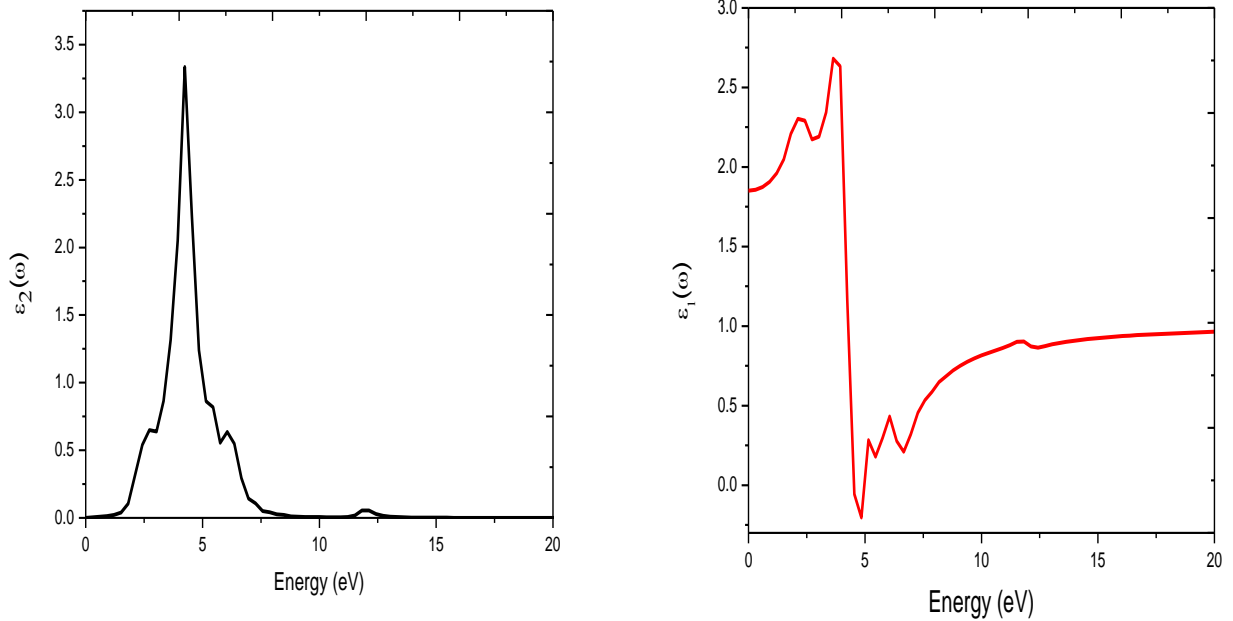


Figure 3. Imaginary and real dielectric function of pure MoTe<sub>2</sub> monolayer

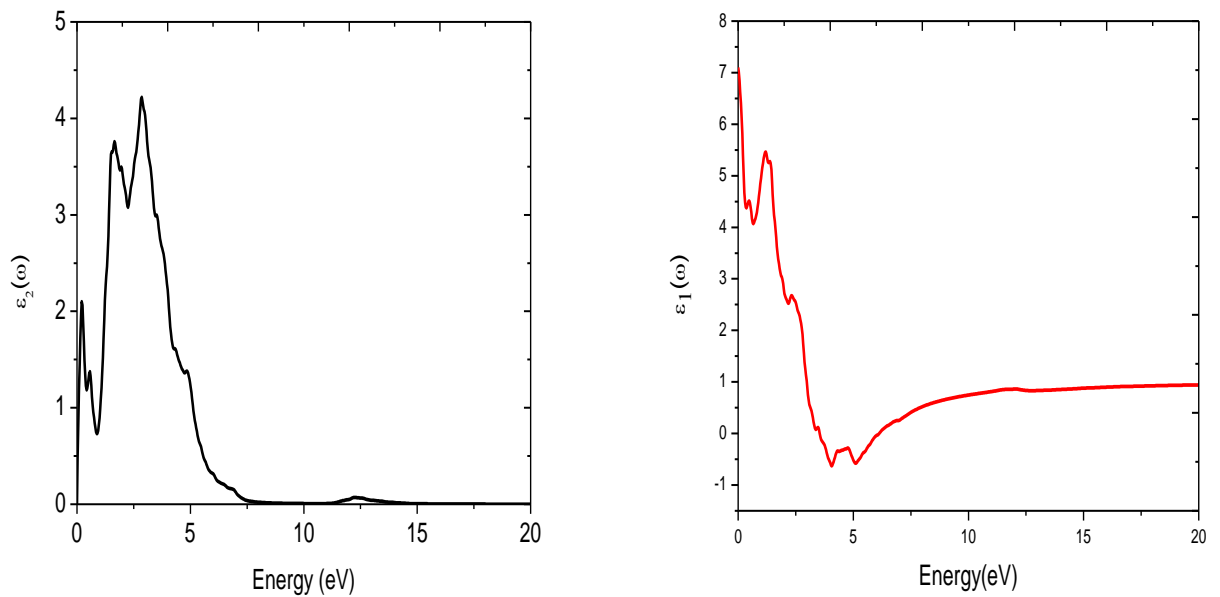


Figure 4. Imaginary and real dielectric function of Cl-doped MoTe<sub>2</sub> monolayer

Table 1. Bond length ( $d_{Mo-cl}$ ), bond angle ( $\theta_{Mo-cl-Mo}$ ), lattice constant ( $a$ ), Energy Band gap and dielectric constants for 2H-MoTe<sub>2</sub> Monolayer.

System	$d_{Mo-cl}$ (Å)	Bond angles		$a$ (Å)	Energy Band gap (eV)	Dielectric constant ( $\epsilon_r$ )
		$\theta_{Mo-Te-Mo}$	$\theta_{Mo-cl-Mo}$			
Pure MoTe <sub>2</sub>	2.73*	122.32	----	3.517	1.13	1.76
Cl-doped MoTe <sub>2</sub>	2.71	124.35	122	3.519	1.45	5.70

\*Mo-Te

### 3. Conclusion

We have investigated the structural, electronic and optical properties of cl-doped and pure 2H-phase MoTe<sub>2</sub> monolayer by first-principles density functional theory (DFT) calculations. The results suggest that both pure and doped compounds are semiconductors having direct band gap energies 1.13eV and 1.45eV respectively, making the materials potentially suitable for photovoltaic applications. Furthermore, the doped material has been identified to have better electronic and optical properties compared to its pure counterpart. As a result, it would be promising for next generation optoelectronics including photovoltaic cells.

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