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Structural and Mechanical Properties of Cl- and Br-doped WSe_2 Monolayer for Possible Application in Flexible Photovoltaic Panel: An ab-initio study

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ABSTRACT

This work investigates the structural and mechanical properties of Chlorine- and Bromine-doped WSe_2 Monolayers. Our result reveals that the introduction of Chlorine impurity into the pristine WSe_2 monolayer is more promising under Se-rich conditions due to the smaller formation energy and may be the most favorable replacement of Se. Further, it is noted that the calculated elastic constants certify the Born stability rule, which is an indication that all the doped materials are mechanically stable, may show considerable resistance to linear compression and behave in a brittle manner. Moreover, our findings suggest a strategy to tailor the mechanical properties of the studied materials for various applications. The study of mechanical properties of 2D materials may further advance the development of ultrathin flexible wearable photovoltaic solar panels and other electromechanical systems.

Keywords: Mechanical stability, structural stability, Born criteria, WSe_2 monolayer**,** Chlorine doped WSe_2, Bromine doped WSe_2

INTRODUCTION

Recently, two-dimensional (2D) transition metal dichalcogenides (TMDCs) have attracted enormous attention of researchers due to their excellent physical properties and potential applications in nanodevices and optoelectronics (Roy & Bermel, 2018). These group of materials are generally represented by the formula MX_2 (where M = transition metal and X = chalcogens Se, S or Te) (Yamusa, Shaari, & Isah, 2022). In TMDCs the inter molecular force i.e. W-W and W-Se are strong covalent bonds, whereas the interlayer force is weak Van der Waals force (Lin, Torsi, Geohegan, Robinson, & Xiao, 2021).

Exposure to high temperature and acute chemical environment during manufacture and domestic uses makes Two-dimensional (2D) Transition metal (TMDCs) liable to imperfections such as cracks and pores, these significantly affect their structural and mechanical properties (Malakar, Thakur, Nahid, & Islam, 2022), therefore understanding structural and mechanical properties of 2D TMDCs is very important for predicting their applications. Among these group of crystals WSe_2 monolayer stands alone by having special properties such as high electron mobility(Rawat, Jena, & De Sarkar, 2018) and very good optical response in the visible band (Ji et al., 2019). These properties make 2D WSe_2 promising, and in fact it has been identified as a potential material for flexible electronic devices (Malakar et al., 2022).

Furthermore, investigations of structural and mechanical stability of a crystal compound is essential before it can be incorporated into an electronic or optoelectronic devices. This is important, so as to avoid quick degradation of

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the devices performance (Lian, Lu, Niu, Zeng, & Zhan, 2018).

It is generally believed that doping or alloying improves/tunes the structural and mechanical properties of materials (X. Zhao et al., 2020) and (Singh et al, 2021). At times n-type semiconductor is needed, for example as electron transport layer in perovskite solar cell (Lin et al., 2021; Roy & Bermel, 2018). Halogen can serve as electron donors to WSe_2 monolayers to obtain higher carrier mobility n-type semiconductor (Loh, Zhang, Bosman, & Eda, 2021; Mohammed, Shu'aibu, Abdu, & Aliyu, 2023).

Moreover, further development and applications of doped WSe_2 monolayers are restricted by the absence of systematic investigation on these characteristics, though structural and mechanical stabilities determine the long term stability of crystal compounds.

In this work, we focus on investigation on structural and mechanical properties of pure, Br- and Cl-doped WSe_2 monolayer by using first principle technique.

COMPUTATIONAL METHOD

In this work, DFT calculations were carried out using Quantum ESPRESSO code (Giannozzi et al., 2009). Our Br- and Cl-doped WSe_2 monolayers are modeled by replacing the Se atom in 3 x3 x 1 WSe_2 monolayers with Br and Cl atom as shown in Fig. 1. These atoms are chosen because the size of Se atom is almost similar to Br and Cl atoms which reduced the change in the super cell (Radzwan et al., 2020). Moreover, doping on chalcogen site is easier experimentally, than on metal site, which may temper with the structural stability of the crystal compound (Lin et al., 2021). The generalized gradient approximation (GGA) with the format of Pardew-Burke-Ernzerhof (PBE) was used for the exchange correlation functional (Itas, Razali, Tata, Idris, & Khandaker, 2023; Itas, Razali, Tata, Kolo, et al., 2023; Perdew, Burke, & Ernzerhof, 1996; Saadu Itas et al., 2023). In our computation, a plane wave basis set with a cut-off kinetic energy of 320 eV was utilized to expand the wave function. Following the Monkhost-Pack scheme (Monkhorst & Pack, 1976), the Brillouin zone is sampled by a 12×12×1 k-point mesh for the PBE calculations. Meanwhile, to avoid any artificial interlayer interaction, a larger vacuum layer of 15 Å was introduced along z direction for the pristine and doped-WSe_2 monolayers (Chhana et al., 2021). All the materials lattice constant and the atomic coordinates were fully optimized before carrying out the mechanical properties calculations using Broyden-Fletcher-Goldfarb-Shannon (B.F.G.S.) algorithm, until the Hellmann-Feynman force on each atom was below 0.001 eV/Å (W. Zhao, 2021). Thermo-pw package was employed for the elastic properties calculations.

RESULTS AND DISCUSSION

Structural Properties

Structural properties have a very strong relation with other physical properties such as electronic, optical and magnetic properties of material (Roknuzzaman, Alarco, Wang, & Ostrikov, 2021). In this work, 2 x 2 supercell of WSe_2 monolayer with 12 atoms (4 W and 8 Se) is taken as the undoped structure (Figure 1). By replacing one Se atom in the supercell with Br and later with Cl we perform all the calculations. This gives a dopant concentration of 8.33 %.

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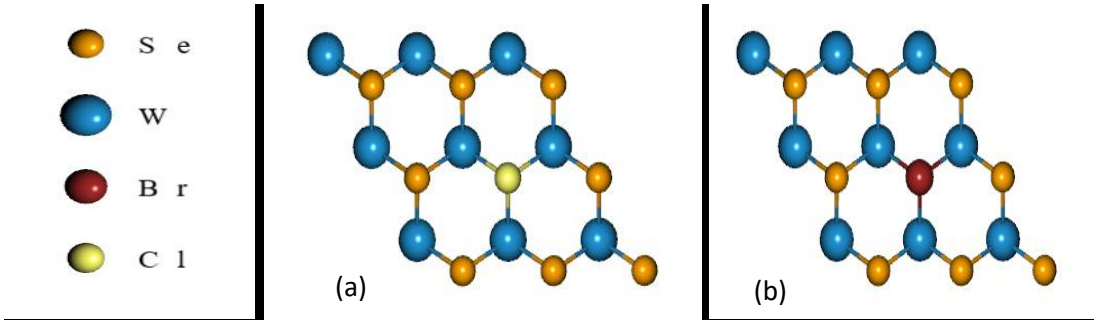

Figure 1: Crystal structure of (a) Cl-doped and (b) Br-doped WSe_2 monolayers

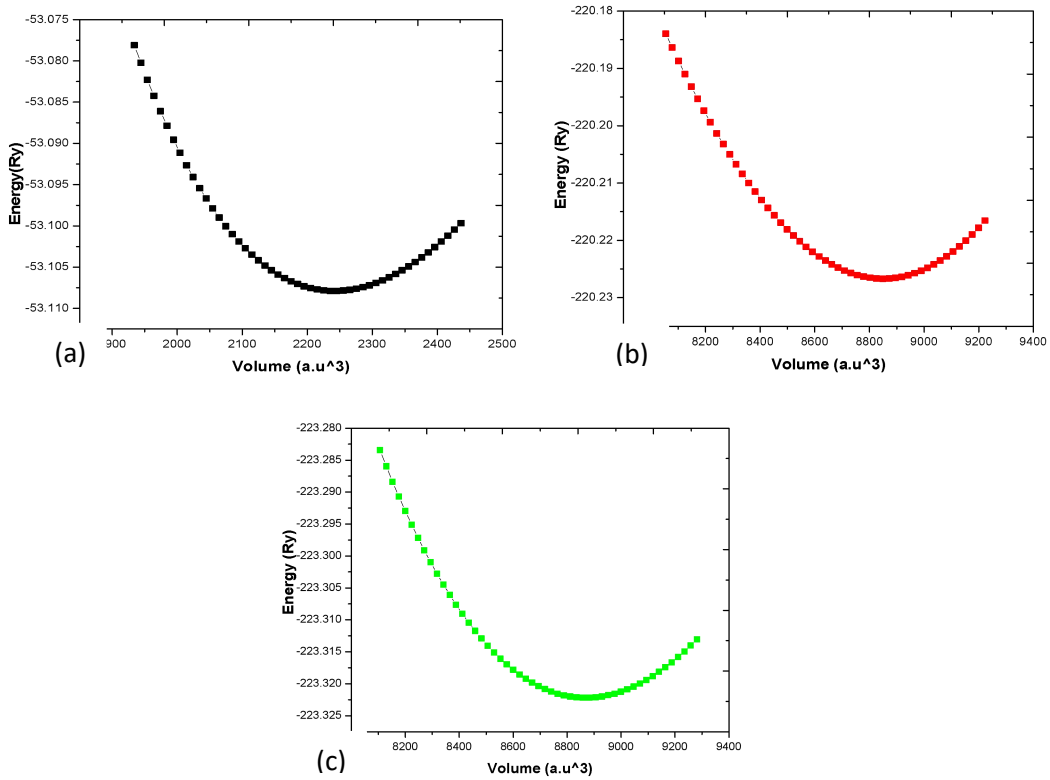

Figure 2: Energy volume curves of pure (a) Br-doped (b) and Cl-doped WSe_2 (c) monolayers

In order to get the equilibrium, ground state structural properties of pure, Br- and Cl-doped WSe_2 monolayers such as the lattice constant, we run structural optimization calculations on the crystal materials in quantum espresso using GGA PBE by minimizing the total energy with respect to volume of the unit cell. The obtained data is fitted to the Birch Mornaghan equation of state (Equation1) (Katsura & Tange, 2019) the calculated equilibrium lattice constants and bulk of modulus are listed in table 2. Figure 2 shows the ground state energy versus volume plots for the pristine and doped crystal compounds of WSe_2 monolayers. The ground state energies are -53.1078, -220.2267 and -223.3221 Ry for pure, bromine and chlorine doped WSe_2 monolayers respectively. These energies indicate that all the materials are structurally stable (Chhana et al., 2021).

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Cl-doped WSe_2 monolayer has the lowest ground state energy (-223.32 Ry) which suggests it is most likely to be the most stable among the studied materials.

$$E_{tot}(a) = E_o + \frac{9V_oB_o}{16}\left\{\left[\left(\frac{a_o}{a}\right)^2 - 1\right]^3 B_o' + \left[\left(\frac{a_o}{a}\right)^2 - 1\right]^2 \left[6 + 4\left(\frac{a_o}{a}\right)^2\right]\right\} \quad (1)$$

Where a_o is equilibrium lattice constant, V_o is the equilibrium volume per atom, B_o is the bulk modulus at zero pressure and the pressure derivative of the bulk modulus $B_o' = \left(\frac{\partial B}{\partial P}\right)_T$

It was observed that all doped structures maintained their original honeycomb like structure resembling graphene compound, though with slight lattice distortion which could be associated with closer atomic radius of Br and Cl to Se atom in periodic table. Furthermore, the bond length around the dopant atoms lengthen as observed from table 1, resulting a small amount of strain around the dopant atom. This could be the reason for the little distortion in the structure.

Structural stability can be studied using formation energy E_f expression given by (Ding, Xiao, Cui, Di, & Pan, 2023; Tanko et al., 2021).

$$E_f = E_{(doped)} - E_{(pure)} + \mu_{se} - \mu_x \quad (2)$$

Where $E_{(doped)}$, $E_{(pure)}$ are the total energies per supercell of the doped and pristine WSe_2 monolayers, respectively. μ_{se} and μ_x stand for the chemical potential of Se atom and Br or Cl dopant respectively.

Formation energy is mostly determined by considering the experimental conditions. Herein, two limiting fabrication conditions have been considered, the W-rich and Se-rich situations. For the W-rich situation, μ_w is assumed to be the energy per W atom in its stable bulk phase. For the Se-rich, μ_{Se} and μ_w are related through (X. Zhao et al., 2020)

$$\mu_w + 2\mu_{se} = \mu_{wse2} \quad (3)$$

Hence, μ_{se} is determined from the energy difference between a Se molecule and one WSe_2 unit that is.

$$\mu_{seo} = \frac{1}{2}(\mu_{wse2} - \mu_w) \quad (4)$$

Chlorine doped WSe_2 has the lowest formation energy, as observed from table 3. This suggests that it is most favorable in terms of structural stability. It has been speculated that halogen (Group vii) doping in TMDCs creates instability. This is true, but in bulk and few layers TMDCs and not in monolayers. The fact is that halogens doping in such materials weaken Van der Waals force, which is interlayer not intralayer force.

Table 1 lists the calculated E_f of the WSe_2 monolayer under both W-rich and Se-rich conditions. The table reveals that the incorporation of Cl impurities into the pure WSe_2 monolayer is thermodynamically preferred under Se-rich conditions than that of W-rich conditions owing to the smaller formation energy of Cl-doped WSe_2.

The fact that E_f of Br-doped WSe_2 case is the smallest, especially for the Se-rich case confirmed it to be the most favorable replacement of Se with Br.

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Table 1: Structural Properties of Pure and doped WSe_2 monolayers within GGA-PBE Functional

Compound	Bond length (Å)	Bond Angle (°)		a(a.u)	Formation Energy (Ry)	
	$d_{W\text{-}D}$	$\Theta_{W\text{-}Se\text{-}W}$	$\Theta_{W\text{-}D\text{-}W}$	-----	W-rich	Se-rich
Pure WSe_2	*2.552	81.33	-----	6.351	--------	--------
Br-WSe_2	2.696	80.67	75.72	12.68	67.71	78.23
Cl-WSe_2	2.588	80.38	79.17	12.66	65.28	72.34

*W-Se bond length

Mechanical Properties

Analysis of elastic constants (C_{ij}) is essential for understanding the mechanical properties of the materials. These constants can be calculated using the energy of the strained system, assuming an applied macroscopic stress. The energy of the strained crystal material is given by (Chiodo, Binder, & Bastien, 2011).

$$E_{(V,\varepsilon)} = E_{(V_o,0)} + V_o\left[\sum_i \tau_i \varepsilon_i \mathfrak{Z}_i + \frac{1}{2}\sum_{ij} C_{ij}\varepsilon_i \mathfrak{Z}_i \varepsilon_j \mathfrak{Z}_j\right] \quad (5)$$

Where $E_{(V_o,0)}$ is the energy of the unstrained material with equilibrium volume V_o, τ_i is element in the stress tensor and $\mathfrak{Z}_i$ is a factor that takes Voit index into consideration

Since all the considered materials are two-dimensional, we consider only two independent elastic constants i.e. C_{11} and C_{12}. The in-plane young modulus (Y) and Poisson ratio (v) can be calculated from the following equations

$$Y = \frac{\left(C_{11}^2 - C_{12}^2\right)}{C_{11}} \quad (6)$$

$$v = \frac{C_{12}}{C_{11}} \quad (7)$$

It should be noted from table 4 and figure 3 that the calculated elastic constants are all positive and they certify the Born stability criteria for monolayer i.e. $C_{11} - C_{12} > 0$, which indicates that all the doped material in consideration are mechanically stable.

The results also imply that the doped structures considered in this study are less stiff than the pristine system.

Pugh (Feldman, 1976) proposed a rule used for understanding the brittle or ductile nature of a given material, according to him if $G/B > 1.75$ the material is ductile while $G/B < 1.75$ indicates brittle material. Our results (Table 2) indicate a G/B value of 0.78187, 0.58351 and 0.8268 for pure, Br- and Cl-doped WSe_2 monolayers respectively. This confirmed that the considered materials show relatively low shear deformation resistance and they all behave in a brittle manner.

Table 3 depicts the calculated elastic constants for both pure and doped WSe_2 monolayers, which are matrix elements obtained from computation run based on equation 5. Among the elastic constants, C_{11}, C_{22} and C_{33} are essential, they indicate resistance to linear compression in the a-, b- and c-direction respectively. It can be observed that Br- and Cl-doped WSe_2 monolayers offered almost equal resistance to linear compression along a-, b- and c-axis.

Poisson's ratio defined as the ratio of transverse contraction strain to longitudinal extension strain under a stretching force (Li,

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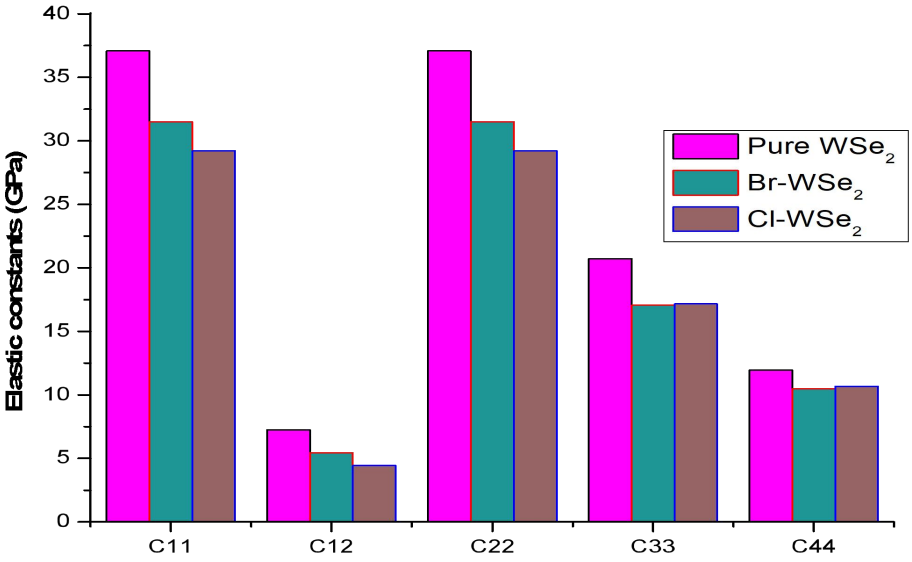
Jia, Zheng, Peng, & Fu, 2020), can be used to determine the stability of a crystal compound. From table 3 all the considered materials have Poisson's ratio greater than 0.25, suggesting all the materials are structurally stable. Zhao et al (X. Zhao et al., 2020) reported a criterion for identifying brittle and ductile material, they suggested that Poisson ratio less than 0.25 indicates brittle nature, while greater than such value means the material is ductile. Based on this, our observations show that our considered materials are brittle in nature. Figure 3 shows that the three elastic constants (C11, C12 and C44) used for calculating the young modulus and Poisson's ratio decrease in value from pure, Br to Cl doped WSe_2 monolayer respectively.

Finally, the mechanical properties (elastic constants, young, bulk moduli, pressure derivative of the bulk modulus and Poisson ratio) display a strong dependent on dopant atoms (Br and Cl).

Table 2: The Bulk modulus, equilibrium Volume, energy and G/B for two dimensional WSe_2 pure and doped obtained from first principle calculations

Compounds	B(GPa)	$B_o^{'}$	V_o(a.u^3)	Energy (Ry)	G/B
Pure WSe_2	16.3439	3.715	2242.6571	-53.1078	0.78187
Br-WSe_2	18.5787	2.859	8842.7904	-220.2267	0.58351
Cl-WSe_2	15.0676	3.654	8876.8273	-223.3221	0.8268



Figyre 3: A bar chart comparing the elastic constants of the pure and doped WSe_2 monolayer

Table 3: Elastic constants (GPa) and Poisson ratio for pristine and doped WSe_2 monolayers

Elastic Constant (GPa)	Compounds		
	Pure-WSe_2	**Br-WSe_2**	**Cl-WSe_2**
C11	37.091	31.505	29.206
C12	7.268	5.443	4.437
C22	37.091	31.505	29.206
C33	20.737	17.055	17.172
C44	11.955	10.479	10.679
Y	3.5666	2.9828	2.8532
v	0.1959	0.1727	0.1519

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CONCLUSION

In this work, we studied the structural and mechanical properties of 2D Br and Cl-doped WSe_2 monolayers. The structural property calculation reveals that the lattice constants calculated are in close agreement with other theoretical and experimental data. The mechanical properties obtained showed that the considered materials are mechanically and structurally stable, exhibit considerable resistance to linear compression and behave in a brittle manner. This suggests that the materials may be promising for photovoltaic and other applications.

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