

PREDICTION OF NEW GENERATION TWO-DIMENSIONAL TERNARY STRUCTURES AND INVESTIGATION OF THEIR FUNDAMENTAL PROPERTIES

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Prediction of new generation two-dimensional ternary structures and
investigation of their fundamental properties

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We certify that we have read this dissertation and that in our opinion it is fully
adequate, in scope and in quality, as a dissertation for the degree of Doctor of
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ABSTRACT

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Consecutive to the isolation of graphene and uncovering its extraordinary properties, the dynasty of two-dimensional (2D) materials has expanded rapidly. A realization of every new member suggests novel features, holding the promise to be used in current and prospective nanodevices. In parallel with the attempts on exploring new 2D systems, the formation of ternary configurations has been suggested as an alternative approach to tailor the inherent properties of the already existing 2D structures. In accordance with recent advancements in ternary 2D systems, in this dissertation, we design and investigate the 2D systems which possess three types of elements in their crystal structure. In this regard, we design Janus $\text{Al}_2\text{XX}'$ (X/X' : O, S, Se, Te) crystals, $1H$, $1T$, and $1T'$ phases of Janus WXO ($X = \text{S, Se, and Te}$) monolayers and Janus BiXY ($X = \text{S, Se, Te, and Y} = \text{F, Cl, Br, I}$) nanosheets and investigate their structural, vibrational, elastic, piezoelectric, and electronic properties by first-principle methods. In addition, inspired by the synthesis of penta-Si nanoribbons, advancements in 2D pentagonal systems, and recent developments on ternary structures, we propose and investigate a new ternary pentagon-based 2D monolayer, namely penta-BNSi. We study the mechanical, electronic, piezoelectric, photocatalytic, and optical properties of penta-BNSi crystal and reveal its suitability to be used in optoelectronics and photocatalytic applications. Then, we focused our attention on new family of MA_2Z_4 monolayers. Based on this motivation, we perform a comprehensive study on physical properties of MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers and suggested novel single layer of InSiN_2 ($\text{In}_2\text{Si}_2\text{N}_4$). For this purpose, in both studies, the ground state configurations of the designed materials are determined, and then the dynamical and thermal stability of these nanosheets are investigated using phonon spectrum analysis and *ab initio* molecular dynamic (AIMD) simulations, respectively. Next, each structure's Raman and infrared

(IR) spectrum are analyzed, and the corresponding atomic displacements of the optical phonon modes are presented. Then, the mechanical properties are studied in terms of in-plane stiffness and Poisson's ratio. The electronic band structures are computed in the electronic properties section, and the corresponding energy band gaps are reported. For MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers, the optical response is examined via calculation of the complex dielectric function by taking many-body interactions into account. In the final study, the effect of an external biaxial strain on the electronic and vibrational properties of the $InSiN_2$ nanosheet is investigated, and the variation of the obtained properties under strain is illustrated. As a result of a thorough theoretical study focusing on ternary 2D materials, it can be said that the examined crystals are stable systems with potential applications in a wide range of nanoelectronics and nanomechanical devices.

Keywords: Density functional theory, Two-dimensional materials, Ternary monolayers, Physical properties, Electronic structure .

ÖZET

TÜRKÇE BAŞLIK

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Grafenin izolasyonunun ve olağanüstü özelliklerinin ortaya çıkarılmasının ardından, iki boyutlu (2B) malzeme ailesi hızla genişlemiştir. Her yeni üyenin sentezlenmesi yeni özelliklerle birlikte, mevcutta ve olası cihazlarda kullanılma imkanı sunar. Yeni 2B sistemleri keşfetme girişimlerine paralel olarak, halihazırda var olan 2B yapının doğasından gelen özelliklerini iyileştirmek için alternatif bir yaklaşım olarak üçlü konfigürasyonların oluşturulması önerilmiştir. Üçlü 2B sistemlerdeki son gelişmelere uygun olarak, bu tezde, kristal yapılarında üç tip element içeren 2B sistemleri tasarlanmış ve çeşitli özellikleri incelenip ortaya çıkarılmıştır. Bu bağlamda, Janus Al_2XX' (X/X' : O, S, Se, Te) kristallerini, tek tabaka WXO ($X = S, Se$ ve Te) sistemlerinin $1H$, $1T$ ve $1T'$ Janus fazlarını ve Janus $BiXY$ ($X = S, Se, Te$ ve $Y = F, Cl, Br, I$) nano tabakalarını dizayn edilerek, bunların yapısal, titreşimsel, elastik, piezoelektrik ve elektronik özelliklerini ilk prensip hesaplamalarıyla incelendi. Ek olarak, penta-Si nanoribbonların sentezlenmesinden ve 2B beşgen sistemler ile üçlü yapılardaki son gelişmelerden esinlenerek, yeni bir üçlü beşgen tabanlı 2B tek tabaka, yani penta-BNSi önerildi ve araştırıldı. Penta-BNSi kristalinin mekanik, elektronik, piezoelektrik, fotokatalitik ve optik özellikleri incelenmiş ve optoelektronik ve fotokatalitik uygulamalarda kullanılmaya uygunluğu ortaya konulmuştur. Ardından, dikkatimizi yeni MA_2Z_4 tek tabakalı aileye odakladık. Bu motivasyondan yola çıkarak tek katmanlı MSi_2Z_4 (M : Pd ve Pt, Z : N and P) in fiziksel özellikleri üzerine kapsamlı bir çalışma gerçekleştirdik ve Z : N ve P) yeni tek katmanlı $InSiN_2$ ($In_2Si_2N_4$) yapısını önerdik. Bu amaçla her iki çalışmada da, tasarlanan malzemelerin temel durum konfigürasyonları belirlenmiş ve daha sonra fonon spektrum analizi ve *ab initio* moleküler dinamik (AIMD) simülasyonları kullanılarak bu nanotabakaların sırasıyla dinamik ve termal kararlılığı incelenmiştir. Daha sonra, her yapının Raman ve kızılötesi (IR) spektrumu analiz edilmiş ve optik fonon modlarının karşılık gelen atomik yer değiştirmeleri sunulmuştur. Daha sonra mekanik özellikler, düzlem içi rijitlik ve Poisson oranı açısından incelenmiştir. Elektronik bant

yapıları, elektronik özellikler bölümünde hesaplanmış ve karşılık gelen enerji bandı boşlukları rapor edilmiştir. MSi_2Z_4 (M : Pd ve Pt, Z : N ve P) tek tabakaları için optik tepki çok-cisim etkileşimlerini hesaba katarak karmaşık dielektrik fonksiyonunun hesaplanması yoluyla incelenir. Son çalışmamızda ise, $InSiN_2$ nanotabakasının elektronik ve titreşimsel özellikleri üzerinde harici bir çift eksenli germenin etkisi araştırılmış ve germe altında elde edilen özelliklerin değişimi gösterilmiştir. Üçlü 2D malzemelere odaklanan kapsamlı bir teorik çalışmanın sonucunda, incelenen kristallerin çok çeşitli nanoelektronik ve nanomekanik cihazlarda potansiyel uygulamaları olan kararlı sistemler olduğu söylenebilir.

Anahtar sözcükler: Yoğunluk fonksiyonel teorisi, İki boyutlu malzemeler, Üçlü tek tabakalar, Fiziksel özellikler, Elektronik yapı.

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Chapter 1

Introduction

When layered materials are thinned down to the monolayer limit, they can exhibit entirely different properties from their bulk counterparts due to the quantum effects and strong electron confinement emerging from dimensional restriction. The best-known example of this phenomenon is graphite and its single atom-thickness crystal, namely, graphene. The successful exfoliation of single-layer graphene [2] from graphite in 2004 has triggered extensive interest in the field of two-dimensional (2D) materials and pioneered the emergence of new ultrathin materials with remarkable properties [3, 4, 5]. Due to its remarkable physical properties, such as high carrier mobility, impressive mechanical properties, and high thermal conductivity, graphene has been intensively studied both theoretically and experimentally [6, 7]. However, one of its major drawbacks is the lack of band gap, which restricts its use in semiconducting applications [8]. This fact led to the exploration of new 2D crystals from a variety of layered van der Waals (vdW) materials, such as boron nitride (h-BN) [9, 10], phosphorene [11, 12] and MoS₂ [13, 14]. In such crystals, the atoms are stacked in the neighboring layers by weak vdW forces, while the atoms within each layer are bonded by strong chemical bonding. The majority of known 3D materials, including silicon, transition metal carbides/nitrides (TMC/TMN), metal dichalcogenides, metal oxides, and group III-V semiconductors, are non-layered [15]. In these materials, since atoms are bonded to each other by strong chemical bonding in three directions,

their 2D forms cannot be obtained through simple mechanical exfoliation. For the synthesis of new 2D materials without 3D stacked crystals, several fabrication techniques, such as top-down and bottom-up growth approaches, have been suggested [16, 17]. In 2017, researchers could successfully fabricate a Janus-type single-layer ternary MoSSe structure via the controllable exchange of S atoms by Se atoms at one surface of a MoS₂ crystal or Se by S at MoSe₂ monolayer [18, 19]. The formation of two surfaces of a 2D material with different atoms enhances the material's functionality, which can be useful in developing novel nanodevices. The characterization results of MoSSe proved that the material possesses strong Rashba spin splitting, large piezoelectric effect, and good catalytic performance [20, 21]. Following the realization of MoSSe monolayer, the formation of ternary configurations from their binary counterparts is considered a new approach to exploring new 2D structures [22, 23]. Motivated by this development, in this dissertation, we tried to design new 2D ternary systems and investigate their fundamental properties.

As a new and exciting family of 2D materials, Group III monochalcogenides (MX , $M = \text{B, Al, Ga, In}$; $X = \text{O, S, Se, Te}$) has received considerable attention due to their outstanding electronic, optical, thermal and mechanical properties and a high surface to volume ratio that makes them promising materials for technological applications in transistors, solar energy absorption and conversation [24, 25]. To date, several members of MX crystals such as GaS [26, 27, 28], GaSe [29, 30], GaTe [31, 32], and InSe [33, 34] have been synthesized, and their unique physical properties have been studied, both theoretically and experimentally. Studies on this family are not limited to their binary forms. The ternary derivatives of group-III monochalcogenides such as Ga_2XX' [35] and In_2XX' [36] monolayers have been theoretically investigated, and they have been proposed as piezoelectric materials with remarkable out of plane piezoelectricity. Accordingly, as the first study on ternary systems, we focused on the family of group III monochalcogenides, exclusively on Al_2XX' monolayers, and the third chapter of this dissertation is dedicated to that study.

Within 2D materials, particular attention has been paid to the family of TMDs and TMOs [37, 38, 39, 40, 41]. Tungsten dichalcogenides (WX_2 , $X = \text{S, Se, Te}$) is

one of prominent members of this family. It possesses three possible geometrical phases ($1H$ -, $1T$ - and $1T'$), in which W atoms are positioned between two layers of X atoms [42, 40, 43]. After the growth of MoSSe, researchers began to consider a similar technique to fabricate WSSe, and could successfully synthesize 2D Janus WSSe crystals in 2020 [44, 45]. Together with experimental studies, several theoretical investigations have been done on ternary WXX' [46, 47]. Motivated by these findings, using first-principles methods, we investigated the formation of Janus WXO monolayers based on oxygenation of WX_2 monolayer, and the obtained results are discussed in the fourth chapter.

Spin-orbit interaction is greatly enhanced in crystals containing heavy elements and broken inversion symmetry [48, 49]. A promising candidate for such a 2D crystal is BiTeI. Due to its giant Rashba spin splitting (RSS) [50, 51, 52], the Bulk form of BiTeI has gained considerable attention. Recently a single layer BiTeI is successfully isolated from its bulk crystal [53]. The monolayer comprises three sublayers, which Bi atoms sandwiched between Te and I plates. Following this development, various 2D bismuth chalcogenide structures, such as BiTeBr [54] and BiTeCl [55], have been synthesized. Motivated by the intriguing physical properties of bismuth chalcogenides, such as giant RSS, large out-of-plane piezoelectricity, and high thermoelectric performance (ZT), we performed a comprehensive and comparative ab initio investigation on the design and characterization of Janus $BiXY$ monolayers and our results on their structural, vibrational, mechanical, piezoelectric, and electronic properties are presented in the fifth chapter.

Single-layer pentagonal materials have garnered less research attention than 2D crystals with hexagonal lattices. In 2015, a 2D carbon allotrope made entirely of pentagonal carbons (pentagraphene) has been predicted [56], and theoretical calculations confirmed its dynamical stability. Following this study, the first 2D pentagonal configuration in 2D penta-PdSe₂ has been realized by exfoliating the monolayer from its bulk crystals [57, 58]. Subsequently, binary and ternary pentagonal structures such as CN_2 [59], CB_2 [60], BN_2 [61], SiC_2 [62] and penta-BCN [63] have been suggested and characterized. Inspired by recent studies, we designed a new ternary pentagon-based 2D nanosheet, namely penta-BNSi, and

comprehensively characterized its physical properties, which the obtained results will be further explained in Chapter 6.

Very recently, the 2D crystals of MoSi_2N_4 and WSi_2N_4 have been successfully synthesized [64] via the chemical vapor deposition (CVD) technique. The fabricated materials are indirect band gap semiconductors that exhibit high tensile strength, and good ambient stability [64]. The growth of MoSi_2N_4 and WSi_2N_4 monolayers led to creation of new class of 2D materials with general formula of MA_2Z_4 [15, 65]. Following the experimental progress, variety of 2D materials within the same class such as TiSi_2N_4 , VSi_2N_4 and CrSi_2N_4 have been suggested and investigated by first principles method [66, 67, 68, 69]. According to stoichiometry of these 2D systems, we constructed and investigated MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers as new members of MA_2Z_4 family and reported our results in Chapter 6 of this dissertation. As the final study on ternary systems, we continued investigations on MA_2Z_4 family. Accordingly, we design the InSiN_2 monolayer and systematically explore its vibrational, elastic, piezoelectric, electronic, and optical properties. As the mechanical strain can significantly tune the vibrational and electronic properties of the materials, we continued studying the strain-dependent vibrational and electronic properties of InSiN_2 monolayer and represented our results in Chapter 8.

Chapter 2

Theoretical Background

As a quantum mechanical analogue to Newton's equations of motion, all information about a quantum system can be obtained from the many-body Schrodinger equation [70]:

$$\hat{H}\Psi_i(r, R) = E_i\Psi_i(r, R) \quad (2.1)$$

Where $\hat{H}$ is the energy operator which is known as the Hamiltonian and the E is the eigenvalue associated with the Hamiltonian operator. For a system with M nuclei and N electrons, the Hamiltonian operator includes terms for all potential interactions between electrons and nuclei.

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{jA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.2)$$

In this case, the first two terms are correlated with the kinetic energy of the electrons and the nuclei, and the remaining terms are related to the Coulomb interaction between the electrons and the nuclei, the electrons, and the nuclei, respectively.

However, this equation is too complex to have a calculable solution in most realistic cases, with the exception of a few simple systems like H or He. To solve this equation, $3N + 3M$ degrees of freedom should be considered. It is quite difficult to solve the Schrodinger equation with a Hamiltonian like this. Thus, various approximations were employed to simplify the solution for $\hat{H}$.

$$\hat{H}\Psi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E_i\Psi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) \quad (2.3)$$

In the equation, N represents the number of electrons and M represents the number of nuclei.

2.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation, which was developed by Max Born and J. Robert Oppenheimer in 1927 basically assumes that nuclei have a mass substantially greater than electrons. Based on this simple assumption, the velocity of nuclei can be considered much lower than the velocity of electrons and can be treated as static, classical particles with respect to electrons. Therefore, the position of the electrons will be determined according to the coordinates of nuclei before the positions of nuclei are changed. According to this assumption, the kinetic term of nuclei in Eq. 2.2 can be removed and this helps to solve the electronic problem, independent of the nuclei movements.

$$\hat{H}_{elect} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{jA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (2.4)$$

Following this simple assumption, the wavefunction that is the solution to this Hamiltonian is merely a function of electron position. Even though the approach is promising, it results in an electronic problem that has $3N$ degrees of freedom which is still difficult to solve.

2.2 Hartree-Fock Approximation

It is obvious that dealing with each particle independently is not practical; instead, they should be considered as distinct particles, and their interactions with others should be averaged. In 1928, Douglas R. Hartree [71] suggested a method to address the electronic problem which was named as Hartree approximation. Based on this approximation, the wave function of a many-body system can be described as the product of one-electron wave functions ($\Psi = \Psi_1 \times \Psi_2 \times \dots \Psi_n$) which satisfies the single-particle Schrodinger equation in a potential field. Therefore, the effect of all electrons can be described as an effective mean-field one-electron potential ν_i

$$\sum_{i=1}^N \sum_{j>1}^N \frac{1}{r_{ij}} \approx \sum_{i=1}^N \nu_i(r_i) \quad (2.5)$$

By using the Hartree technique, after finding an initial effective potential for the system, iterative calculations should be carried out until a self-consistent solution is obtained that minimizes the total energy. However, this method has a major drawback since two essential principle of quantum mechanics such as Pauli's exclusion (exchange) principle and anti-symmetry are not taken into consideration. Thus, the computed value of total energy by this method is a naive estimation of the energy. Hartree's method can be formulated by the inclusion of the Pauli exclusion principle and the total wave function can be expressed better with writing it as Slater determinant which is known as the Hartree-Fock method [72].

$$\Phi_{SD} = \frac{1}{\sqrt{N!}} \det \{ \chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \dots \chi_N(\vec{x}_N) \} \quad (2.6)$$

where, $\frac{1}{\sqrt{N!}}$ is the factor of normalization, and χ_i are orbital wave function. As a result of this approximation, $3N$ degrees of freedom are reduced to 3, and numerical calculations are simplified. Despite the fact that this approximation

takes into account the exchange effect, the correlation between the many-body electron system is entirely ignored [73].

2.3 Density Functional Theory

First attempts were made by Thomas and Fermi [74, 75] in the early 1920s to determine the electronic many-body problem by taking into account density of the electrons as the fundamental variable. In spite of the fact that this approximation failed to take into account exchange-correlation terms, it provided the basis for the rise of the Density Functional Theory (DFT). In 1964, Hohenberg and Kohn [76] proposed the principles of DFT. In their proposal, they stated that the ground-state electron density of a many-body electronic system can provide all the information related to the properties of the ground state. Hohenberg and Kohn's first theorem states that the external potential is a distinctive functional electron density.

$$E_0[n_0] = \int n_0(\vec{r})V_{ex}d\vec{r} + T[n_0] + E_{ee}[n_0] \quad (2.7)$$

where, n_0 is the ground-state electron density, V_{ex} is the external potential, T and E_{ee} are the kinetic and exchange-correlation terms, respectively. Based on the second Hohenberg-Kohn theorem, only the actual ground state density gives the minimum energy, which opens up the possibility of using the variational principle to find the ground state. In other words, instead of dealing with the complicated electronic wave functions, they showed that it is possible to minimize the total energy of a system by taking advantage of the simpler total electron density rather than dealing with the complicated electronic wave functions,

$$E_0 \leq E[\tilde{n}] = T[\tilde{n}] + E_{ext}[\tilde{n}] + E_{ee}[\tilde{n}] \quad (2.8)$$

Then, in 1965, Kohn and Sham [77] suggested that the kinetic energy of the

interacting electrons can be replaced by the kinetic energy of an equivalent non-interacting system to minimize the kinetic energy under predetermined density constraints. Once the solution to the kinetic term of the equation has been determined, the remaining terms of the equation, which represent the exchange and correlation terms of the system, can be expressed as functional of the full electron density. However, the accurate expression has yet to be determined. Initially, we begin with an initial conjecture of electron density, for a naive configuration of ionic coordinates. We then calculate the effective potential correlated to this assumed density. After that, the Kohn-Sham orbitals are computed by inserting the estimated effective potential into Kohn-Sham equations. According to the Kohn-Sham ansatz, for the ground state of a many body system, the new and old electron densities ought to be equal. Thus, whenever, the difference is smaller than a predetermined threshold, the desired accuracy has been attained, and the self-consistency loop will stop. On the other hand, if the difference exceeds the allowable limit, the loop will keep going until the self-consistency is reached.

2.4 Exchange and Correlation

In DFT, the exchange and correlation energy of a many-electron system is considered to be an essential quantity. Exchange energy is generally characterized in terms of Pauli exclusion principle because in these systems we are dealing with electrons, which are recognized as fermions. This concept states that when two electrons interact, their overall wave function will be antisymmetric, resulting in an energy exchange. However, correlation energy is usually described as the difference between a quantum mechanical system's total energy and its Hartree energy. In order to deal with these two terms, there are two known approximations that are widely used in calculations based on DFT. The local density approximation (LDA), and the generalized gradient approximation (GGA).

Local Density Approximation(LDA) :

Within this approximation, the system is divided into infinitesimally small

volumes, each of which has a constant electron density. For each piece, it is assumed that the exchange-correlation energy corresponds to the density-uniform electron gas energy. The exchange correlation energy of LDA can be written as

$$E_{xc}^{LDA}[n] = \int n(r) \varepsilon_{xc}^{uni}[n] dr \quad (2.9)$$

where ε_{xc}^{uni} is exchange-correlation energy per electron. As a general principle of LDA, the concept is based on the notion that the inhomogeneous electronic systems can be regarded as local homogeneous ones, and then the exchange correlations can be used for the calculations that correspond to the homogeneous electron gas. In this respect, LDA provides better approximations in systems with a higher degree of homogeneity [78].

Generalized Gradient Approximation(GGA) :

Due to the fact that the local uniform density does not provide a satisfactory approximation for rapidly varying electron densities, in such systems the gradient of the electron density, $\nabla n(r)$, should also be considered. In order to calculate the total energy functional in GGA, we use a general functional combining the two electron density and its gradient [79, 80]. Therefore we have;

$$E_{xc}^{GGA}[n] = \int f^{GGA}(n(r), \nabla n(r)) dr \quad (2.10)$$

The GGA approximation introduces semi-locally inhomogeneities of the density, by means of expanding a series of exchange-correlation functions and including terms such as the density and what it is gradiented from. Thus, the GGA method shows an improvement in the binding energies, bond lengths, and atomic energies of atoms in comparison to the results that can be obtained from the LDA approximation.

Hybrid Functionals :

In Hartree's definition, the self-interaction of electrons is unphysically considered. In 1993, Becke [81] developed a hybrid approach to construct the E_{xc} term

by a linear combination of Hartree-Fock's precise exchange functional and any number of exchange and correlation functional, which are derived using LDA or GGA approaches. To enhance the computational efficiency of the exchange term, the hybrid method uses a Coulomb potential with error-function screened estimations. Heyd-Scuseria-Ernzerhof (HSE06) is a well-known Hybrid Functionals that has been widely used in DFT calculations and can be calculated as follows;

$$E_{xc}^{HSE} = aE_x^{\text{HF,SR}}(\lambda) + (1 - a)E_x^{\text{PBE,SR}}(\lambda) + E_x^{\text{PBE,LR}}(\lambda) + E_c^{\text{PBE}} \quad (2.11)$$

The use of HSE hybrid functional results in a more accurate estimation of energy bandgap in which HF and PBE are mixed with a parameter $\mathbf{a}$, and the range of interaction is screened by λ . HF,SR and PBE,LR represent the short-range Hartree-Fock and long-range components of PBE, respectively. Generally, in HSE06 calculations, the screening length of HSE and the mixing rate of the Hartree-Fock exchange potential were taken as $\lambda = 0.2 \text{ \AA}^{-1}$ and $\mathbf{a} = 0.25$, respectively.

2.5 Theory of Phonons and Molecular Dynamics (MD)

To determine whether a material is dynamically stable at equilibrium or under strain, the materials' phonon-band dispersion through Brillouin Zone can be computed. A crystal is composed of many atoms vibrating around a particular equilibrium position. Their movement obeys Hooke's Law. According to this law, restoring forces that the atoms experience while displaced from their equilibrium position cause vibrations. Therefore, to determine the phonon band dispersion of a crystal, the variation of the restoring forces as a function of the displacement should be calculated. Initially, to obtain the dispersion, the force constants in the form of a matrix should be estimated. In this dissertation, the phonon spectra are calculated within the DFT framework using the small displacement

method. In this methodology, a sufficiently large supercell of the crystal should be constructed to satisfy the harmonic motion in the system. Then, based on the Hellman-Feynmann theorem [82], the ionic forces between atoms and the stress tensor can be calculated by;

$$F_i = \frac{dE}{dR_i} \quad (2.12)$$

$$C_{ij} = \frac{dF}{dR_j} \quad (2.13)$$

Where E , F_i and C_{ij} represent the system's total energy, force on the nucleus, and inter-atomic force constant. After acquiring the Hellmann-Feynman forces, the dynamical matrix can be constructed. Once the matrix is calculated, it is possible to solve the eigenvalue equation of the matrix. Using the eigenvalues of the dynamical matrix, the phonon frequencies of each phonon at any wave vector, $\mathbf{q}$, can be determined. Acquiring the phonon dispersion allows the calculation of various parameters such as specific heat (C_v), effective charges, and electron-phonon interactions.

As the next step in determining the stability of materials, an *ab initio* molecular dynamics (AIMD) simulation is performed to explore the effect of temperature on the lattice structure. To remove the size constraint, the exact supercell sizes that were considered in the phonon spectrum analysis are used. AIMD calculation is performed using a microcanonical ensemble at finite temperatures with a scaled velocity approach (keeping temperature constant). The calculation duration is considered long enough to see the effect of temperature on the material.

2.6 Calculation of Raman spectra

A brief explanation of the intensity of a vibrational mode is necessary before we can calculate the Raman activity of the vibration. The intensity of an output

that comes from a physical source can be described as a ratio between the average power and the area in which the scattering rate is observed.

$$I = \frac{P}{A} \quad (2.14)$$

where P denotes the average power radiated by the source, and A is the area. In Raman spectroscopy experiments, an incident light beam interacts with vibrating atoms in the material and scatters inelastically due to Raman scattering. It is known from classical electrodynamics that a dipole in oscillation radiates with an average total power of $\mathbf{P}$ (watts) given by;

$$p = \frac{4\pi^3 v_0^4 |\mu|^2}{3\varepsilon_0 c^3} \quad (2.15)$$

Then the intensity of a transition from v to v' can be obtained as;

$$P = \frac{4\pi^3 v_0^4}{3A\varepsilon_0 c^3} \langle v' |\mu|^2 v \rangle \quad (2.16)$$

where c is the velocity of light, v_0 is the frequency of the incident light, and μ is the electric dipole moment of the oscillating dipole which is correlated to incident electric field by;

$$\mu = \alpha E \quad (2.17)$$

where α is the polarizability of the material. The Raman intensity for each eigenmode can be computed using;

$$I_{Raman} = a\tilde{\alpha} + b\beta \quad (2.18)$$

where a and b are constants, $\tilde{\alpha}$ and β correspond to the isotropic and anisotropic parts of the derivative of polarizability tensor, respectively, and can

be calculated as;

$$\tilde{\alpha} = \frac{1}{3}(\tilde{\alpha}_{xx} + \tilde{\alpha}_{yy} + \tilde{\alpha}_{zz}) \quad (2.19)$$

$$\beta = \frac{1}{2}\{(\tilde{\alpha}_{xx}-\tilde{\alpha}_{yy})^2+(\tilde{\alpha}_{yy}-\tilde{\alpha}_{zz})^2+(\tilde{\alpha}_{zz}-\tilde{\alpha}_{xx})^2+6[(\tilde{\alpha}_{xy})^2+(\tilde{\alpha}_{yz})^2+(\tilde{\alpha}_{zx})^2]\} \quad (2.20)$$

By displacing the atoms along the eigenvectors of each phonon mode twice, $\tilde{\alpha}$ (per volume) can be calculated via using DFPT approach.

2.7 Mechanical Properties of Materials

As part of the characteristics of materials, mechanical properties play an essential role because they provide information about the stability of the structure under external forces. The information about a material's mechanical properties depends on the material's structure because interatomic forces which resist any structural change characterize the material's behavior [83]. Basically, the mechanical response of homogeneous 2D materials in the elastic region can be defined in terms of in-plane stiffness (Y_{2D}), Poisson's ratio (ν), and ultimate tensile strength (UTS). Whenever a material is loaded only in its elastic region, it will be able to restore to its original shape any time that the applied load is removed, with no permanent change in the material's structure. Therefore, a material's elastic property can be considered the reversible deformation process. To obtain the mechanical properties, we must first obtain the elastic tensors. The elasticity tensor, which correlates to the applied load (stress) to the strain tensor, has 6×6 dimensions given by;

$$\begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1131} & C_{1112} \\ C_{2211} & C_{2222} & C_{2233} & C_{2223} & C_{2231} & C_{2212} \\ C_{3311} & C_{3322} & C_{3333} & C_{3323} & C_{3331} & C_{3312} \\ C_{2311} & C_{2322} & C_{2333} & C_{2323} & C_{2331} & C_{2312} \\ C_{3111} & C_{3122} & C_{3133} & C_{3123} & C_{3131} & C_{3112} \\ C_{1211} & C_{1222} & C_{1233} & C_{1223} & C_{1231} & C_{1212} \end{bmatrix}$$

where C_{ijkl} 's are elastic constants with symmetry qualities such as $C_{ijkl} = C_{jikl}$, $C_{ijkl} = C_{ijlk}$, and $C_{ijkl} = C_{klij}$. In this thesis, the elastic constants are obtained within the DFT framework by DFPT approach.

Young's Modulus and In-plane Stiffness :

A modulus can be described as the numerical value (constant) corresponding to a physical property of the material when an external force applying to it. The modulus of elasticity, often known as Young's Modulus (E), is a mechanical property of a material that measures rigidity (or flexibility) and can be formulated as;

$$E = \frac{\sigma}{\varepsilon} \quad (2.21)$$

$$\sigma = E\varepsilon \quad (2.22)$$

where σ is the applied stress and ε is the change in the dimension of the material along the direction of the applied stress. σ is described as force (F) per unit area (A), and strain is the ratio of elongation (ΔL) of the material to its original length (L), as given in Equations below;

$$\sigma = \frac{F}{A} \quad (2.23)$$

$$\varepsilon = \frac{\Delta L}{L} \quad (2.24)$$

The Young's modulus (E) has a SI unit of GPa. As defined in Eq.2.21, the slope of a linear segment of a stress-strain relation will correspond to the value of Young's modulus (E). When elastic modulus is measured on the atomic scale, strain is viewed as the small changes in the interatomic spacing and the stretching of interatomic bonds. In the 2D limit, the modulus of elasticity can be termed as in-plane stiffness (Y_{2D}). Due to the absence of periodic boundary conditions along the out-of-plane direction in the 2D limit, in-plane stiffness should be related to the stress and strain along the in-plane directions. Therefore we have;

$$\sigma_{xx} = Y_{2D(xx)} \times \varepsilon_{xx} \quad (2.25)$$

$$\sigma_{yy} = Y_{2D(yy)} \times \varepsilon_{yy} \quad (2.26)$$

xx and yy are specific direction in 2D crystal structures. In the case of isotropic materials, the value of Y_{2D} in any direction will be the same. This is due to the interatomic bonding symmetry of the material. However, in 2D anisotropic materials, the value of Y_{2D} in different directions will be different. Therefore, the orientation-dependent mechanical properties of these systems should be calculated.

Poisson's ratio :

Poisson's ratio (ν) is defined as the negative ratio of the transverse contraction strain to the axial extension strain in the direction of the stretching force.

$$\nu = -\frac{\varepsilon_{trans.}}{\varepsilon_{long.}} \quad (2.27)$$

Generally, ν of isotropic materials is positive, meaning they shrink transversely

when stretched (See Fig.2.1). On the other hand, an entirely different class of materials, known as auxetic materials, exhibits a negative ν and becomes wider in the transverse direction when the axial tension is applied to them. According to Christensen's criterion [84], in 2D crystal structures, the threshold for the ductile/brittle transition is $2/7$. Thus, the crystal structures with larger $\nu > 2/7$ can be considered ductile, and those with $\nu < 2/7$ possess a brittle character.

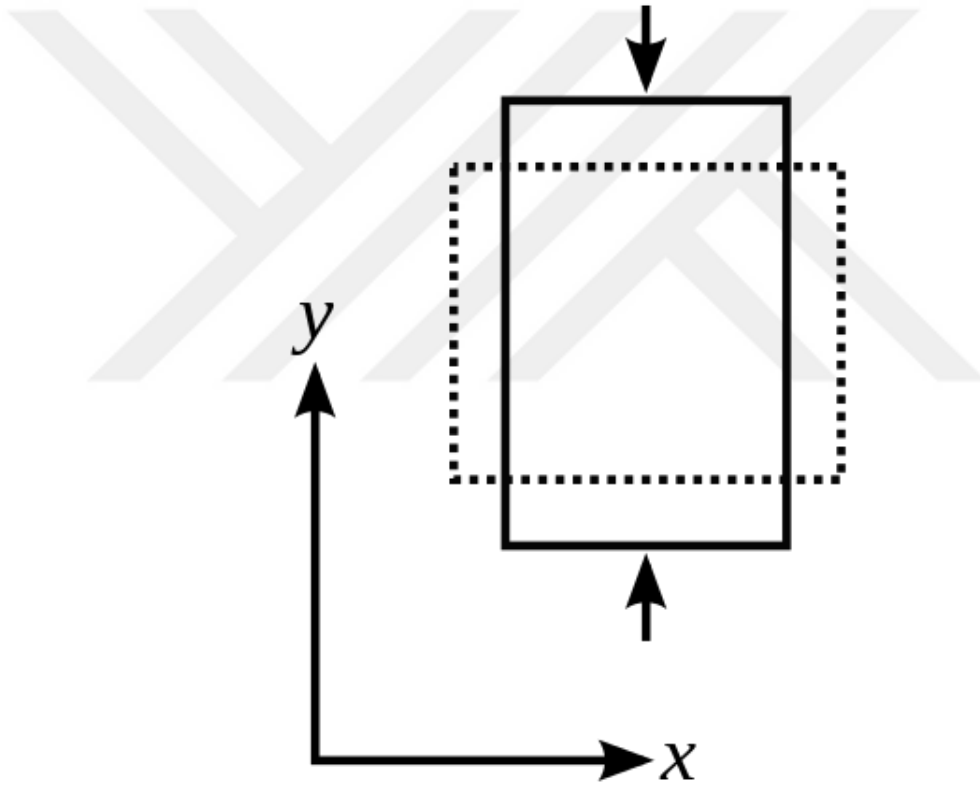


Figure 2.1: Geometrical deformation of conventional 2D crystal under applied stress [1].

Stress-Strain Relation :

A stress-strain curve is a graph that illustrates the relationship between stress and strain in a material. Figure 2.2 [83] illustrates the critical points in a stress-strain diagram. The linear region on the stress-strain curve, known as the elastic region, is where the material can deform, and this deformation is reversible. As stress levels increase, this relationship between stress and strain can take different

forms, and the material can undergo non-reversible deformations. Depending on the type of materials, stress-strain curves can exhibit different regions, such as linear elastic, uniform plastic, or nonuniform plastic regions. The term plastic region or plastic deformation is usually associated with metal crystal structures since dislocations are the most common factor causing plastic deformation in metal crystals. This is an important region in the stress-strain curve since it gives information about the brittleness or ductility of the material as well as mechanical properties such as ultimate tensile strength (UTS) and fracture point. UTS is an essential inherent mechanical feature of materials and is defined as the amount of tensile stress that a material can withstand before breaking. Generally, in 2D crystals, dynamical instability occurs before the material reaches the ultimate strength point. Thus, this means that at this point, the crystal structure is not deformed, but it is no longer dynamically stable. Additionally, the fracture strain can be defined as the strain value that the material breaks.

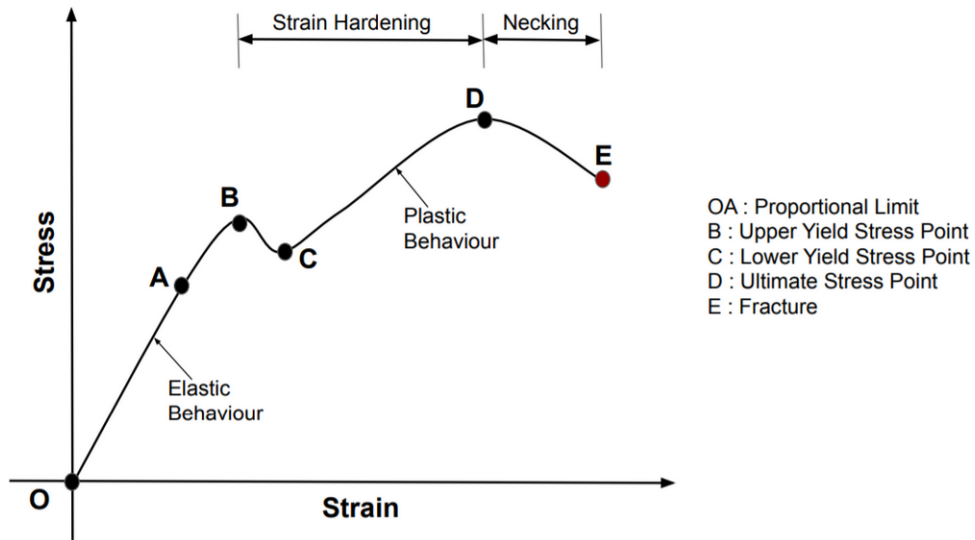


Figure 2.2: Schematic representation of stress-strain diagram [1].

2.8 Piezoelectric Properties

Piezoelectric effect is a unique material property which is described as the creation of electric dipole moment as a result of applied external stress (and vice

versa) in noncentrosymmetric materials. Theoretical studies and experimental observations have demonstrated the enhancement of piezoelectric coefficients in 2D limit compared to their 3D counterparts[85, 86]. The piezoelectric stress tensor, e_{ijk} , can be formulated as the coupling between electrical polarization (P_i) and strain (ε_{jk}) tensor

$$e_{ijk} = \frac{\partial P_i}{\partial \varepsilon_{jk}} \quad (2.28)$$

where i, j and k correspond to the x, y and z Cartesian directions, respectively. For 2D materials, the piezoelectric stress tensor, e_{ij} , must be re-normalized by the unit of lattice parameter along the z axis, i.e. $e_{ij}^{2D} = z \cdot e_{ij}^{3D}$. The e_{ij}^{2D} can be described as sum of electronic e_{ij}^{el} and ionic e_{ij}^{ion} contributions.

$$e_{ij} = e_{ij}^{el} + e_{ij}^{ion} \quad (2.29)$$

In this dissertation, the values of e_{ij} is calculated via DFPT method and the values of piezoelectric strain tensors, d_{ij} are derived using the following relation;

$$e_{ij} = d_{ik} C_{kj}. \quad (2.30)$$

where C_{ij} is the elastic constants of the related materials.

The number of independent components of piezoelectric tensors (e_{ij} and d_{ij}) are determined by the symmetry of structures.

Chapter 3

Janus $\text{Al}_2\text{XX}'$ (X/X' : O, S, Se, Te) Monolayers

Recently the 2D group -III monochalcogenides have become the focus of numerous studies, as they possess remarkable electronic, optical, thermal, and mechanical properties [87, 88]. Until now, 2D crystals of GaS [26, 27, 28], GaSe [29, 30], GaTe [31, 32], and InSe [33, 34] have been synthesized and their unique properties have been characterized. Their possible applications such as photocatalysts for water splitting [89], field-effect transistors (FETs) [90], and solar photovoltaics [91] have also been proposed. In addition to experimental efforts, the entire class of group-III monochalcogenides (MX , $M = \text{B, Al, Ga, In}$; $X = \text{O, S, Se, Te}$) have been examined by first-principles methods and stable structures among them have been predicted [92]. MX monolayers are semiconductors with indirect band gaps, which span a wide range from deep ultraviolet to near infrared [93, 92]. It has been shown that along with GaX , an unusual band inversion (Mexican-hat dispersion) [94, 93] is also noticed in monolayers of AlX , the class of which should be further analyzed. Recently, it has been reported that AlX monolayers exhibit outstanding thermoelectric performance, which make them promising candidate matrices in high efficiency thermoelectric nanocomposites [95]. Additionally, nanosheets of aluminum oxides have been found to be dynamically stable [96, 97], indicating the possible realization of AlX systems in the near future.

In parallel with the attempts on exploring new 2D systems, the formation of ternary (Janus) configurations has been suggested as an alternative approach to tailor the inherent properties of already existing 2D structures [19, 98]. In this regard, computational studies have revealed that $\text{Ga}_2\text{XX}'$ can be designed and utilized in many applications such as ultraviolet photodetectors [99] and piezoelectric materials [35] as well as photocatalytic water splitting [100]. Furthermore, oxygenation of gallium monochalcogenides (Ga_2XO) has been investigated and it has been demonstrated that while GaX monolayers are indirect band gap semiconductors, Ga_2XO monolayers have direct band gaps and oxygenation also tuned their mechanical properties [101]. In another study, the stability of In_2SSe Janus monolayer has been predicted and a tunable direct band gap under strain has been reported [36]. These studies on group -III monochalcogenides have indicated that the addition of a third element and broken structural symmetry can lead to new and more interesting features in this family which exhibit great potential for numerous applications [22, 102, 103]. Following recent developments in ternary 2D crystals, in this chapter, we design and systematically investigate the monolayers of $\text{Al}_2\text{XX}'$ ($\text{X/X}'$: O, S, Se, and Te), which is one of the prominent groups within MX .

3.1 Methodology

For this study, we performed first-principles calculations based on density functional theory (DFT) [104, 105] as implemented in the Vienna *Ab initio* Simulation Package (VASP) [106, 107, 108, 109]. The projector augmented wave (PAW) [110] method was utilized to portray the potentials of Al, O, S, Se, and Te elements. The exchange-correlation term was described within the generalized gradient approximation (GGA) as parameterized by Perdew-Burke-Ernzerhof (PBE) [111]. In addition to GGA-PBE, Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional was adopted to correct the underestimated electronic band gaps [112, 113]. A plane wave basis set with a cutoff energy of 530 eV was taken. The Γ -centered $16 \times 16 \times 1$ uniform k-point mesh was used to sample the Brillouin zone [114].

A vacuum space of $\sim 20 \text{ \AA}$ was employed to hinder any interaction in the non-periodic direction. All ionic positions and lattice constants were relaxed until the force on each atom was less than $0.01 \text{ eV/\AA}$. The convergence criterion for electronic steps was set to 10^{-5} eV . The phonon spectrum analyses were carried out for $6 \times 6 \times 1$ supercell by using the finite displacement method which is implemented in the PHONOPY package [115]. To analyze the thermal stability of the considered structures, *ab initio* molecular dynamics (AIMD) calculations were performed for $6 \times 6 \times 1$ supercell considering micro-canonical ensemble simulation at elevated temperatures. Bader charge analysis was used to estimate the charge transfers between the atoms [116].

3.2 Results and Discussion

3.2.1 Structural Properties and Energetics

We start with the structural optimization of binary AlX (X : O, S, Se, Te) monolayers. The geometry of AlX belongs to the D_{3h} symmetry group and consists of four sublayers ($X\text{-Al-Al-X}$) which are held together with strong covalent bonds [92]. The Al planes are surrounded by two chalcogen layers exhibiting mirror symmetry in the vertical direction. The calculated structural parameters of the binary systems, which are in good agreement with the literature, are summarized in Table 3.1 [92, 89]. After obtaining the binary systems, one of the X layers is fully replaced with a different chalcogen atom (X') to design the Janus $\text{Al}_2\text{XX}'$ (X/X' : O, S, Se, Te) monolayer. The prototype structure is shown in Figure 3.1. Taking account the broken symmetry in z -direction, the lattice constants ($\mathbf{a}$ and $\mathbf{b}$) are relaxed separately, but found to be equal. This indicates that the hexagonal lattice is also preserved in ternary systems. The calculated structural parameters, which are lattice constants ($\mathbf{a}$), bond length between Al-Al ($d_{\text{Al-Al}}$), Al- X ($d_{\text{Al-X}}$), Al- X' ($d_{\text{Al-X}'}$), thickness (h), and the angle between Al and X/X' atoms (θ and θ') for both binary AlX and ternary $\text{Al}_2\text{XX}'$, are summarized in Table 3.1. It is found that for fixed X , the structural parameters of $\text{Al}_2\text{XX}'$ vary

regularly with the size of X' and the obtained results are the average of $\text{Al}X$ and $\text{Al}X'$. Accordingly, all parameters are analyzed with respect to the type of X' for a given subset of X throughout the study.

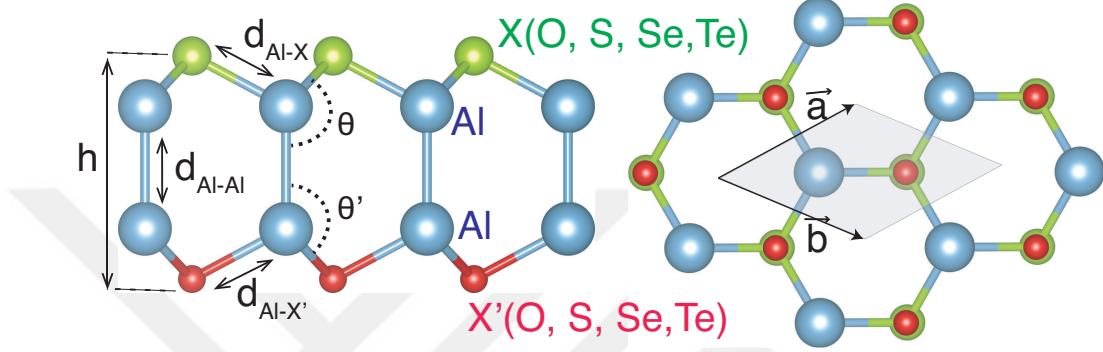


Figure 3.1: Top and side views of the prototype structure of the predicted ternary Al_2XX' monolayers. The relevant structural parameters are shown.

The distribution of $\mathbf{a}$ for all the considered binary and ternary systems is shown in Figure 3.2(a). Accordingly, it turns out that $\mathbf{a}$ increases down the group of X' for each subset of X . As an example, for $X = \text{S}$, $\mathbf{a}$ follows a sequence of $\text{Al}_2\text{SO} < \text{Al}_2\text{SS} < \text{Al}_2\text{SSe} < \text{Al}_2\text{STe}$ and a similar relation holds for the other choices of X following a similar trend for $\text{Al}X$. In coherence with $\mathbf{a}$, $d_{\text{Al}-X}$ and $d_{\text{Al}-X'}$ also elongate and h thickens with the size of X' . On the other hand $d_{\text{Al}-\text{Al}}$ slightly shortens with increasing $\mathbf{a}$ and this is related to decreasing charge transfer from Al atoms to X and/or X' .

The cohesive energy per atom (E_C) can be calculated by using the following relation:

$$E_C = \frac{N_{\text{Al}}E_{\text{Al}} + N_XE_X + N_{X'}E_{X'} - E_{\text{Al}_2XX'}}{N_{\text{Al}} + N_X + N_{X'}} \quad (3.1)$$

where $E_{\text{Al}_2XX'}$ is the total energy of the Al_2XX' monolayer; E_{Al} , E_X , $E_{X'}$ (N_{Al} , N_X , $N_{X'}$) are the single atom energies (total number) of Al, X , X' elements, respectively. As shown in Figure 3.2(b), there is an inverse proportion between E_C and $\mathbf{a}$, and cohesive energy decreases down the group of X' . The elongation of $\mathbf{a}$ together with $d_{\text{Al}-X}$ and $d_{\text{Al}-X'}$ indicates bond weakening and explains the descent in E_C . Additionally, as shown in Figure 3.2(c) the average charge donated by Al atoms ($\Delta\rho$) decreases with increasing $\mathbf{a}$ associated with

the electronegativity difference ($\Delta\chi$) between X/X' and Al (Table 3.1) and supports the variation of E_C . The isolation of AlO (and Al_2XO) from other binary (ternary) monolayers [92] is correlated with the very high χ of oxygen atom [117]. When compared with their binary counterparts, E_C of $\text{Al}_2\text{XX}'$ lies between those of AlX and AlX' .

Table 3.1: The lattice constant (a), bond lengths ($d_{\text{Al-Al}}$, $d_{\text{Al-X}}$, and $d_{\text{Al-X}'}$), thickness (h), bond angle between $X\text{-Al-X}$ and $X\text{-Al-X}'$ (θ and θ'), cohesive energy per atom (E_C), electronic band gap at the level of PBE and HSE (E_g^{PBE} and E_g^{HSE}), Poisson's ratio (ν), in-plane stiffness (Y_{2D}), electronegativity difference ($\Delta\chi$), and average charge transfer from Al to X/X' ($\Delta\rho$) for monolayers of AlX and $\text{Al}_2\text{XX}'$. * indicates that no feature is calculated for that case.

	a	$d_{\text{Al-Al}}$	$d_{\text{Al-X}}$	$d_{\text{Al-X}'}$	h	θ	θ'	E_C	E_G^{PBE}	E_G^{HSE}	ν	Y_{2D}	$\Delta\chi$	$\Delta\rho$
<i>Type</i>	(Å)	(Å)	(Å)	(Å)	(Å)	(deg)	(deg)	(eV)	(eV)	(eV)	-	(J/m ²)	-	(e ⁻)
AlO	2.87	2.61	1.80	1.80	4.01	105.9	105.9	5.67	1.06	1.61	0.36	155.0	1.83	1.69
Al_2SO	3.28	2.61	2.24	1.96	4.34	94.0	113.1	4.76	1.71	2.63	0.28	111.3	1.40	1.60
Al_2SeO	3.46	2.60	2.38	2.05	4.36	92.9	115.1	4.44	0.94	1.66	0.30	94.0	1.38	1.54
AlS	3.58	2.60	2.32	2.32	4.73	100.6	100.6	4.22	2.09	2.88	0.25	79.9	0.97	1.49
Al_2SSe	3.71	2.58	2.36	2.45	4.77	103.4	98.4	4.03	1.97	2.74	0.25	74.1	0.95	1.44
AlSe	3.78	2.58	2.47	2.47	4.91	99.6	99.6	3.87	2.00	2.73	0.24	68.3	0.94	1.39
Al_2TeO	3.79	2.58	2.61	2.21	5.78	93.0	117.5	3.84	0.58	1.07	*	*	1.16	1.42
Al_2STe	3.96	2.57	2.45	2.65	4.79	108.1	96.5	3.65	1.57	2.23	0.24	64.4	0.73	1.35
Al_2SeTe	4.06	2.57	2.56	2.68	4.90	104.9	98.4	3.53	1.58	2.35	0.23	60.3	0.72	1.29
AlTe	4.11	2.57	2.70	2.70	5.13	99.4	99.4	3.28	1.84	2.48	0.24	55.0	0.49	1.22

3.2.2 Dynamical Stability

After revealing the structural features, the dynamical stability of $\text{Al}_2\text{XX}'$ monolayers is examined firstly by calculation of the phonon dispersion spectra as shown in Figure 3.3. Except Al_2TeO , the phonon frequencies are found to be real for the considered structures indicating the stability at low temperature. The instability of Al_2TeO results from the strong asymmetry in the accumulated charge on O and Te due to the large electronegativity difference between these atoms. Similar

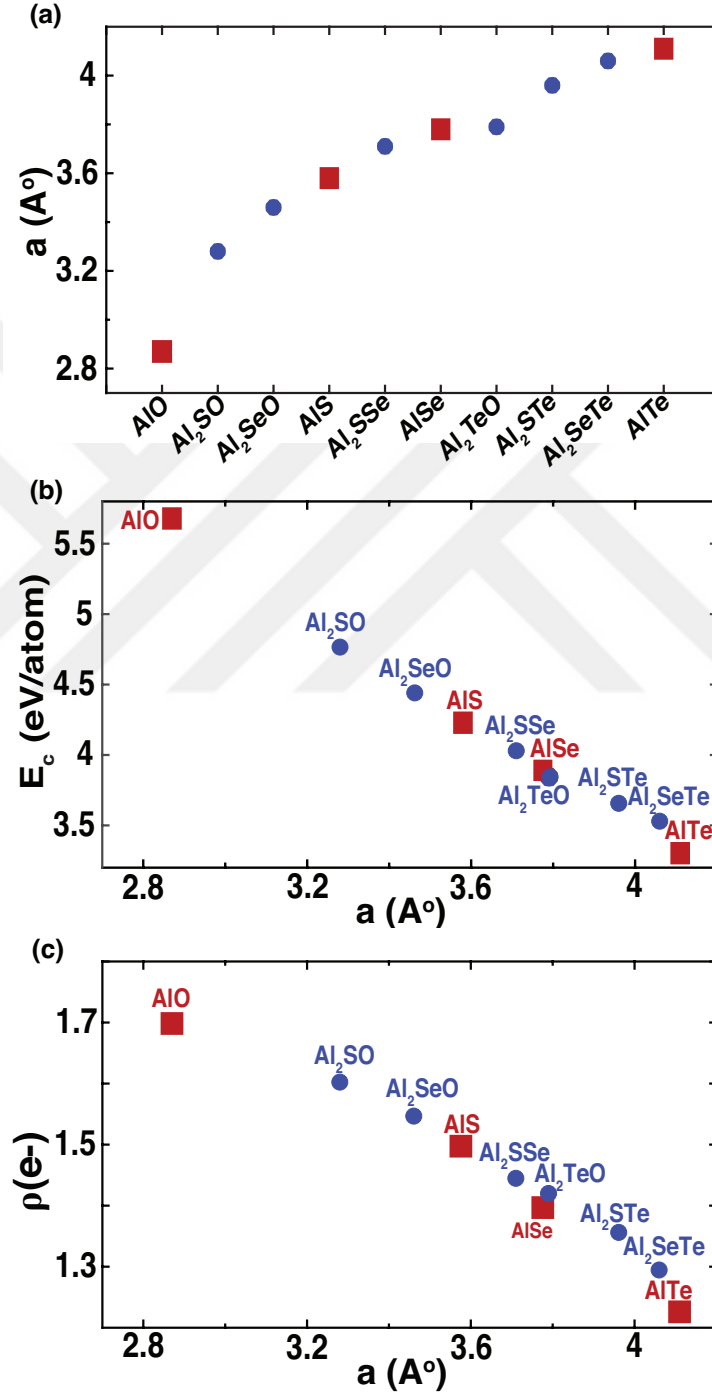


Figure 3.2: (a) The distribution of lattice constant (a) for all the considered $\text{Al}_2\text{XX}'$ and AlX monolayers, (b) the variation of cohesive energy (E_c) and (c) the average charge transfer (ρ) from Al to chalcogenide atoms with the lattice constant.

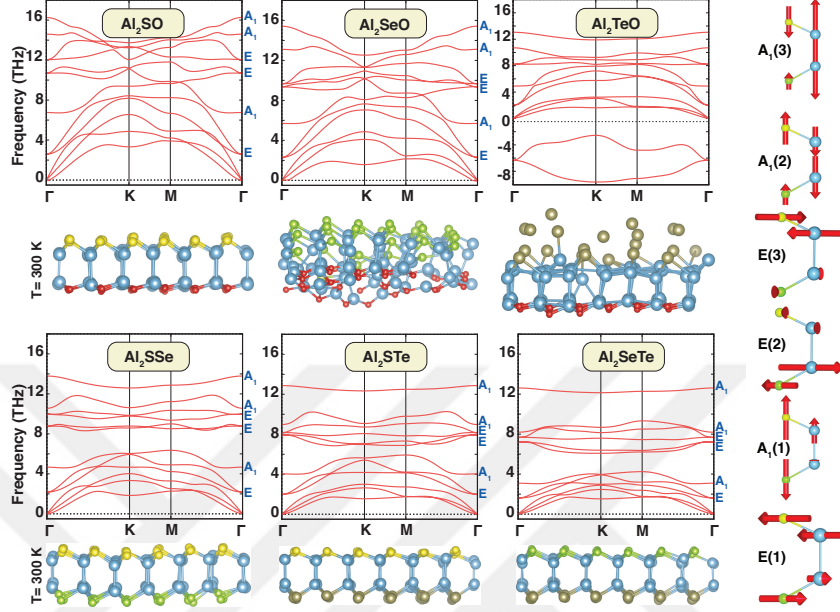


Figure 3.3: Phonon dispersion diagrams and AIMD simulation snapshots at $T=300$ K. The blue, yellow, green, brown, and red spheres represent Al, S, Se, Te, and O atoms, respectively. The representative eigenvectors calculated at Γ point are also shown. The red arrows on the atoms demonstrate the eigenmodes.

result was also reported for Ga_2TeO monolayer [101]. Phonon spectra not only provide information about stability of the structures but also they help to analyze the eigenmodes. The primitive cell of $\text{Al}_2\text{XX}'$ monolayer contains four atoms, resulting in twelve phonon branches, three of which are acoustic and the rest are optical. The symmetry of $\text{Al}_2\text{XX}'$ is described by $P3m1$ space group (C_{3v} point group). Accordingly, the optical phonon modes at the Γ point are expected to be either non-degenerate or doubly degenerate. The group theory analysis reveals that the corresponding irreducible representation for phonon modes in the spectrum is given by $\Gamma = 3E + 3A_1$, where all E phonon modes are attributed to the doubly degenerate in-plane vibrations whereas all non-degenerate A_1 phonon modes represent vibrations along the z -direction. E and A_1 modes are both infrared and Raman active as these modes correspond to the linear and quadratic functions in C_{3v} symmetry. Therefore, $\text{Al}_2\text{XX}'$ monolayers should exhibit six peaks at Raman- and six peaks at IR-spectrum. The atomic displacements of six distinct phonon modes are illustrated in Figure 3.3. As X and X' have different atomic masses, the vibrations of AlX and AlX' pairs are not symmetric. The

first optical mode with the lowest frequency is owned by E representation. In this mode, AlX pair moves in the opposite in plane direction of AlX' pair. The first E mode is followed by A_1 mode and in this mode, AlX and AlX' pairs vibrate in the opposite out of plane direction. In the higher segment of the phonon spectrum, there are two doubly degenerate E modes and their energies are very close to each-other. For the second E mode, the vibration of AlX' pair is significantly larger than the AlX while Al and X' atoms vibrate in the opposite in plane direction. The same trend can be found for the third E mode. However, in this mode, the vibration of AlX' is smaller than AlX pair and can be ignored. The character of the second A_1 mode reveals that each of the four atomic planes in the monolayer vibrates in the opposite out of plane direction. Finally, when the eigenvectors of the third non-degenerate A_1 mode are analyzed, it is found that Al atoms and X/X' atoms move in the opposite direction along z-axis while the vibrations of Al atoms dominate those of the chalcogenide atoms. Additionally, it is noticed that the phonon modes are softened when the average atomic mass increases as seen in Figure 3.3. Similar to the AlX monolayers, the highest frequency phonon band originated from the Al atoms. While the phonon modes of Al_2XO monolayers are interwoven, a gap is noticed between lower and higher frequency optical branches for Al_2SSe , Al_2STe , and Al_2SeTe . The bond strength and the mass differences between the constitute atoms in the $\text{Al}_2\text{XX}'$ monolayers are the origins of the phonon band gaps. Recently, it has been shown that phonon band gaps play an important role in determining and controlling thermal conductivity through material design [118, 119]. In this respect, low thermal conductivity is expected for Al_2XO systems due to strong acoustic and optical scattering [120, 121].

We further explore the high temperature stability by performing AIMD simulations. To alter the unit cell constraint, a $6 \times 6 \times 1$ super cell is constructed for all models and simulations are performed at $T=300$ K and 600 K within 2 ps total simulation time. The final snapshots of the resulting geometries are represented in Figure 3.3. For Al_2TeO , Te atoms detached from the system at 300 K and thus the ternary structure is destroyed confirming the phonon spectrum results. Although the Al_2SeO appears to be stable according to all real phonon

modes, the structure deforms at 300 K, indicating a plausible instability at elevated temperatures. For the case of Al_2SO , the last member of Al_2XO , the structure preserves its geometry up to 600 K, but small distortions are noticed. On the other hand, Al_2SSe , Al_2STe , and Al_2SeTe maintain their structures even at high temperatures. Accordingly, it can be concluded that oxygenation weakens the strength of the bonds and can induce instability in ternary monolayers. In addition, although the stability at ambient conditions can be assumed based on experimental studies on GaX systems [122, 123, 124], further investigation (i.e. stability against oxidation) [125] is required to reveal this issue for practical applications.

3.2.3 Mechanical Properties

After revealing the stability of the predicted structures, the elastic constants (C_{ij}) tensor is calculated to obtain the mechanical properties by following the stress theorem [126, 127]. C_{ij} 's are found to be positive for all $\text{Al}_2\text{XX}'$ monolayers other than Al_2TeO , fulfilling the Born stability criterion. The results for Al_2TeO are anticipated as its instability has already been demonstrated by phonon dispersion analysis and AIMD simulations. Accordingly, no mechanical feature is examined for Al_2TeO . Firstly, in plane stiffness Y_{2D} , which is the measure of the rigidity, is calculated. For a hexagonal lattice [128], it can be obtained with the following formula; $Y_{2D} = (C_{11}^2 - C_{12}^2)/C_{11}$. As shown in Figure 3.4(a), Y_{2D} decreases with the elongation of $\mathbf{a}$. This can be associated with the reduction of bond strength among the atoms since E_C also follows a similar trend. Additionally, for the designated X , Y_{2D} decreases down the group of X' . $\text{Al}_2\text{OX}'$ monolayers have higher Y_{2D} than the other Janus structures as the AlO sets the upper limit. Similar to structural features, Y_{2D} of $\text{Al}_2\text{XX}'$ is in between that of binary counterparts. It should be noted that Y_{2D} can be converted to bulk units by dividing it with effective thickness [128]. Next, the Poisson's ratio is calculated by utilizing the relation; $\nu = C_{12}/C_{11}$. Although to a lesser extent, ν also decreases with elongation of $\mathbf{a}$ as shown in Figure 3.4(b). As $\nu < 1/3$ for all cases, it can be concluded that $\text{Al}_2\text{XX}'$ monolayers are brittle according to the Frantsevich rule [129]. Similar

to Y_{2D} , ν of $\text{Al}_2\text{OX}'$ are larger than those of the other systems. In other words, as only AlO has a ductile character with $\nu=0.36$, the oxygenation makes AlX monolayers less stiff.

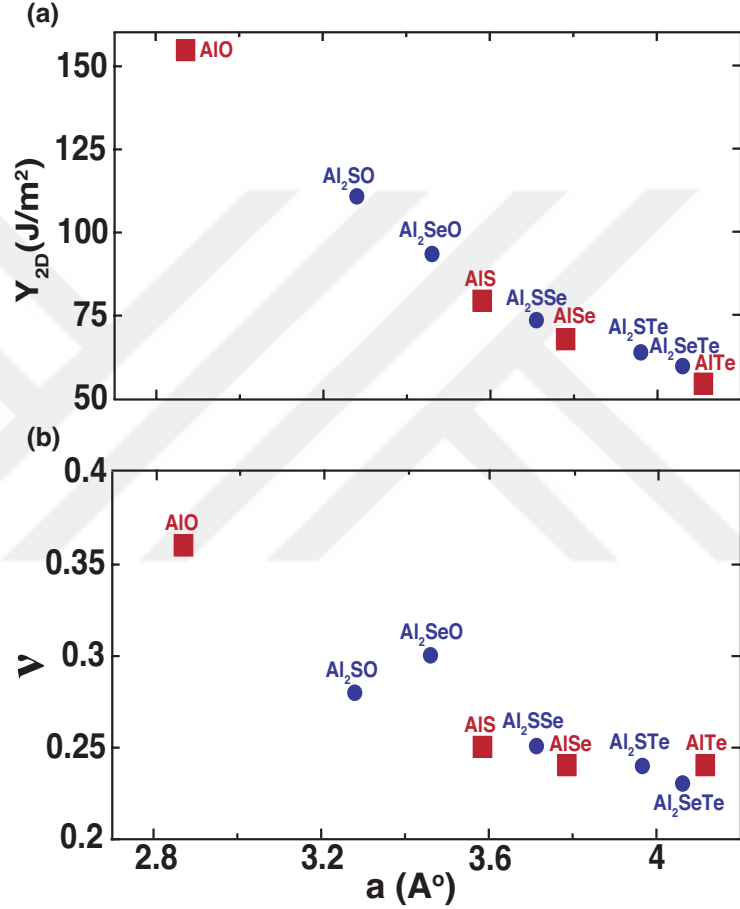


Figure 3.4: (a) The variation of in plane stiffness (Y_{2D}) and (b) Poisson's ratio (ν) with the lattice constant of $\text{Al}_2\text{XX}'$ and AlX monolayers.

3.2.4 Electronic Properties

Finally, the electronic properties of AlX and $\text{Al}_2\text{XX}'$ monolayers are investigated. It should be noted that the precursor AlX monolayers are indirect band gap semiconductors [92]. AlO has a different electronic band profile among other binary structures and has the narrowest band gap. While the highest valence band (HVB) is localized and mainly composed of Al- p_z and X- p_z orbitals for AlS,

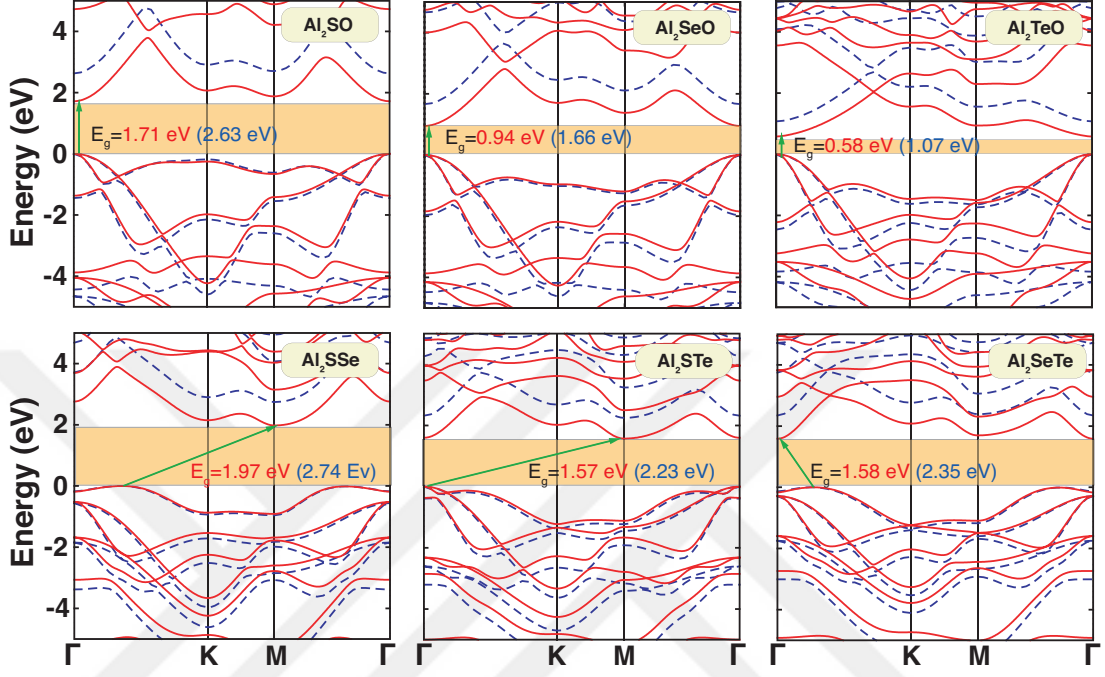


Figure 3.5: The electronic band structures calculated at the level of GGA-PBE (red solid lines) and HSE06 (dashed blue lines) for $\text{Al}_2\text{XX}'$ monolayers. The band gap values, E_g^{PBE} (E_g^{HSE}) are shown with blue (red). The Fermi level is set to zero.

AlSe , and AlTe , HVB is very dispersive for AlO and in addition to $\text{Al-}p_z$ and $\text{O-}p_z$ orbitals, significant contribution from O-s orbital is noticed. This feature can be clarified by band-decomposed charge analysis [92]. While the electronic states of AlO at the K point are accumulated between Al atoms and have a σ -character, the states at the Γ -point concentrated around O atoms and have a π -character. Accordingly, the states at Γ -point have lower energy with respect to K -point due to $\Delta\chi$ between Al and O atoms. On the other hand, the lowest conduction band (LCB) is dispersive with two valleys at K - and M -points (Mexican-hat dispersion) [94] and has a similar character for all AlX systems. This type of band dispersion induces Fermi-ring of states, which can give rise to unique features including itinerant magnetism and superconductivity [130]. Revealing the electronic properties of binary systems, the electronic band structures $\text{Al}_2\text{XX}'$ monolayers are calculated and shown in Figure 3.5. While all the precursor AlX monolayers are indirect band gap semiconductors, indirect to direct band gap transition is

noticed for Al_2XO . The same trend was also reported for Ga_2XO [101]. This transition is induced firstly due to the dramatic modification of HVB with inclusion of oxygen (see above). Secondly, the first and second LCB has multiple valleys at high symmetry points and when the intrinsic strain (two surfaces are under different types of induced biaxial strains, i.e., the O side undergoes tensile strain whereas the X side is compressed) is large enough, it not only shifts the bands but also alters the order of band extremums. Accordingly, for Al_2XO monolayers, because of these two affects, valence band maximum and conduction band minimum are shifted to Γ -point and system turns into a direct band gap semiconductor. The indirect-direct (or vice versa) transition is also reported for other Janus system [36, 131]. For the remaining $\text{Al}_2\text{XX}'$ monolayers, systems remain to be indirect band gap semiconductors (for Al_2STe , the difference between the indirect and direct band gap is reduced to ~ 25 meV, and it can also be considered as a direct band gap material at the ambient conditions). The electronic band structure features resemble their binary constituents and Mexican-hat dispersion is preserved.

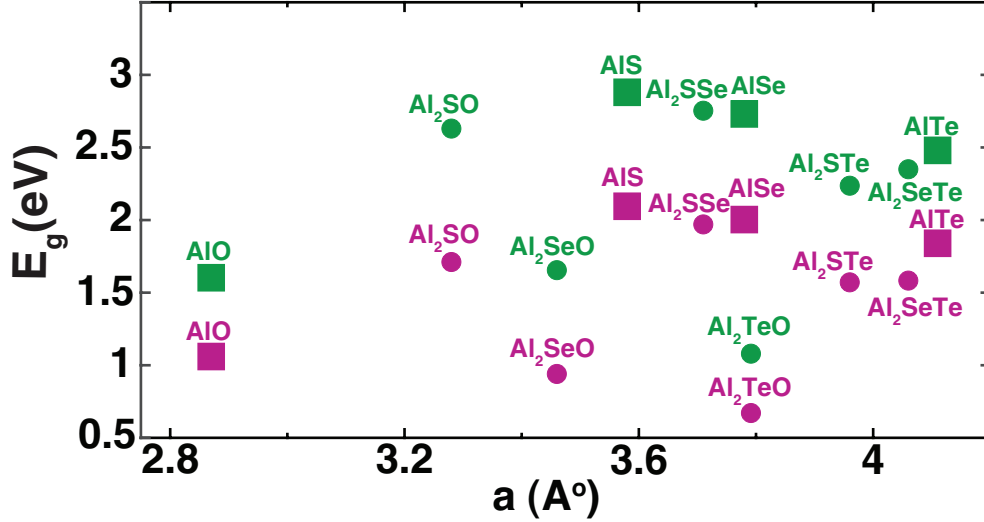


Figure 3.6: The variation of E_g^{PBE} (in purple) and E_g^{HSE} (in green) with lattice constant values.

The variation of E_g^{PBE} and E_g^{HSE} with a is shown in Figure 3.6. Different from other features, an apparent trend with respect to a is not noticed. As discussed above, the band profile is significantly influenced by inclusion of O

atoms for Al_2XO , and also by the intrinsic strain on both sides due to the broken symmetry, thus the alternation of E_g cannot be classified simply with the type of X atom. Moreover, while the calculated features for Janus monolayers are the average of their binary constituents, E_g does not fit in this trend, E_g of $\text{Al}_2\text{XX}'$ can be even narrower than AlX and AlX' . As the effect of intrinsic strain on the electronic structure is found to be substantial, we also examine the variation of E_g^{PBE} with compressive/tensile biaxial strain for both AlX and $\text{Al}_2\text{XX}'$ monolayers, and the results are shown in Figure 3.7. The non-monotonic variation of E_g^{PBE} under strain can be revealed by examining the change of bands in the vicinity of Fermi level (E_F). For AlS , AlSe , and AlTe , while HVB is not significantly affected by tensile strain, the energy of LCB is lowered, resulting in a band gap narrowing. It should also be mentioned that conduction band edge at Γ -point is lowered with tensile strain and the energy difference between M -point is closed gradually. On the other hand, E_g^{PBE} increases up to -2% as it is expected but then starts to decrease beyond this level. The compressive strain not only shifts LCB but also alters the energy levels of valleys (band extremums) at high symmetry points. Conduction band minimum is switched from K to M -point and band gap narrows once again. While the effect of strain is more dramatic for AlTe , it is less significant for AlS , and this can be associated with the bond strength. AlO behaves differently than the other monolayers; E_g widens with tensile strain whereas a narrowing is anticipated. This is correlated with the dispersive HVB which is the distinctive feature of AlO . While the effect of tensile strain on LCB is similar to other binary monolayers, the dispersion of HVB is altered significantly and becomes less dispersive. The combined effect gives rise to an increase in E_g . Accordingly, the complex effect of strain on electronic structure of $\text{Al}_2\text{XX}'$ can be explained by comparison with binary AlX monolayers. Whereas the variation of E_g for Al_2SeO and Al_2TeO resembles AlO , that of Al_2SO is a combination of AlS and AlO . The oxygenation of AlS makes it more sensitive to strain, and E_g of Al_2SO narrows dramatically with increasing tensile strain. The irregular pattern above -3% for Al_2TeO (-5% for AlSeO) can be linked with the structural instability. As discussed above, the intrinsic strain is stated as one of factors that leads to indirect to direct band gap transition in Al_2XO . In a similar manner, direct to indirect transition is noticed in Al_2XO monolayers with applied strain.

E_g of Al_2SSe , Al_2STe , and Al_2SeTe follow a similar trend to that of AlSe (or AlTe). These results indicate that the electronic structure of $\text{Al}_2\text{XX}'$ is sensitive to elongation/contraction of $\mathbf{a}$ and their E_g can be easily modified by applied strain.

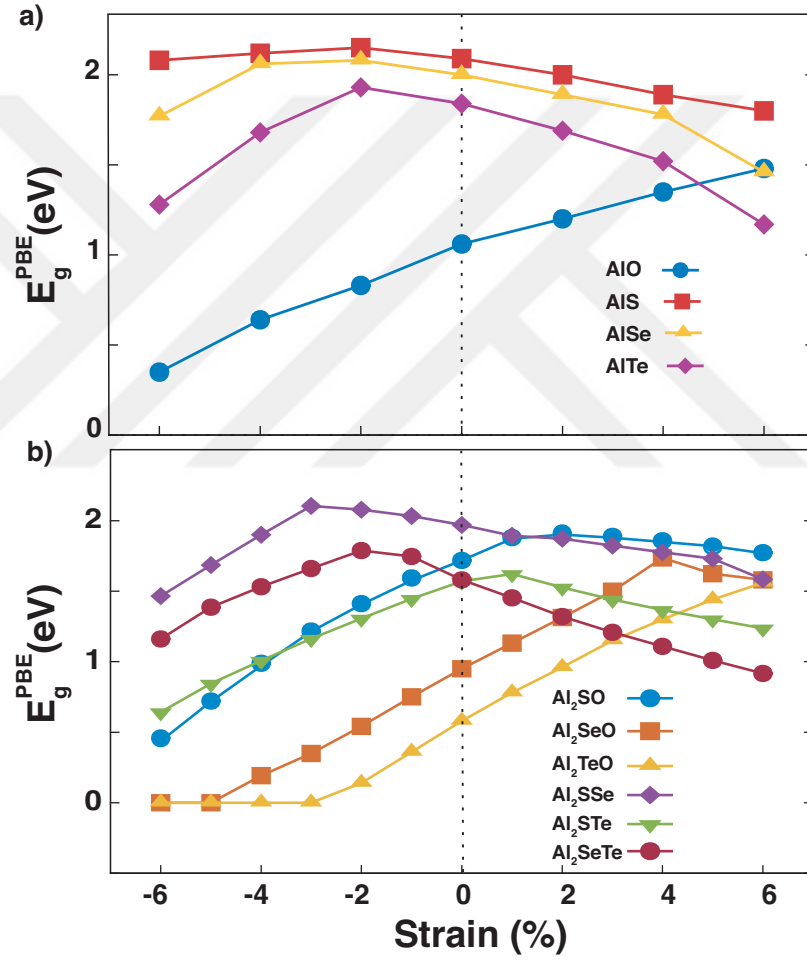


Figure 3.7: The variation of E_g^{PBE} of (a) AlX and (b) $\text{Al}_2\text{XX}'$ monolayers under compressive (-) and tensile (+) biaxial strain.

3.3 Conclusion

In conclusion, we design and analyze the monolayers of $\text{Al}_2\text{XX}'$ (X/X' : O, S, Se, Te). Our stability analyses, performed by phonon dispersion calculations and AIMD simulations, indicate that while Al_2TeO is dynamically unstable, and Al_2SeO is prone to instability at elevated temperatures, the other predicted Janus systems are stable at ambient conditions. The calculated cohesive energies of $\text{Al}_2\text{XX}'$ are in between their binary constituents and they decrease with elongation of the lattice constant due to weakening of the bonds and reduced charge transfer between Al and X/X' atoms. The Young's modulus of $\text{Al}_2\text{XX}'$ decreases down the group of X' for a given X subset following the same trend with cohesive energy. All calculated Poisson's ratios are less than 1/3 indicating a brittle character, but oxygenation makes $\text{Al}_2\text{XX}'$ monolayers less stiff. Similar to their binary counterparts, ternary monolayers are also semiconductors but indirect to direct band gap transition is noticed for Al_2XO and Al_2STe as a result of anisotropic strain on both sides of the Janus structures. However the variation of band gap does not follow a regular pattern, it is found to be very sensitive to strain and thus can be easily tuned by the applied compressive/tensile strain.

Chapter 4

Janus Two-dimensional WXO (X : S, Se, Te) Monolayers

Within the 2D dynasty, transition metal dichalcogenides (TMDs) and transition metal oxides (TMOs) (with the general chemical formula MX_2 where M refers to a transition metal atom and X is a chalcogen atom) [37, 38, 39, 40, 41] have obtained considerable attention due to their stability and remarkable electronic properties ranging from semiconducting, metallic to superconducting[132, 133, 134]. One of the prominent members of this family is WX_2 , and it possesses three possible structural phases, in which W atoms are sandwiched between two layers of X atoms. Depending on the coordination arrangement of W and X atoms, monolayer WX_2 can be formed either in the honeycomb[42] ($1H$ - WX_2 , trigonal prismatic structure), the centered honeycomb[40] ($1T$ - WX_2 , octahedral) or distorted[43] ($1T'$ - WX_2 , distorted octahedral) structures. $1H$ - WX_2 is the most stable configuration under ambient conditions and can be obtained by mechanical exfoliation from its bulk counterpart or can be synthesized via chemical vapor deposition (CVD)[135, 136, 137]. The metallic $1T$ - WX_2 has been shown to be unstable [138, 139], and transforms to $1T'$ - WX_2 due to the Peierls distortion, which also results in the formation of charge density waves (CDW)[140, 141]. 2D WS_2 crystals exhibit superior optical properties[142, 143] and larger spin-orbit coupling[144] than 2D MoS_2 , which makes them interesting

for optoelectronic and spintronic applications. Similar to WS_2 , WSe_2 monolayer in the $1H$ phase is a semiconductor with a direct band gap of ~ 1.6 eV and carrier mobility around $250 \text{ cm}^2/\text{V.s}$ [145]. In addition, the monolayer of WSe_2 has been reported to be the first TMD presenting a p-type conductive behavior with a large work function (with palladium contacts)[145, 146]. Recently, it has been shown that $1T'$ - WTe_2 monolayer is a type-II Weyl semimetal with a large non-saturating magnetoresistance[147, 148]. In addition to binary systems, several 2D Janus TMDs have been fabricated recently, following the realization of MoSSe monolayers[18, 19], and subsequently WSSe [44, 45], and synthesis of 2D single-layer crystals of Janus SPtSe on $\text{Pt}(111)$ [149]. In Janus TMDs, chalcogen atoms in one of the layers are fully replaced with another chalcogen atom (e.g., S with Se) which results in structural symmetry breaking along the vertical direction. This broken out-of-plane symmetry and the additional degree of freedom lead to distinct features, including the enhancement of the piezoelectric constants, especially in the out-of-plane direction[21]. Together with experimental progress, various 2D Janus systems have been predicted and characterized by *ab initio* methods[22, 21, 23, 150, 101, 151, 152]. For instance, the electronic, mechanical, and piezoelectric properties of Janus MoSTe monolayer in $1H$ and $1T'$ phases have been investigated, and it was found that the out of plane piezoelectric coefficient is non-zero[131]. In another study, it was reported that WSTe monolayer has large Rashba spin splitting parameters which are tunable by in-plane strain[46]. The energy difference between the $1H$ and $1T'$ phases of Janus WSeTe monolayer are small allowing for an electrostatically driven reversible phases transition between the stable phases plausible[47]. Like the Janus systems based on TMDs, the monolayer of MoSO was also found to be dynamically stable and possess a strong out-of-plane piezoelectricity which originates from the large charge difference between the S and O surfaces[131]. Additionally, a new member of TMOs[153], tungsten oxysulfide[154] (WO_yS_x) has been discovered and shown to be a highly efficient catalyst in hydrogen evolution reactions (HER). Despite the variety of studies on Janus WXX' systems, the realization of Janus WXO monolayers based on oxygenation of WX_2 have not been investigated. In this chapter, motivated by the already synthesized 2D ternary TMDs and TMOs, as well as the novel properties of binary WX_2 systems, we design and study the

structural, vibrational, thermal, mechanical, piezoelectric, and electronic properties of $1H$, $1T$, and $1T'$ phases of WXO ($X = S, Se, \text{ and } Te$) Janus monolayers by first-principle methods.

4.1 Methodology

First-principles calculations were carried out in the framework of density functional theory (DFT) [104, 105] as implemented in the Vienna *Ab initio* Simulation Package (VASP)[106, 107, 108, 109]. The projector augmented wave (PAW)[155] method was used to portray the potentials of W, O, S, Se, and Te elements. The exchange-correlation potential was treated by the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) form[80]. A plane-wave basis set with the kinetic energy cut off $\hbar^2 |\mathbf{k}+\mathbf{G}|^2/2m = 520$ eV was used for all calculations. The convergence value for electronic relaxation between the sequential steps in the total energy calculations is taken to be 10^{-5} eV. For the optimization of the ionic positions and lattice constants, the conjugate gradient method was employed until the Hellmann-Feynman forces on each atom were less than 0.01 eV/Å. To prevent any artificial interaction between neighboring images, a vacuum spacing of ~ 20 Å was set in non-periodic direction. The spin-orbit coupling (SOC) was taken into account during the calculation of electronic band structures. In order to obtain more accurate electronic band gaps, the hybrid functional of Heyd-Scuseria Ernzerhof (HSE06) with SOC was adopted and compared with GGA-PBE results[112, 113]. The screening length of HSE06 and the mixing rate of the Hartree-Fock exchange potential were taken as $\lambda = 0.2$ Å $^{-1}$ and 0.25, respectively. The Brillouin zones (BZ) of $1H$ -, $1T$ -, and $1T'$ - WXO were sampled by using Γ -centered $24 \times 24 \times 1$, $24 \times 24 \times 1$, and $24 \times 16 \times 1$ uniform k -point meshes, respectively[114]. The phonon spectrum analyses were performed by $5 \times 5 \times 1$ supercells for $1H$, $1T$ and $6 \times 4 \times 1$ supercells for $1T'$ structures using the small-displacement method as implemented in PHONOPY[115].

The first-order off-resonant Raman spectrum of each phonon mode was obtained by calculating the macroscopic dielectric tensor using the small difference

method at the Γ -point[20]. To obtain the piezoelectric stress coefficients, the density functional perturbation theory (DFPT) method with a sufficiently large k -point grid and cutoff energy of 700 eV was used. To examine the dynamical stability of the optimized structures, *ab initio* molecular dynamics (AIMD) calculations were performed by implementing micro-canonical ensemble simulation at constant temperatures (300K and 600K) with a total simulation time of 3 ps. In order to understand the bond characteristics of the structures, charge transfer calculations between the atoms are conducted by employing the Bader method[116].

4.2 Results and Discussion

4.2.1 Atomic Structure and Energetics

Prior to the design of Janus WXO ($X = \text{S, Se, Te}$) systems, we start with investigating the structural properties of the three common phases of binary WX_2 monolayers. The geometry of $1H$, $1T$, and $1T'$ belong to the D_{3h} , D_{3d} , and C_{2h}^2 space groups, respectively. The calculated structural properties are summarized in Table 4.1, which are in good agreement with previous studies[156, 157].

Once the binary WX_2 systems are obtained, Janus WXO monolayers are constructed by substituting X atoms of the top layer by O atoms. Top and side views of $1H$ -, $1T$ -, and $1T'$ -WXO are illustrated in Figs. 4.1(a)-(b). Notice that the lattice constants ($\mathbf{a}$ and $\mathbf{b}$) of $1H$ - and $1T$ -WXO monolayers increase down the chalcogen group. The bond length between W and X atoms (d_{W-X}) and the thickness of the crystals (h) follows a similar trend as d_{W-X} elongates and h thickens with an increasing atomic radius of X atoms. Not surprisingly, the bond length between W and O atoms (d_{W-O}) remains almost the same for all the systems. Our results also indicate that the lattice parameter of WXO is between those of WX_2 and WO_2 monolayers. Therefore, up and down sides of these

Table 4.1: The lattice constants ($\mathbf{a}$) and ($\mathbf{b}$); atomic bond lengths in the crystals (d_{W-X}); thickness (h); bond angle between X -W- X atoms (θ); average charge depletion from W to X ($\Delta_{\rho(W-X)}$); cohesive energy per atom (E_C); electronic band gaps at the level of GGA-PBE, E_g^{GGA} ; PBE + SOC, $E_g^{PBE-SOC}$, HSE06 + SOC, $E_g^{HSE-SOC}$ and locations of VBM and CBM edges over the BZ.

Crystal	a	b	d_{W-X}	$h(h_1/h_2)$	$\Delta_{\rho(W-X)}$	E_C	E_g^{PBE}	$E_g^{PBE-SOC}$	$E_g^{HSE-SOC}$	VBM/CBM
Phase	(Å)	(Å)	(Å)	(Å)	(e $^-$)	(eV/atom)	(eV)	(eV)	(eV)	-
1H-WO ₂	2.84	2.84	2.05	2.48	0.92	6.98	1.33	1.31	1.90	Γ /K
1H-WS ₂	3.19	3.19	2.42	3.14	0.63	5.76	1.79	1.54	1.97	K/K
1H-WSe ₂	3.32	3.32	2.55	3.35	0.48	5.15	1.53	1.24	1.62	K/K
1H-WTe ₂	3.55	3.55	2.74	3.62	0.29	4.51	1.06	0.74	1.04	K/K
1T-WO ₂	2.91	2.91	2.06	2.40	1.01	6.80	M	M	M	—
1T-WS ₂	3.20	3.20	2.43	3.15	0.67	5.28	M	M	M	—
1T-WSe ₂	3.30	3.30	2.56	3.43	0.50	4.64	M	M	M	—
1T-WTe ₂	3.52	3.52	2.75	3.71	0.30	4.02	M	M	M	—
1T'-WO ₂	2.95	5.04	2.03/2.04	1.93/2.67	0.96	6.79	SM	SM	SM	Γ - X/S -Y
			2.11/2.12							
1T'-WS ₂	3.20	5.71	2.40/2.43	2.65/3.49	0.62	5.58	SM	0.08	0.17	Γ - X/ Γ - S
			2.47/2.51							Γ / Γ - S
1T'-WSe ₂	3.31	5.94	2.53/2.56	2.80/3.78	0.47	5.06	SM	0.05	0.18	Γ - X/ Γ - X
			2.62/2.65							
1T'-WTe ₂	3.49	6.31	2.71/2.73	2.95/4.18	0.27	4.53	SM	SM	0.07	Γ / Γ - X
			2.83/2.85							

structures undergo different types of induced biaxial strain (i.e., the O-side experiences tensile strain whereas X -side is under compressive strain). Similar to binary counterparts, 1T-WXO transforms into 1T' phase due to Peierls distortion. This distorted phase has been found to be energetically more favorable than the 1T phase in various systems including RuSe₂[158], ReS₂[159], MoX₂[160, 138, 161], and WX₂[147, 138, 161] monolayers. To model 1T'-WXO monolayers, firstly 1×2 supercell is constructed, and then the same design principles are applied. As summarized in Table 7.1, similar to other phases, $\mathbf{a}$, $\mathbf{b}$, d_{W-X} , h of the 1T'-WXO structures increase down the chalcogen group. It should be noted that due to the broken symmetry, the bond lengths are not uniform, and additionally, two thicknesses (h_1 and h_2) are labeled (Fig. 4.1(b)).

In order to analyze the strength of the binding between the atoms, the cohesive

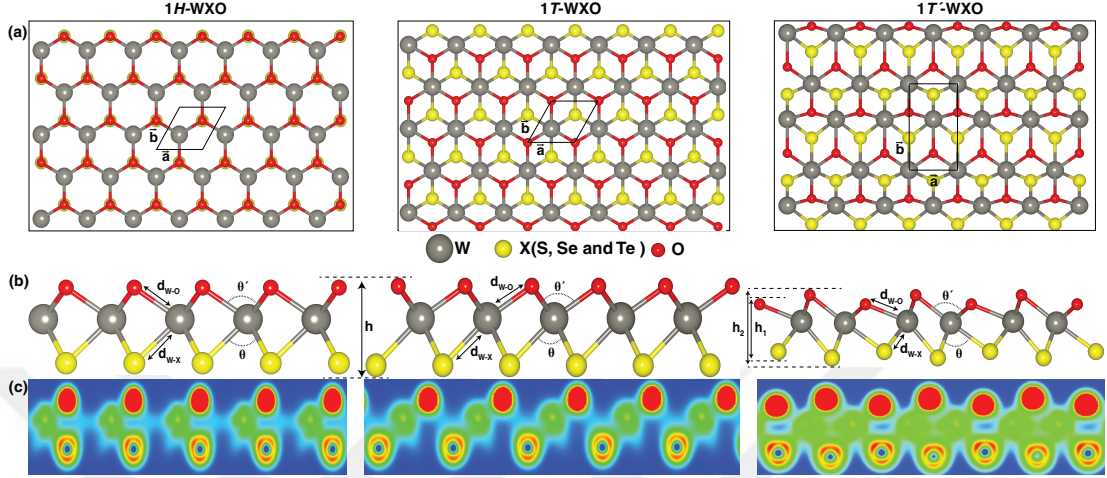


Figure 4.1: (a) Top, (b) side views of the structures, and (c) total charge distribution profile of 1H-, 1T-, and 1T'-WXO monolayers. A color scheme with linear scaling from blue(lowest) to red(highest) is used for charge profile. The relevant structural parameters are labeled. In (a) the unit cell is shown by the black polygon.

energy per atom (E_C) of the WXO structures is calculated with the following formula:

$$E_C = \frac{[N_W E_T(W) + N_X E_T(X) + N_O E_T(O)] - [E_T(WXO)]}{[N_W + N_X + N_O]} \quad (4.1)$$

where $E_T(W)$, $E_T(X)$, and $E_T(O)$ are the single atom energies of W, X and O elements, respectively; $E_T(WXO)$ corresponds to the total energy of the WXO monolayer; N_W , N_X , and N_O are the total number of W, X and O elements in the unit cell. All calculated E_C 's, which are summarized in Table 7.1, are positive and relatively large, indicating strong binding between the constituent atoms. The covalent character of the bonds is also shown in Fig. 4.1(c). Similar to the binary counterparts, E_C decreases down the chalcogen group in parallel with the variation of $\mathbf{a}$ (or $\mathbf{b}$) and d_{W-X} . The highest E_C 's are obtained for the 1H phase, except WTeO, where 1H and 1T' phases have almost the same energy. As expected, E_C 's of 1T' phase are larger than those of the 1T phase due to the energy lowering as a consequence of the Peierls distortion. According to the Bader charge analysis, while the charge depletion from W to O atoms ($\Delta\rho_{(W-O)}$) remains almost constant in all the structures, the average charge transfer between X and W atoms ($\Delta\rho_{(W-X)}$) decreases down the chalcogen group associated with

Table 4.2: For monolayers of $1H$ -, $1T$ - and $1T'$ -W X O, we present the optimized lattice constants, $\mathbf{a}$ and $\mathbf{b}$; atomic bond lengths, d_{W-X} and d_{W-O} ; thickness, h ; bond angle between X -W- X , θ and O-W-O, θ' ; average charge transfer from W to X , $\Delta\rho_{(W-X)}$ and W to O, $\Delta\rho_{(W-O)}$; and the cohesive energy per atom, E_C .

Crystal	$\mathbf{a}$	$\mathbf{b}$	d_{W-X}	d_{W-O}	h	θ	θ'	$\Delta\rho_{(W-X)}$	$\Delta\rho_{(W-O)}$	E_C
Phase	(Å)	(Å)	(Å)	(Å)	(Å)	(deg)	(deg)	(e $^-$)	(e $^-$)	(eV/atom)
$1H$ -WSO	3.01	3.01	2.38	2.09	2.80	78.2	91.8	0.59	0.97	6.27
$1H$ -WSeO	3.07	3.07	2.50	2.10	2.91	75.5	93.6	0.42	0.98	5.87
$1H$ -WTeO	3.19	3.19	2.69	2.13	3.04	72.5	96.8	0.22	1.01	5.36
$1T$ -WSO	3.05	3.05	2.41	2.08	2.75	78.6	94.0	0.65	1.01	5.97
$1T$ -WSeO	3.09	3.09	2.54	2.09	2.90	74.8	95.4	0.47	1.01	5.63
$1T$ -WTeO	3.21	3.21	2.74	2.10	3.02	71.4	99.3	0.27	1.03	5.22
$1T'$ -WSO	3.06	5.42	2.36/2.38	2.03/2.06	2.30/3.05	69.2/79.4	77.9/88.2	0.61	0.99	6.08
			2.43/2.45	2.24/2.29		82.1/93.0	98.1/108.4			
$1T'$ -WSeO	3.09	5.69	2.49/2.53	2.02/2.03	2.38/3.23	65.0/77.7	77.1/88.3	0.43	0.98	5.73
			2.57/2.58	2.29/2.63		81.5/94.8	97.7/108.5			
$1T'$ -WTeO	3.17	6.43	2.69/2.76	1.97/2.06	2.39/3.41	60.1/78.3	80.4/92.4	0.26	0.98	5.38
			2.78/2.85	2.16/3.57		86.5/105.5	93.5/104.3			

the decreasing electronegativity difference between W and X atoms ($\Delta\chi$). As $\Delta\rho_{(W-X)}$ strongly depends on $\Delta\chi$, the variation over the different structural phases is not significant. The change of E_C with X atom is in line with the variation of $\Delta\rho_{(W-X)}$. Additionally, E_C of W X O Janus crystals are in between those of the WX_2 and WO_2 binary constituents. In other words, oxygenation of WX_2 increases the cohesive energy of the system.

4.2.2 Dynamical Stability

To examine the dynamical stability of the proposed structures, vibrational frequency analysis is performed, and corresponding phonon band diagrams are represented in Fig. 4.2. All phonon spectra of $1H$ -W X O are found to be free

from any imaginary frequencies over the whole Brillouin Zone (BZ), indicating structural stability. It is seen that the phonon band gap between acoustical and optical modes becomes narrower, and the frequencies of phonon modes (including the maximum phonon frequency, ω_{max}) gradually decrease from $1H$ -WSO to $1H$ -WTeO, as a result of increasing the weight the X atom. A careful analysis of the force constant matrices reveals that this reduction is not only due to the increased mass of the X atoms, but also to the weakening of inter-atomic bonding between the atoms. However, the phonon spectra of $1T$ -WXO monolayers have imaginary frequencies labeled with solid red lines in Fig. 4.2. These soft acoustic modes indicate that metallic $1T$ -WXO monolayers are prone to instability and transform to $1T'$ phase due to Peierls distortion. These imaginary frequencies in the phonon spectrum are removed in the $1T'$ phase. (Notice that $1T'$ -WSeO and $1T'$ -WTeO possess small imaginary frequencies around the Y high symmetry point which can be correlated with charge density waves[162]). They disappear if we allow for charge density waves. Based on 1×2 reconstruction, phonon spectra of the Janus $1T'$ -WXO crystals have eighteen discrete phonon modes composed of three acoustical and fifteen optical branches. All these modes are non-degenerate because of the broken structural symmetry.

To further investigate the structural stability of the WXO monolayers at high temperatures, AIMD simulations are performed. To remove the size constraint, the same super cell sizes that were considered in the phonon spectrum analysis are used. The AIMD simulations are carried out at 300K and 600K for a total simulation time of 3 ps. Apart from small fluctuations of the atoms around their equilibrium positions, the crystalline morphology of $1H$ and $1T'$ phases are preserved, confirming the dynamical stability of these systems at and above ambient temperature. The final snapshots of the resulting atomic structures taken at 300 K and 600 K are shown in Figs 4.3 and 4.4, respectively. It should be noted that even Janus WXO monolayers are structurally stable, their free-standing form can be curled due to the stress on the outer layers[163, 164].

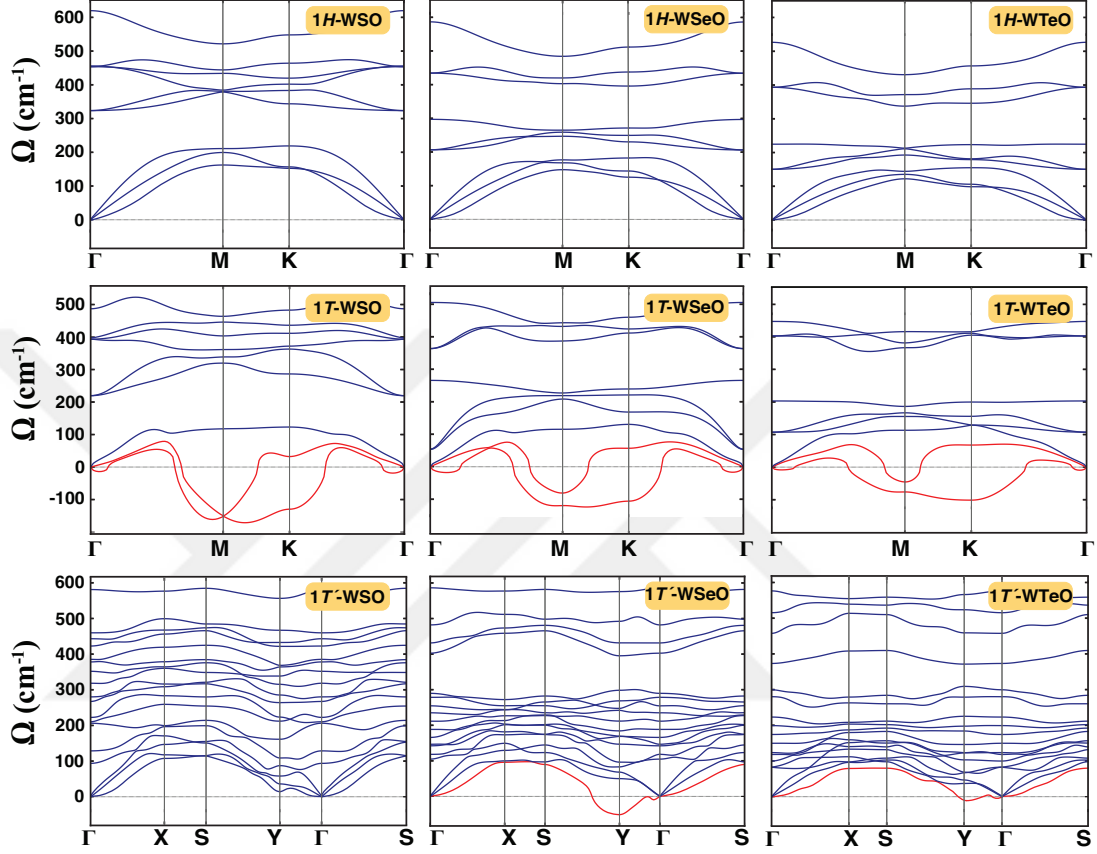


Figure 4.2: Phonon spectra of Janus $1H$ -, $1T$ -, and $1T'$ -WXO monolayers. Imaginary frequencies are indicated by red color.

4.2.3 Vibrational Properties

Raman spectroscopy analysis and the vibrational characteristics of phonon modes at the Γ -point are useful techniques to investigate the lattice symmetries and crystallographic phase-dependent properties of a material. $1H$ -WX₂ monolayers belong to the D_{3h} space group and consist of three atomic sublayers (X -W- X), which are held together via covalent bonding. By replacing one of the chalcogenide layers with O atoms, the out-of-plane symmetry is broken, and additional Raman active modes appear. $1H$ -WXO monolayers have C_{3v} symmetry, and the corresponding irreducible representation for phonon modes in their spectrum is given by $\Gamma = 2A_1 + 2E$, in which the A_1 and E modes are both IR and Raman active. All nondegenerate A_1 eigenmodes are attributed to the vibration

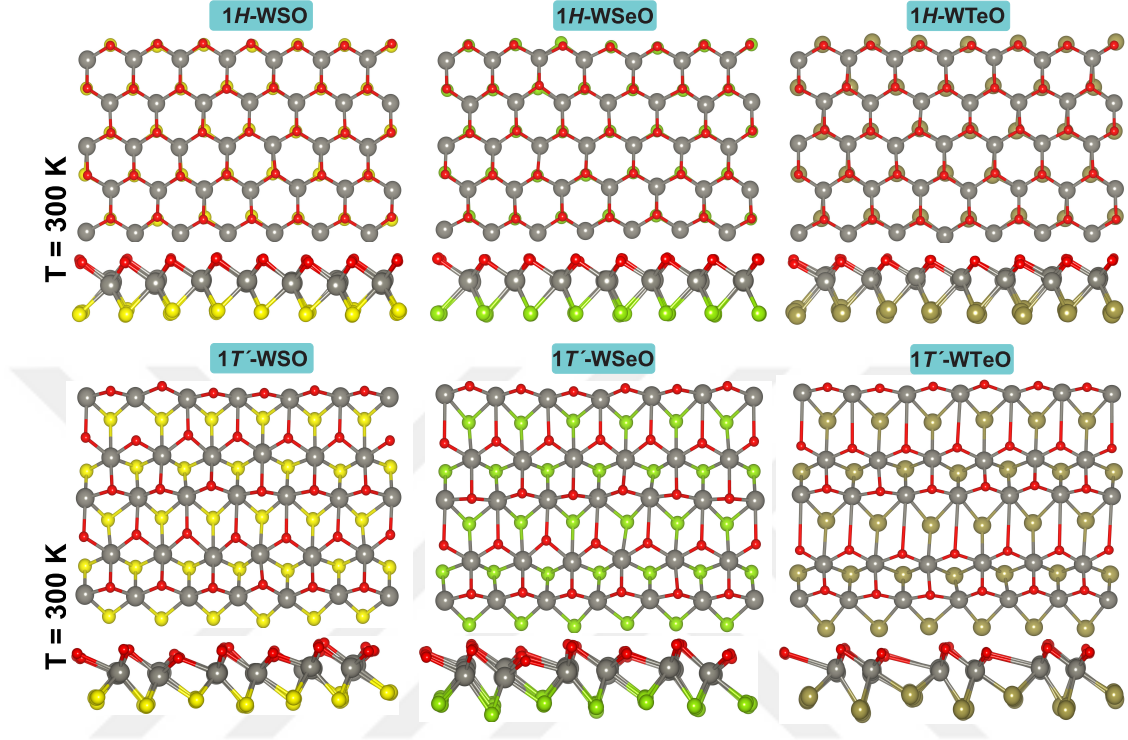


Figure 4.3: The Snapshots of *ab initio* molecular dynamics(AIMD) simulations of 1*H*- and 1*T'*-WXO Janus monolayers at 300 K.

along the *z*-direction, whereas *E* phonon modes represent the doubly degenerate in-plane vibrations. Therefore, in total, there are four Raman active modes in the 1*H*-WXO monolayers. As can be seen from Fig. 4.5(a), in 1*H*-WXO, the Raman activity of $A_1^{(W-X)}$ is very robust, which originates from the relatively higher contribution of the out-of-plane macroscopic dielectric constants to the Raman tensors. For the sake of comparison, the calculated Raman spectra of 1*H*-WX₂ monolayers are also depicted. The frequencies of the $A_1^{(W-X)}$ mode in the 1*H* phases are 456 cm^{-1} , 297 cm^{-1} , and 224 cm^{-1} for WSO, WSeO, and WTeO monolayers, respectively. As shown in Fig. 4.5(b), there are four distinct eigenmodes present in the optical spectrum of the 1*H* Janus structures. In the lower energy *E* phonon mode, the *X* atom moves in opposite in-plane directions of the W-O couple, whereas in the higher frequency *E* mode, the O atoms, and the W-*X* pairs vibrate in the opposite in-plane direction of each other and the magnitude of the O eigenvectors are significantly larger than those of W-*X*. The $A_1^{(W-X)}$ mode arises from the out-of-plane vibration of *X* and W atoms in the

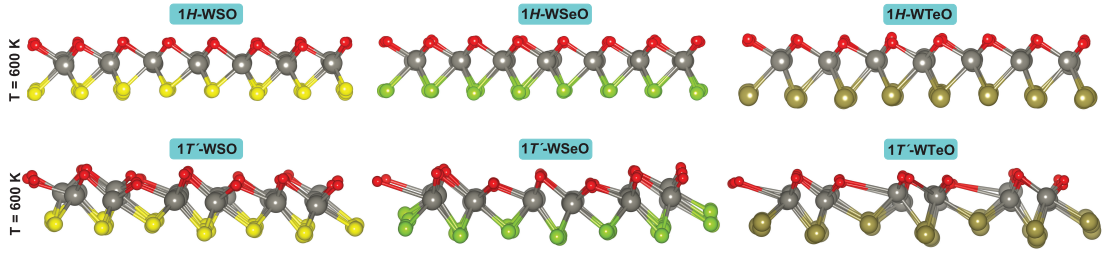


Figure 4.4: The Snapshots of *ab initio* molecular dynamics (AIMD) simulations of 1H- and 1T'-WXO Janus monolayers at 600 K.

opposite directions. Unlike WX_2 systems, the center of mass in the Janus 1H-WXO structures are not at the W layer; thus the center of vibration is in between the W-X bonds for $A_1^{(W-X)}$ vibrational mode. The $A_1^{(W-O)}$ phonon mode originates from the strong bond stretching of W-O atoms. In this mode, W and O atoms vibrate in the z-direction against each other, and the displacement of the O atoms is more significant.

As mentioned, the space group of the 1T'- WX_2 monolayers belongs to C_{2h}^2 . Our analyses shows that the irreducible representation for the optical spectrum in the 1T'- WX_2 structure can be described by $\Gamma = 2A_u + 4B_u + 6A_g + 3B_g$, in which six optical modes (A_u and B_u) and the other nine modes (A_g and B_g) are IR and Raman active, respectively. Due to the broken symmetry along the z-direction by replacing O atoms with the chalcogenide atoms in the 1T'- WX_2 structures, the symmetry of the new structures (1T'-WXO) is described by C_{2v}^7 space group. Similar to its binary counterpart, the 1T'-WXO monolayer consists of six atoms within the primitive cell, resulting in fifteen optical branches. All optical phonon modes in the 1T'-WXO structures are non-degenerate and Raman active. The calculated Raman activity of 1T'-WXO crystals are shown in Fig. 4.5(c). Notice from Figs. 4.5 (a) and (c) that two different structural phases of the WXO monolayers exhibit completely different Raman spectra. The prominent peaks in the Raman spectra of 1T'-WSO are labeled with numbers, and the vibrational motion of the corresponding peaks are illustrated in Fig. 4.5(d). The I and II peaks are mostly dominated by in-plane and out-of-plane vibration of W atoms, respectively. The Raman modes labeled as III and IV, all atoms in the primitive

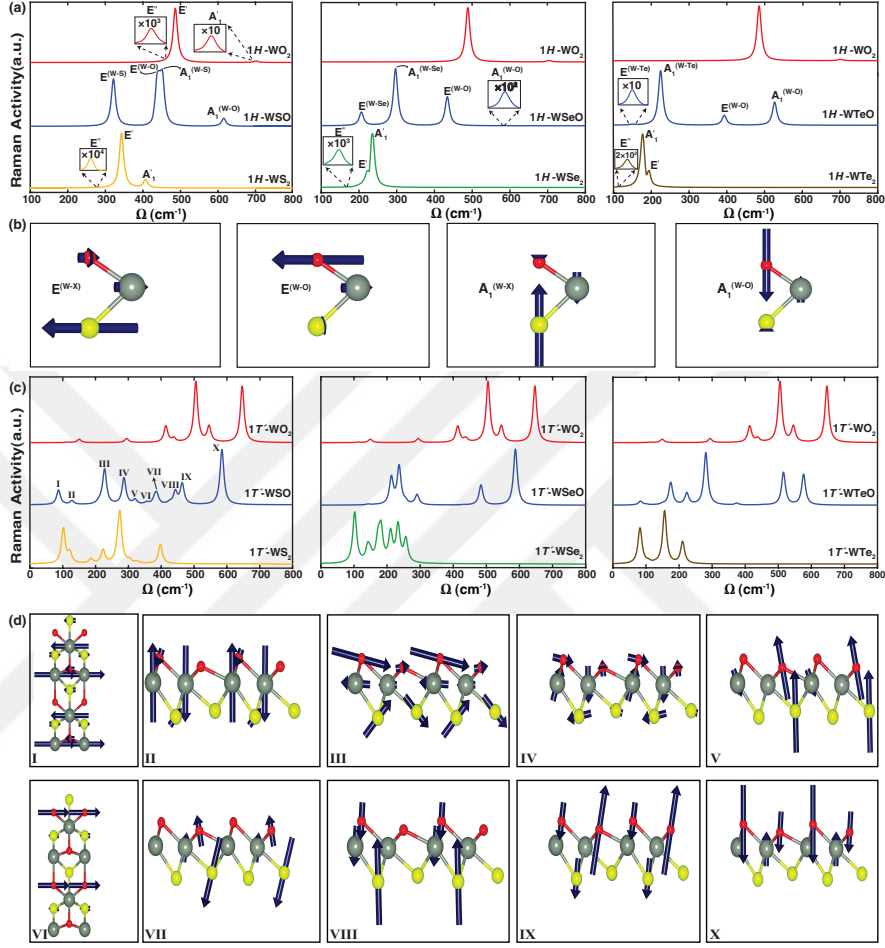


Figure 4.5: The normalized Raman activity spectra (a,c) and corresponding atomic displacement (b,d) of the Raman activity modes of 1H (a,b) and 1T' (c,d), phases of WX₂ and WXO monolayers

cell vibrate along different directions. The V peak mode is attributed to the vibration of O and S atoms in the out-of-plane direction. The peak VI (with the frequency of 377 cm⁻¹) corresponds with a dominant in-plane vibration of O atom in the unit cell. For the peaks VII and VIII, the out of plane vibration of the outer S atoms against O atoms is more dominant, while in the remaining peaks the strong out-of-plane vibration of O atoms is the reason for the robust peaks in the Raman activity diagram. It can be concluded that the Raman spectra of the 1T' structures are significantly different from those of 1H phase.

4.2.4 Thermal Properties

Having obtained the phonon spectra, we also investigated the isovolume heat capacity (C_V) of WXO monolayers, which is related to the ability of a material to store heat for a given temperature range. It is known that the lattice vibrations in ultra-thin materials give the dominate contribution to the specific heat capacity, while the role of the free conduction electrons is negligible[165, 166]. Fig. 4.6 presents C_V of 1*H*- and 1*T'*-WXO structures up to 600 K, at which structural stability is still maintained. Our results reveal that similar to bulk systems, C_V increases with temperature and approaches the classical Dulong-Petit limit i.e., $3Nk_B$, where N is the number of atoms in the unit cell, and k_B is the Boltzmann constant. Up to room temperature, C_V moderately increases down the chalcogen group for both phases, and this can be correlated with the shift of the optical phonon modes with X [167]. C_V varies more rapidly for the high-frequency optical branches than for the low-frequency acoustic branches at low temperatures. Moreover, it has been reported that the C_V of 2D materials at low temperatures scales with $T^{2/n}$ ($n > 0$). n is obtained from the following relation, $\omega = q^n$ where ω is the frequency of vibration and q is the wave vector of the acoustical phonon modes around the Γ point [166, 165]. Accordingly, n is estimated as 1.01 - 1.05 and 1.12 - 1.15 for 1*H* and 1*T'* phases, respectively. Accordingly, while C_V of 1*H*-WXO varies with T^2 , it increases with $T^{1.75}$ for 1*T'*-WXO. In addition, with this analysis, it is found that the main contribution to the C_V arises from in-plane LA-TA modes, and out-of-plane ZA mode for 1*H*-WSO and 1*T'*-WSO monolayers, respectively.

4.2.5 Linear-Elastic and Piezoelectric Properties

The mechanical response of 2D materials in the elastic regime can be represented by two linear-elastic constants: the in-plane stiffness (C) and the Poisson ratio (ν). In the present study, these constants are obtained from the elastic-strain tensor elements, c_{ij} , and their values for two specific orientations, namely zigzag (zz) and armchair (ac), can be calculated using the relations below;

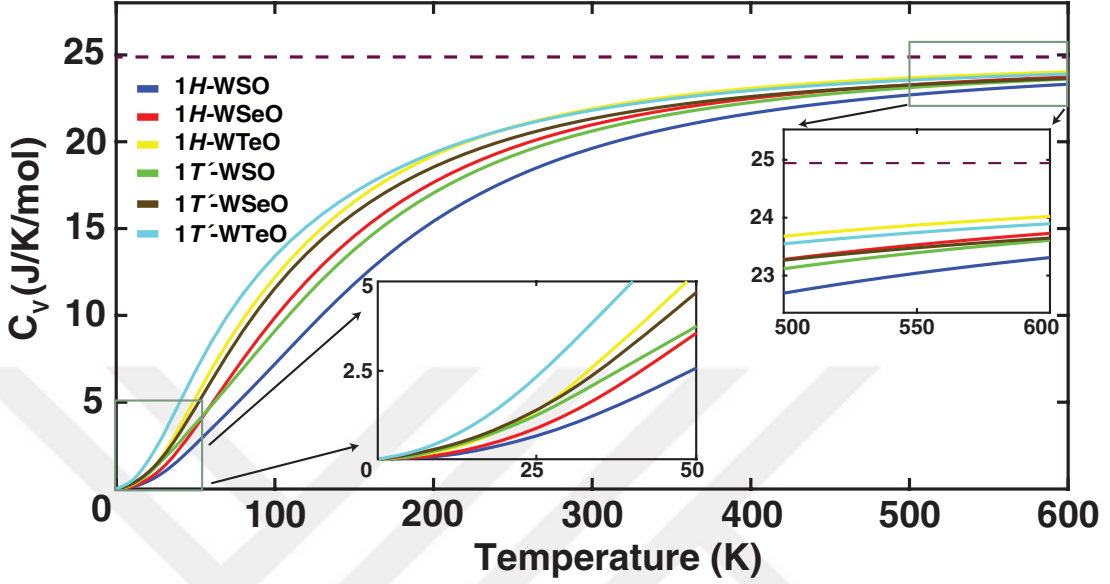


Figure 4.6: Variation of isovolume heat capacity (C_V) for the 1H- and 1T'-WXO monolayers with temperature. The low and high temperature limits are shown as insets.

$$C_{zz} = \frac{(c_{11}c_{22} - c_{12}^2)}{c_{22}}, \quad C_{ac} = \frac{(c_{11}c_{22} - c_{12}^2)}{c_{11}} \quad (4.2)$$

and similarly the Poisson's ratio can be written as;

$$\nu_{zz} = \frac{c_{12}}{c_{22}}, \quad \nu_{ac} = \frac{c_{12}}{c_{11}} \quad (4.3)$$

The in-plane stiffness, C , is the measure of the rigidity of a material in the 2D limit analogous to Young's modulus in 3D structures. C is isotropic for 1H-WXO and has the same value along all orientations. In Table 4.3, C_{zz} and C_{ac} , are given for the sake of comparison with the T' -phase. Notice that C decreases with increasing atomic radius of the X atoms along with elongation of d_{W-X} . The calculated C 's are 182, 169, and 150 N/m for monolayers of 1H-WSO, 1H-WSeO, and 1H-WTeO, respectively. In contrast, 1T'-WXO structures are shown to possess in-plane anisotropy arising from the formation of W-W chains in the crystal. It was already observed in $M\text{Te}_2$ ($M = \text{Mo}$ or W) layered crystals that due to the large atomic radius of Te atoms, Mo or W atoms tend to get closer and form M-M chains which lead to in-plane anisotropy

Table 4.3: The relaxed-ion elastic coefficients, c_{ij} ; in-plane stiffness, C ; and Poisson's ratio, ν along two orientations, namely zigzag (zz or a) and armchair (ac or b) for $1H-$ and $1T'$ -W X O.

Crystal	c_{11}	c_{22}	c_{12}	C_{zz}	C_{ac}	ν_{zz}	ν_{ac}
Structure	(N/m)	(N/m)	(N/m)	(N/m)	(N/m)	(-)	(-)
$1H$ -WSO	196	196	52	182	182	0.27	0.27
$1H$ -WSeO	179	179	44	169	169	0.24	0.24
$1H$ -WTeO	158	158	34	150	150	0.22	0.22
$1T'$ -WSO	132	130	18	130	128	0.14	0.13
$1T'$ -WSeO	142	44	9	140	43	0.21	0.06
$1T'$ -WTeO	91	28	7	89	27	0.26	0.08

[168]. The anisotropy becomes more evident as the atomic radius difference between the O and X atoms increases. The reason for the increasing anisotropy degree in WSeO and WTeO can be related to the induced surface strains on O and X sites. Therefore, the response of the lattice to the applied external load is different as one of the chalcogen layer of WX_2 is replaced by O. C_{zz} (C_{ac}) are calculated as 130 N/m (128 N/m), 140 N/m (43 N/m), and 89 N/m (27 N/m) for $1T'$ -WSO, $1T'$ -WSeO, and $1T'$ -WTeO, respectively. Apparently, the difference between zigzag and armchair orientations increases down the chalcogen group. Additionally, bond weakening results in a decrease in stiffness. As compared to the stiffness values predicted for other Janus TMDs, (ranges between 106-117 N/m for $1H$ -MoXY and 139-146 N/m for $1H$ -WXY)[169], $1T'$ -WTeO is quite softer especially along the ac -orientation. The significant decrease of the stiffness along this direction for $1T'$ -WSeO and $1T'$ -WTeO can be attributed to the increasing surface strain on the O-site. As the atomic radius of the X atom increases with Se or Te atoms on one side, the perpendicular distance between W-W chains increases, and thus, the W-O distance increases also. The increasing W-O distance, therefore, results in the weakening of the stiffness along W-O

direction. Poisson's ratio (ν) is defined as the negative ratio of the transverse strain to the longitudinal strain and correlates the deformation along the applied stress to the deformation in the vertical direction. Similar to C , ν is also isotropic and has the value 0.27, 0.24, and 0.22 for 1H-WSO, 1H-WSeO, and 1H-WTeO, respectively. As $\nu < 0.33$, 1H-WXO monolayers are brittle according to the Christensen criterion[170] similar to their WX₂ counterparts. The predicted ν values for WS₂, WSe₂, and WTe₂ were reported to be 0.21, 0.26, and 0.34, respectively, and display a different behavior than 1H-WXO due to the presence of O atoms on one side[169]. In the case of 1T'-WXO monolayers, the anisotropy becomes more drastic as the difference in atomic radius of X and O atoms increases. ν_a (ν_b) are estimated as 0.14 (0.13), 0.21 (0.06), and 0.26 (0.08) for 1T'-WSO, 1T'-WSeO, and 1T'-WTeO, respectively. Similar to 1H-phase, 1T'-WXO monolayers are also brittle and being $\nu_b \sim 0.1$ indicates enhanced covalent bonding character in that direction[170].

Table 4.4: The relaxed-ion piezoelectric stress, e_{ij} , and the corresponding piezoelectric strain coefficients, d_{ij} for the 1H- and 1T'-WXO monolayers. Note that the values for e_{ij} are multiplied by 10^{-10} order.

Crystal	e_{11}	e_{13}	e_{14}	e_{21}	e_{22}	d_{11}	d_{13}	d_{14}	d_{21}	d_{22}
Phase	(C/m)	(C/m)	(C/m)	(C/m)	(C/m)	(pm/V)	(pm/V)	(pm/V)	(pm/V)	(pm/V)
1H-WSO	2.5	1.1	—	—	—	1.8	0.4	—	—	—
1H-WSeO	2.6	1.2	—	—	—	1.9	0.5	—	—	—
1H-WTeO	3.4	1.2	—	—	—	2.8	0.6	—	—	—
1T'-WSO	—	—	13.4	16.1	8.2	—	—	25.8	15.4	3.3
1T'-WSeO	—	—	5.6	19.1	7.4	—	—	12.7	16.3	35.6
1T'-WTeO	—	—	1.3	3.3	1.9	—	—	1.7	5.1	4.6

Piezoelectricity is described as the generating electric dipole moment as a result of applied external stress (and vice versa) in non-centrobinary structures [171]. Experiments have demonstrated enhanced piezoelectric constants in the 2D limit[85].

For the 1H-phase, d_{ij} are given by the relations;

$$d_{11} = \frac{e_{11}}{c_{11} - c_{12}}, \quad d_{13} = \frac{e_{13}}{c_{11} + c_{12}}. \quad (4.4)$$

It should be noted that while e_{13} is zero in $1H-WX_2$, broken out-of-plane symmetry adds a degree of freedom to piezoelectricity in $1H-WXO$, and e_{13} is no longer zero. The e_{11} coefficients are calculated to be 2.5×10^{-10} , 2.6×10^{-10} , and 3.4×10^{-10} C/m for $1H-WSO$, $1H-WSeO$, and $1H-WTeO$ crystals, respectively. Besides, the out-of-plane components of the piezoelectric stress tensor are found to be quite significant, 1.1, 1.2, and 1.2 pm/V, which are much larger than those of Janus MoSSe. This is related to the large charge difference on both surfaces arising from the O atoms.

As the structural symmetry changes from $1H$ to $1T'$, the number of non-zero piezoelectric tensor elements becomes e_{14} , e_{21} , and e_{22} . As listed in Table 4.4, e_{14} and e_{22} decreases as X atoms changes from O to Te. The two coefficients represent the induced dipole moment along $x - y$ and y directions when the external strain is applied along x and y directions (i.e., zz and ac), respectively. Therefore, the decreasing trend indicates a decline in the in-plane dipole moment caused by the charge density difference on X and O atoms.

The related d_{ij} values are calculated by using the following relations,

$$d_{14} = \frac{e_{14}}{c_{44}}, \quad d_{21} = \frac{2e_{21}c_{12} + e_{21}c_{11} + e_{22}c_{11}}{3c_{11}c_{12} + c_{11}^2}, \quad d_{22} = \frac{e_{21}c_{12} - e_{22}c_{11}}{3c_{22}c_{12} + c_{11}c_{22}} \quad (4.5)$$

and found to be one-order larger than those for the isotropic $1H$ -phase structures. It is important to note that the formation of distorted Janus structures of WXO creates in-plane piezoelectricity, which is absent in binary $1T'-WX_2$. Therefore, the creation of out-of-plane asymmetry is important not only for out-of-plane piezoelectricity but also for the in-plane components in the distorted phase of TMDs. Prediction of distorted Janus materials will enrich the family of piezoelectric materials[86].

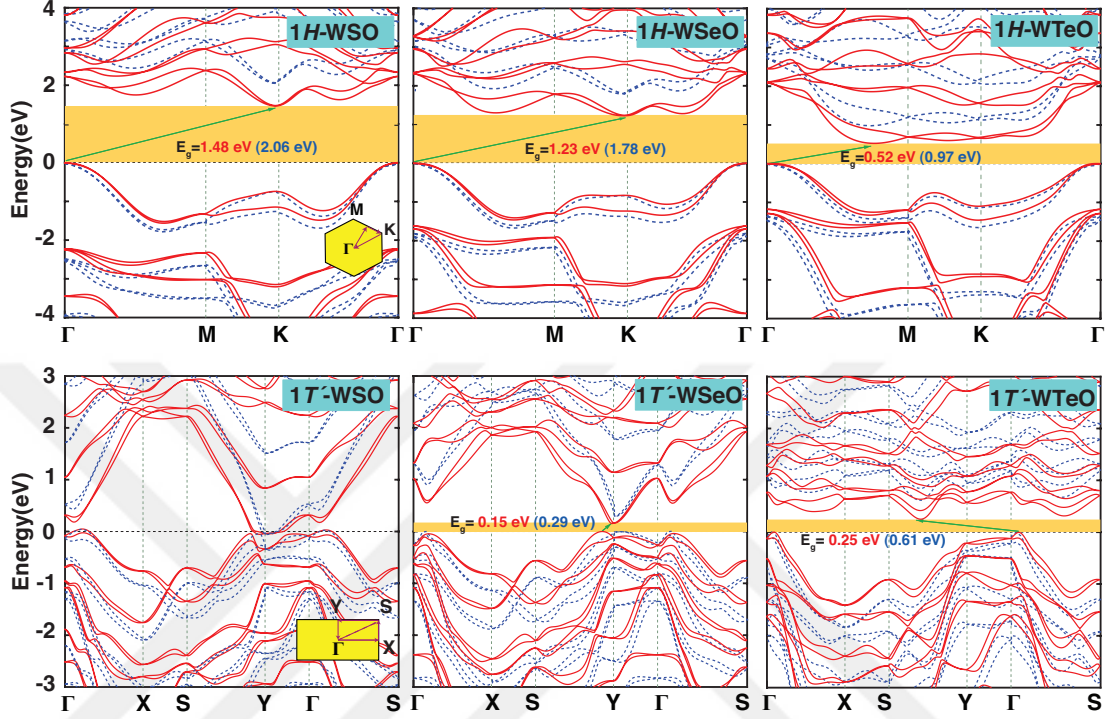


Figure 4.7: The electronic band structures of Janus 1H- and 1T'-WXO monolayers. The results based on GGA-PBE + SOC and HSE06 + SOC are shown by red solid and dashed blue lines, respectively. The band gap values at the level of PBE + SOC are shaded by light orange rectangles. $E_g^{PBE-SOC}$ and $E_g^{HSE-SOC}$ values are given. The Fermi level is set to zero.

4.2.6 Electronic Properties

Lastly, the electronic properties of 1H- and 1T'-WXO monolayers are investigated. The calculated electronic band structures and orbital projected density of states (PDOS) are presented in Fig. 4.7, 4.8 and 4.9, respectively. As summarized in Table 4.1 while 1H-WX₂ (X= S, Se, and Te) monolayers are direct band gap semiconductors, 1H-WO₂ monolayer has an indirect band gap. Therefore, 1H-WXO systems are found to be indirect band gap semiconductors, as shown in Fig. 4.7. Direct to indirect band gap transition can also be related with the induced strain on the outer layer (i.e, while O-side undergoes tensile strain, the X-side experiences a compressive strain). The calculated band gap values at the level of GGA-PBE (E_g^{PBE}) are 1.52, 1.28, and 0.71 eV for 1H-WSO,

1*H*-WSeO and 1*H*-WTeO monolayers, respectively. It is noticed that E_g^{PBE} decreases down the group of chalcogen atoms in line with the variation of $\Delta\rho_{(W-X)}$. E_g^{PBE} of 1*H*-WXO are narrower than those of WX_2 systems but follow the same trend. The inclusion of spin-orbit coupling (SOC) decreases the band gap values ($E_g^{PBE-SOC}$), and expectedly the impact is more prominent for 1*H*-WTeO, being Te is the heaviest element among the chalcogens. Similar trends with wider band gap values ($E_g^{HSE-SOC}$) are obtained when calculations are repeated with hybrid functionals with the inclusion of SOC. As can be seen from Table 4.1, 1*T'*- WX_2 monolayers other than 1*T'*-WO₂ are semiconductors, which is correlated with the Peierls distortion [172, 173]. The metallic *T*-phase is prone to instability and transforms to *T'*-phase, and results in a metal to semiconductor transition. Similar results are also obtained for 1*T'*-WXO. As discussed above, 1*T*-WXO monolayers are unstable, and a phase transition from 1*T* to 1*T'* is realized. As 1*T'*-WO₂ is a semi-metal, the band gap variation of 1*T'*-WXO does not follow a clear trend. As shown in Fig. 4.7, while 1*T'*-WXO is a semi-metal, E_g^{PBE} of 1*T'*-WSeO and 1*T'*-WTeO are 0.25 and 0.41 eV, respectively. The increase in band gap is correlated with the structural deformation (Table 7.1). Akin to 1*H*-phase, the inclusion of SOC lowers the band gap ($E_g^{PBE-SOC}$), and similar band profiles with wider band gap ($E_g^{HSE-SOC}$) are obtained with hybrid functionals. All calculated band gaps together with the location of valence band maximum (VBM) and conduction band minimum (CBM) are summarized in Table 4.5.

Table 4.5: Energy band gaps at the level of GGA-PBE, E_g^{PBE} ; GGA-PBE + SOC, $E_g^{PBE-SOC}$; HSE06 + SOC, $E_g^{HSE-SOC}$; and the locations of VBM and CBM edges for 1*H*- and 1*T'*-WXO monolayers.

Crystal	E_g^{PBE}	$E_g^{PBE-SOC}$	$E_g^{HSE-SOC}$	VBM/CBM
Phase	(eV)	(eV)	(eV)	-
1 <i>H</i> -WSO	1.52	1.48	2.06	Γ/K
1 <i>H</i> -WSeO	1.28	1.23	1.78	Γ/K
1 <i>H</i> -WTeO	0.71	0.52	0.97	Γ/Γ-M
1 <i>T'</i> -WSO	SM	SM	SM	Γ- X/S -Y
1 <i>T'</i> -WSeO	0.25	0.15	0.29	S -Y/Y
1 <i>T'</i> -WTeO	0.41	0.25	0.61	Γ- S/S -Y

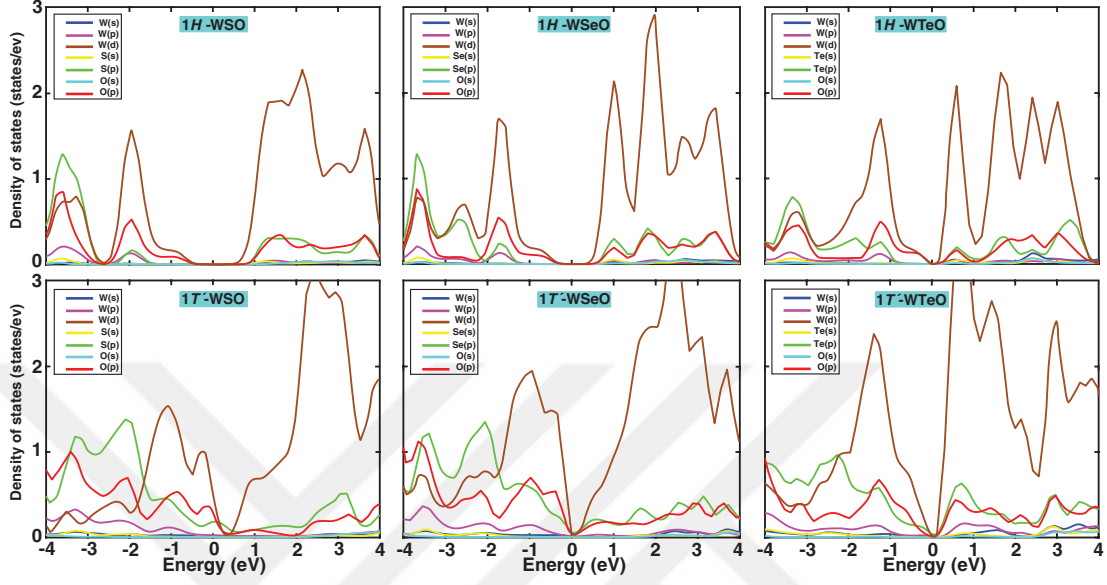


Figure 4.8: The projected density of states (PDOS) of 1H- and 1T'-WXO (X: S, Se and Te) monolayers

4.3 Conclusion

The stability and fundamental properties of 1H-, 1T-, and 1T' phases of Janus WXO ($X = \text{S, Se, and Te}$) monolayers were investigated. Our vibrational frequency analysis revealed that the 1T-WXO monolayers are prone to instability, and transform to 1T'-phase similar to their binary counterparts. On the other hand, 1H- and 1T'-WXO monolayers retain their crystalline structures up to 600K. Raman spectrum analysis showed that the formation of Janus WXO monolayers results in new Raman active phonon modes (four for 1H- and ten for 1T'-phase) different from WX_2 systems. The heat capacity (C_V) of 1H- and 1T'-WXO monolayers varies with T^2 and $T^{1.75}$ for low temperature range and expectedly converges to classical limit as temperature increases. The mechanical properties of 1H-phase were found to be isotropic, and the calculated in-plane stiffness values (C) are larger than the corresponding binary counterpart. Accordingly, the oxygenation makes the systems stiffer. On the other hand, mechanical response of 1T-WXO monolayers was calculated to be orientation-dependent, and the anisotropy along armchair and zigzag direction becomes more evident down the chalcogen group. The estimated Poisson's ratio range indicated that

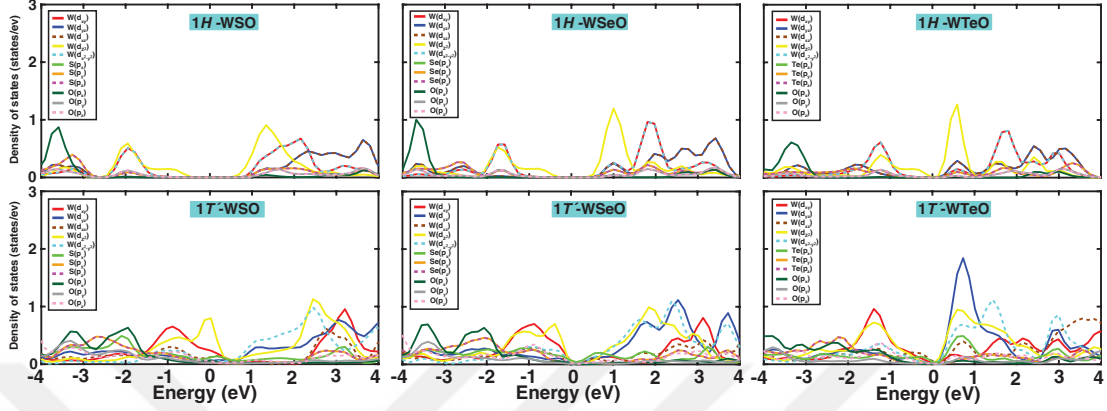


Figure 4.9: Orbital projected partial electronic density of states of W(d), X(p) (X: S, Se and Te) and O(p) elements in 1H- and 1T'-WXO monolayers

both phases are brittle. Following the calculation of elastic tensor elements, the piezoelectricity in 1H- and 1T'-WXO crystals was investigated, and large out-of-plane piezoelectric coefficients were shown to appear in both of the phases due to the broken out-of-plane symmetry. It was obtained that while 1H-WX₂ monolayers have direct band gaps, 1H-WXO systems are indirect band gap semiconductors, and the band gap narrows down the chalcogen group. The direct to indirect transition is linked to the induced strain on X- and O-sides, and also correlated with the band structure profile of 1H-WO₂. Except 1T'-WSO, 1T'-WSeO and 1T'-WTeO are narrow band gap semiconductors due to the Peierls distortion. The inclusion of spin-orbit coupling lowers the band gap for both phases, and the effect is found to be more distinct as X atoms get heavier.

Chapter 5

Janus $\text{Bi}XY$ ($X = \text{S, Se, Te}$ and $Y = \text{F, Cl, Br, I}$) monolayers

Two-dimensional (2D) ternary metal chalcogenides (i.e., MXY) [21, 18, 174, 150, 175, 176, 177, 178] are emerging as next-generation 2D semiconductors beyond their binary counterparts [179, 180]. Especially, bismuth-based ternary compounds, such as bismuth oxychalcogenides (Bi_2O_2X with $X = \text{S, Se, and Te}$), have been realized and attracted considerable interest due to their remarkable properties, including high carrier mobility and stability at ambient conditions [181, 182]. Furthermore, recent experimental studies show that bismuth oxyhalides (BiOX with $X = \text{Cl, Br and I}$) have excellent photocatalytic performance owing to their unique electronic properties [183]. Another important family of bismuth-based ternary structures is bismuth tellurohalides (BiTeX with $X = \text{Cl, Br and I}$), which has been shown to possess a strong Rashba spin splitting (RSS) [184, 185]. Recently, single-layer (SL) BiTeI composed of three sublayers, with Bi atoms are sandwiched between Te and I plates, has been isolated by exfoliation from bulk form [53]. Following this achievement, fascinating properties of BiTeI , including giant RSS [50, 51, 52], large out of plane piezoelectricity [186, 187] and high thermoelectric performance (ZT) [188, 189] have been investigated extensively. In addition to BiTeI , various bulk bismuth chalcogenides structures (BiXY with $X = \text{S, Se, Te}$ and $Y = \text{Cl, Br, I}$) composed of weakly coupled

layers have been synthesized. For instance, bulk BiTeBr [54], BiTeCl [55], BiSeI [190], and BiSI [191, 192] have been realized in their multilayered form, and their fundamental physical properties have been studied, both theoretically and experimentally [193, 194, 195, 196]. In this regard, thermoelectric properties of bulk and SL-BiTeBr have been investigated by using first-principles calculations and enhanced thermoelectric performance of SL-BiTeBr compared to the bulk structure (owing to reduced thermal conductivity) has been revealed [197]. In another experimental study, it has been reported that the BiTeCl is a semiconductor with an electronic bandgap of 0.77 eV at room temperature, which makes it a suitable material for infrared detector and sensing applications [198, 199]. The vibrational properties of bulk and exfoliated flakes of BiTeCl have been examined by Raman spectroscopy, providing basic information on lattice dynamics [200]. Furthermore, theoretical calculations and experimental analysis have demonstrated pressure-induced topological phase transition and superconductivity in BiTeX crystals [201, 202, 203]. Additionally, bulk crystals of BiSI and BiSeI, which are stable at high temperatures, have been synthesized in large quantities by a ball milling method and shown to exhibit suitable optical bandgaps for solar cell applications [204]. Lately, highly crystalline 2D BiTeCl and BiTeBr nanosheets, which can be utilized in spintronics [205], have been directly synthesized via epitaxial growth [206]. Despite promising outcomes of experimental and theoretical research on bismuth chalcogenides, a comprehensive and comparative study focusing on the design and characterization of BiXY monolayers has not been performed. With this motivation, we studied the structural, vibrational, mechanical, piezoelectric, and electronic properties of the Janus BiXY ($X = \text{S, Se, Te}$, and $Y = \text{F, Cl, Br, I}$) monolayers using first-principles methods.

5.1 Methodology

In this study, we utilized the Vienna *Ab initio* Simulation Package (VASP) [106, 107, 108, 109] to perform first principles calculations based on density functional theory (DFT) [104, 105] with project-augmented wave (PAW) [155] potentials. For the exchange-correlation interaction, Perdew-Burke-Ernzerhof (PBE) functional

within the generalized gradient approximation (GGA) was considered[80]. A plane-wave basis set with the kinetic cutoff energy of 520 eV was employed for all calculations. The Brillouin zone (BZ) was sampled uniformly by a Γ -centered $16 \times 16 \times 1$ k -point mesh based on the Monkhorst–Pack scheme[114]. The total energy convergence criterion for relaxation between the sequential steps was set to 10^{-5} eV. The ionic positions and lattice constants of the structures were optimized until the Hellmann-Feynman forces on each atom were decreased below 0.01 eV/Å, while the pressure on the lattice was reduced below 1.0 kbar. To hinder the artificial interactions in the non-periodic direction, a vacuum space of ~ 15 Å was inserted. During the calculation of electronic band structures, the spin-orbit coupling (SOC) effect was also taken into account. [48]. Additionally, the hybrid functional of Heyd-Scuseria Ernzerhorf (HSE06) was adopted with SOC to obtain corrected bandgaps[112, 113]. The HSE06 functional was designed by mixing 25% of nonlocal Fock exchange with 75% of PBE exchange and 100% of PBE correlation energy. The phonon dispersions were calculated for $4 \times 4 \times 1$ supercell by using a small displacement method as implemented in PHONOPY[115]. To check the thermal stability of the proposed structures, *ab initio* molecular dynamics (AIMD) calculations were carried out via implementing a micro-canonical ensemble method for a total simulation time of 2 ps with 1 fs time step. The vibrational modes and atomic displacements were obtained by a direct diagonalization of the force constant matrix. The corresponding first-order off-resonant Raman spectrum of each vibrational mode was determined via calculating the macroscopic dielectric tensor at the Γ -point of the BZ by using a small difference method[20]. Due to the net electric dipole moment occurring in the polar surface calculations, the dipole correction was taken into account[207]. Both elastic constants and piezoelectric stress coefficients were calculated by employing the density functional perturbation theory (DFPT) method with a $48 \times 48 \times 1$ k -point grids and cutoff energy of 700 eV. To analyze the net charge on atoms and the bond characteristics of the structures, the Bader technique was applied[116].

5.2 Results and Discussion

5.2.1 Atomic Structure and Energetics

The geometric structure of the Janus BiXY ($X = \text{S, Se, Te}$ and $Y = \text{F, Cl, Br, I}$) monolayers is constructed based on the crystal structure of the realized BiTeI monolayer. The schematic representation of the Janus BiXY monolayers is depicted in Fig.5.1. The primitive cell of SL-BiXY consists of three atomic sub-layers where Bi is in the center while X and Y atoms are located on the top and bottom layers, respectively. Their symmetry belongs to the P3m1 space group and C_{3v} point group. Additionally, similar to several Janus TMD monolayers[22, 23] their structure lacks the reflection symmetry with respect to the center atom. The calculated structural parameters of BiXY monolayers are listed in Table 7.1. The obtained results are in good agreement with the available data on BiTeCl, BiTeBr, and BiTeI [208, 209, 187, 186]. Additionally, our calculated lattice constant (4.42 Å) is comparable to the in-plane lattice constant of synthesized bulk BiTeI (4.33 Å)[210]. The bond length between Bi and X/Y atoms ($d_{\text{Bi}-X}$ and $d_{\text{Bi}-Y}$) elongates going down in chalcogen and/or halogen group. This is due to the increase in the atomic radius of X and/or Y atoms in the structures. Accordingly, BiTeI and BiSF monolayers possess the longest and shortest bond lengths, respectively. The lattice constant ($\mathbf{a}$) follows a similar trend with the bond length, and for each subset of X , $\mathbf{a}$ enlarges down the halogen group and vice versa. The thickness of the Janus BiXY crystals (h) increases with elongation of $d_{\text{Bi}-X}$ and $d_{\text{Bi}-Y}$ as it is proportional with the bond length. On the other hand, for a given X , the bond angle θ' ($\angle Y\text{-Bi-}Y$) narrows down the halogen group, whereas θ ($\angle X\text{-Bi-}X$) represents an opposite behavior. This is due to the fact that when the electronegativity difference between X and Y atoms ($\Delta\chi$) increases, more electrons accumulate around the atom with higher electronegativity, in turn, the atoms start to repel each other, which results in widening of bond angle.

The cohesive energy per atom (E_C) for the proposed structures are calculated

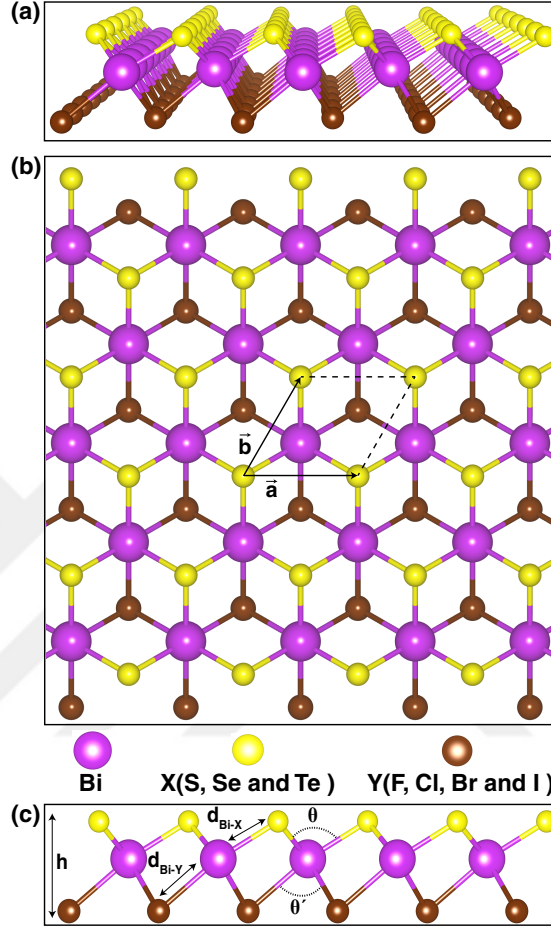


Figure 5.1: (a) Perspective, (b) top, and (c) side views of Janus BiXY monolayers. The corresponding lattice vectors (a , b), bond lengths ($d_{\text{Bi-X}}$, $d_{\text{Bi-Y}}$), bond angle between $X\text{-Bi-X}$ and $Y\text{-Bi-Y}$ (θ and θ') and thickness (h) are shown.

via the following relation:

$$E_C = \frac{[E_T(\text{Bi}) + E_T(X) + E_T(Y)] - [E_T(\text{BiXY})]}{3} \quad (5.1)$$

where $E_T(\text{Bi})$, $E_T(X)$, and $E_T(Y)$ are the single atom energies of Bi, X , and Y elements, respectively; $E_T(\text{BiXY})$ corresponds to the total energy of the Janus BiXY structures. All obtained results are given in Table 7.1. Correlated with the bond weakening, E_C gradually decreases as a enlarges. In a similar manner, for each subset of X (Y), E_C decreases moving down the chalcogen (halogen) group. High cohesive energy implies strong binding between the constituent elements and is a notable parameter to quantify the stability of a material. Accordingly, BiSF

and BiTeI are the most and the least stable structures among Janus BiXY monolayers. It should be noted that the computed E_C 's are comparable to the other bismuth-based systems. For instance, E_C of 2D Bi₂Se₃, Bi₂Te₂S and Bi₂Te₂Se are reported to be 2.89, 2.77 and 2.67 eV/atom[211], respectively, which are within the same cohesive energy range of the BiXY monolayers.

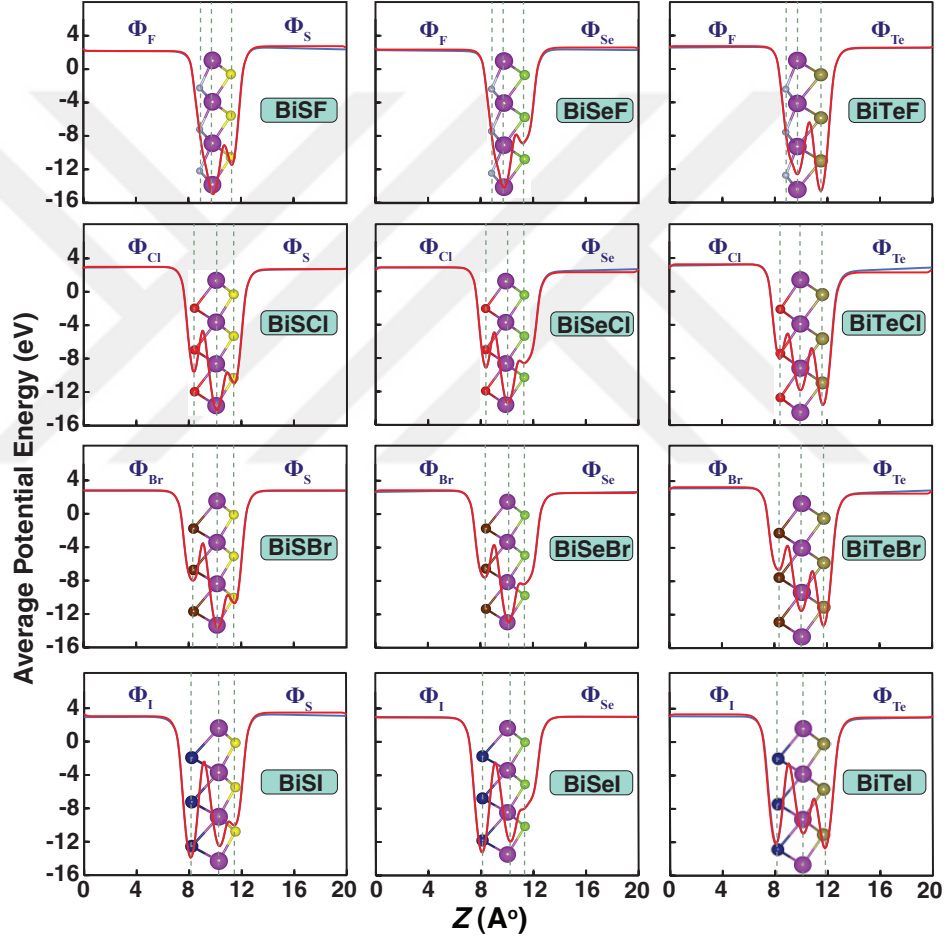


Figure 5.2: Planar average of the electrostatic potential along the z -axis for Janus BiXY monolayers with (red) and without (blue) dipole correction. The vertical dashed lines represent the positions of the Bi, X, and Y atoms. Φ_X and Φ_Y denote the work function of the X and Y surfaces, respectively.

In BiXY systems, the size difference of atoms, electronegativity difference ($\Delta\chi$), and different types of bonding between Bi-X and Bi-Y (double and single bonding, respectively) give rise to in-equivalent charge distributions. The corresponding data from Bader analysis demonstrate that the charge depletion from Bi

to X and Y elements ($\Delta\rho_{(\text{Bi}-X)}$ and $\Delta\rho_{(\text{Bi}-Y)}$) decreases with increasing $\mathbf{a}$ which is correlated with the aforementioned factors and also support the variation of E_C . The general features of charge partitioning between the atoms reveal that the Bi layer in all structures is positively charged, whereas the X and Y layers are negatively charged. As an example, the results of Bader analyses show that 0.42 e^- and 0.41 e^- transferred from Bi to Te and I atoms, respectively, which are consistent with those of previous studies on BiTeI crystals [186]. The unbalance charge between the X and Y sides generates a net electric field, between Bi layer and $X(Y)$ layer, the direction of which points Bi layer to $X(Y)$ layer. Furthermore, the charge difference between the surfaces affects the magnitude of the thermionic work function (Φ) on each side. Accordingly, to identify the inherent electric field in Janus BiXY crystals, the work function from X and Y sides are calculated. The planar average of the electrostatic potential and the related work functions for Bi- X and Bi- Y surfaces (Φ_X and Φ_Y) are displayed in Fig. 5.2. It is noticed that the difference between Φ_X and Φ_Y ($\Delta\Phi$) is proportional with magnitude of the dipole moment in the structures and is in parallel with the Helmholtz equation [212], $\mu = \frac{e}{\varepsilon_0} \times \frac{\Delta\Phi A}{\theta}$. Based on the Helmholtz model, the surface dipole (μ) is linearly proportional with the work function difference ($\Delta\Phi$), slab surface area (A) and elementary charge (e) and has inverse relation with the surface coverage (θ) and vacuum permittivity (ε_0)[212]. In addition, the electrostatic potential difference between X and Y surfaces increases when $\Delta\chi$ is larger. For the BiXF monolayers, the potential energy on the side of F is minimal, which is due to the strong electronegativity of F atoms that causes the accumulated electrons cannot offset it. The electrostatic potential energy diagram demonstrates information about the charge distribution between the constituent elements in the structures. Generally, a high electrostatic potential implies the deficiency of electrons on that element, whereas the low electrostatic potential indicates an abundance of electrons. Since the F atom has the highest electronegativity value, it attracts the majority of the electrons, decreasing the electrostatic potential energy. Moreover, the change in the work function of the BiTeBr monolayer is almost twice as large as the one for BiTeI which results in a larger dipole moment in the BiTeBr, as it was also previously verified by earlier work[50].

Table 5.1: The optimized lattice constant (a), atomic bond lengths ($d_{\text{Bi-X}}$, and $d_{\text{Bi-Y}}$), thickness (h), bond angle between $X\text{-Bi-X}$ and $Y\text{-Bi-Y}$ (θ and θ'), cohesive energy per atom (E_C), the amounts of charge transfer, $\Delta\rho_{(\text{Bi-X})}$ and $\Delta\rho_{(\text{Bi-Y})}$, the calculated work functions for two different surfaces, Φ_X and Φ_Y and their differences $\Delta\Phi$.

	a	$d_{\text{Bi-X}}$	$d_{\text{Bi-Y}}$	h	θ	θ'	E_C	$\Delta\rho_{(\text{Bi-X})}$	$\Delta\rho_{(\text{Bi-Y})}$	Φ_X	Φ_Y	$\Delta\Phi$
Structure	(Å)	(Å)	(Å)	(Å)	(deg)	(deg)	(eV/atom)	(e ⁻)	(e ⁻)	(eV)	(eV)	(eV)
BiSF	3.94	2.73	2.50	2.55	92.4	103.7	3.58	0.74	0.76	6.09	5.52	0.57
BiSCl	4.06	2.75	2.93	3.18	95.4	87.7	3.06	0.75	0.58	5.85	6.13	-0.28
BiSBr	4.11	2.75	3.07	3.35	96.4	83.9	2.90	0.75	0.51	5.69	5.70	-0.01
BiSI	4.19	2.76	3.25	3.51	98.6	80.1	2.75	0.76	0.40	5.70	5.28	0.42
BiSeF	4.01	2.84	2.52	2.64	89.7	105.5	3.42	0.60	0.76	5.77	5.52	0.25
BiSeCl	4.15	2.86	2.94	3.28	92.6	89.7	2.92	0.61	0.59	5.49	6.07	-0.58
BiSeBr	4.19	2.87	3.07	3.45	93.5	85.7	2.77	0.61	0.51	5.41	5.74	-0.33
BiSeI	4.27	2.88	3.27	3.64	95.5	81.6	2.61	0.62	0.41	5.30	5.20	0.10
BiTeF	4.15	3.02	2.55	2.74	86.8	108.2	3.24	0.40	0.77	4.74	4.92	-0.18
BiTeCl	4.31	3.06	2.96	3.38	89.7	93.3	2.77	0.42	0.59	5.08	6.05	-0.97
BiTeBr	4.35	3.06	3.09	3.56	90.4	89.2	2.62	0.42	0.52	4.98	5.74	-0.76
BiTeI	4.42	3.07	3.28	3.78	92.1	84.6	2.46	0.42	0.41	4.84	5.24	-0.40

5.2.2 Dynamical Stability

The structural stability of Janus BiXY monolayers are examined by phonon spectra analyses, and Fig.5.3 shows that the dispersion of the phonon modes are free from any imaginary frequencies, and all twelve structures are confirmed to be stable. The primitive cell of the SL- BiXY crystals consists of three atoms, resulting in 9 vibrational modes. The three acoustic phonon modes are the flexural acoustic(ZA) branch, the transverse acoustic (TA), and the longitudinal acoustic (LA) branches. The ZA phonon mode has quadratic dispersion while TA and LA phonon modes have linear dispersion near Γ -point as in other 2D systems anticipated by continuum elasticity theory[213]. It can be seen from Fig.5.3 that when the atomic mass of the elements becomes heavier for a given structure, all

phonon modes are pushed towards lower frequencies, and overall phonon spectra are narrowed. Additionally, in BiXF and BiTeY monolayers, a gap is noticed between acoustical and optical frequencies, which is due to the large mass differences between the constituent elements and weakened bond strength between the atoms. For the remaining structures, the low-frequency optical and acoustic branches overlap. The phonon bandgap reduces the phonon-phonon scattering rate (i.e., long phonon relaxation time) and leads to enhanced thermal conductivity[119, 120, 121].

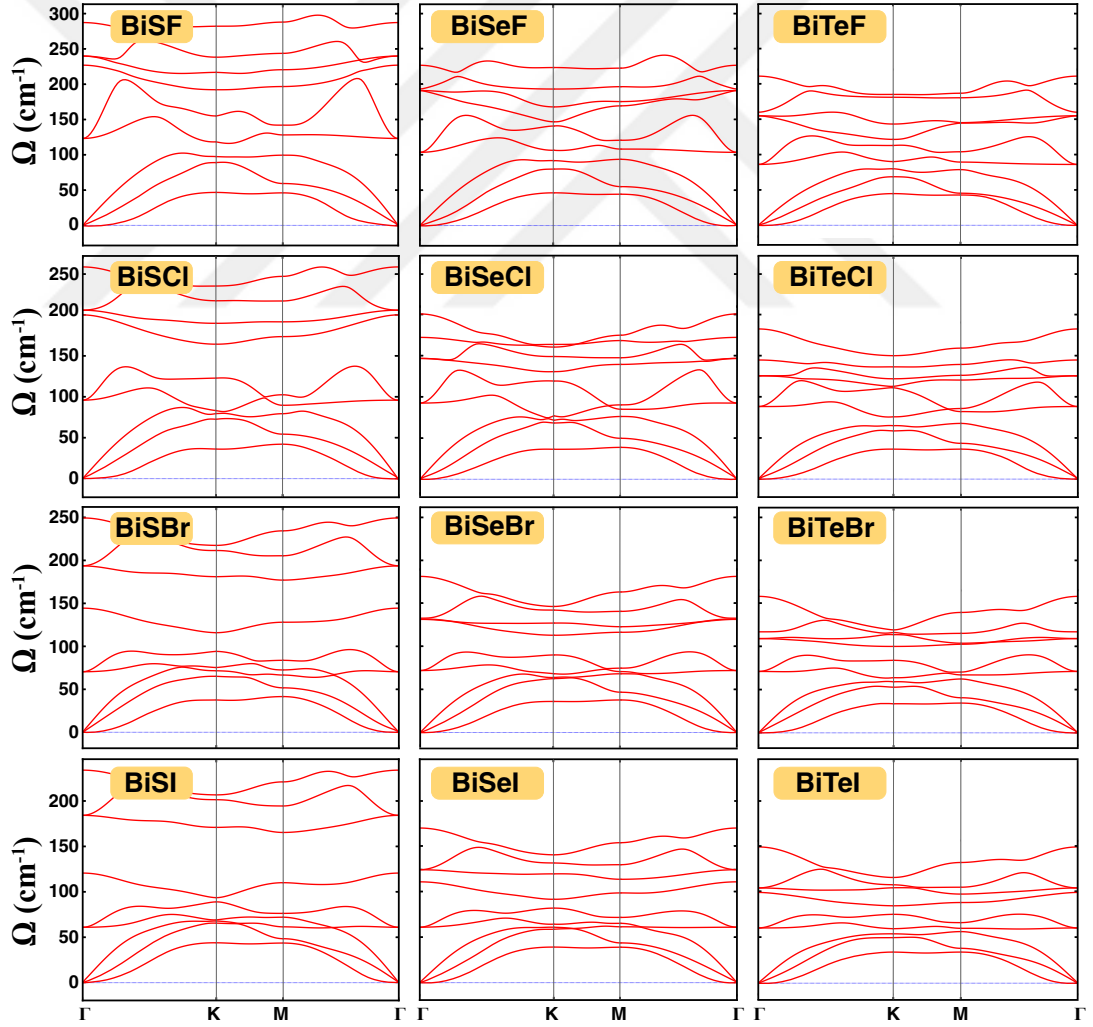


Figure 5.3: Phonon band diagrams of the Janus BiXY monolayers.

To test the stability of the structures at high temperatures, *ab initio* molecular dynamics (AIMD) simulations were carried out at 300 K and 600 K for 2 ps. To

alter the unit cell size constraint, $4 \times 4 \times 1$ supercell was used for BiXY monolayers. The variation of energy as a function of simulation time and the final snapshots of the resulting structures at 300 K and 600 K are illustrated in Fig.5.4, and Fig.5.4. AIMD simulations indicate that apart from slight distortions, which are not sufficient enough to break the Bi-X and Bi-Y bonds, the crystalline form of BiXY monolayers are preserved even at elevated temperatures and confirm the thermal stability.

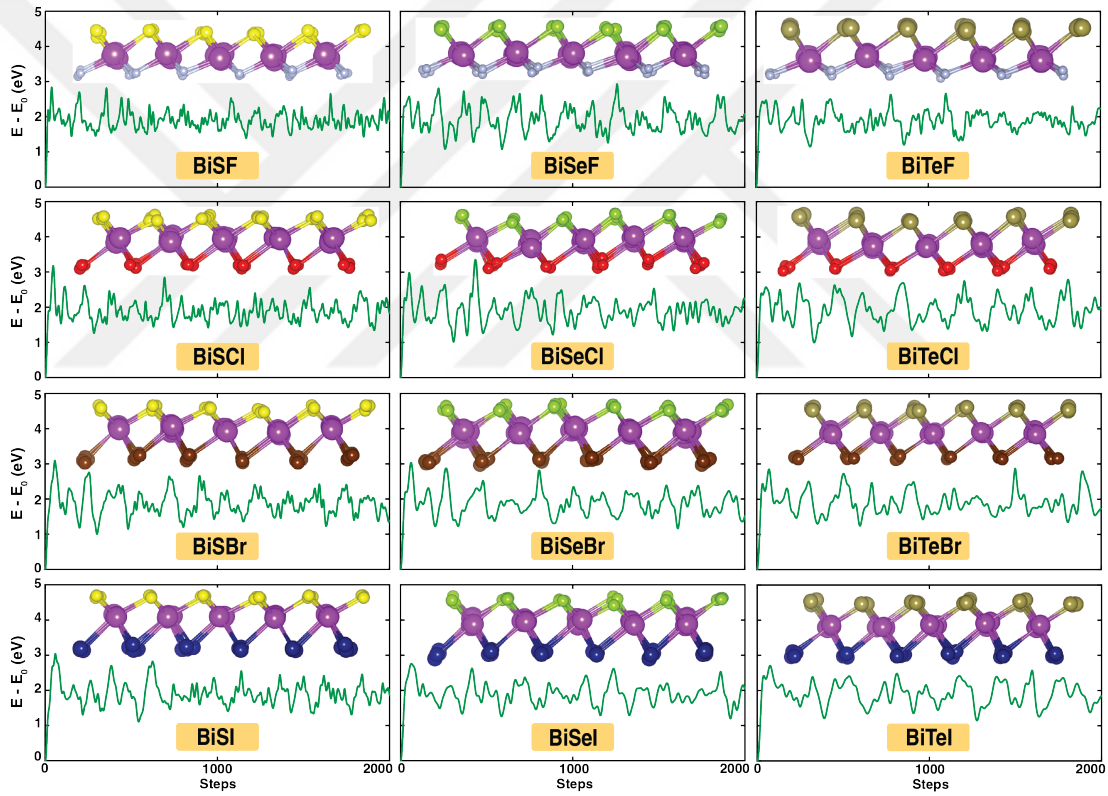


Figure 5.4: The variation of energy with respect to the number of steps at 300 K for Janus BiXY crystals. The insets show the snapshots of atomic configurations at the end of *ab initio* molecular dynamics (AIMD) simulations for each structure.

5.2.3 Vibrational Properties

Vibrational properties and the corresponding Raman spectra are closely related to the geometrical structure of the materials, and their analysis could be a useful

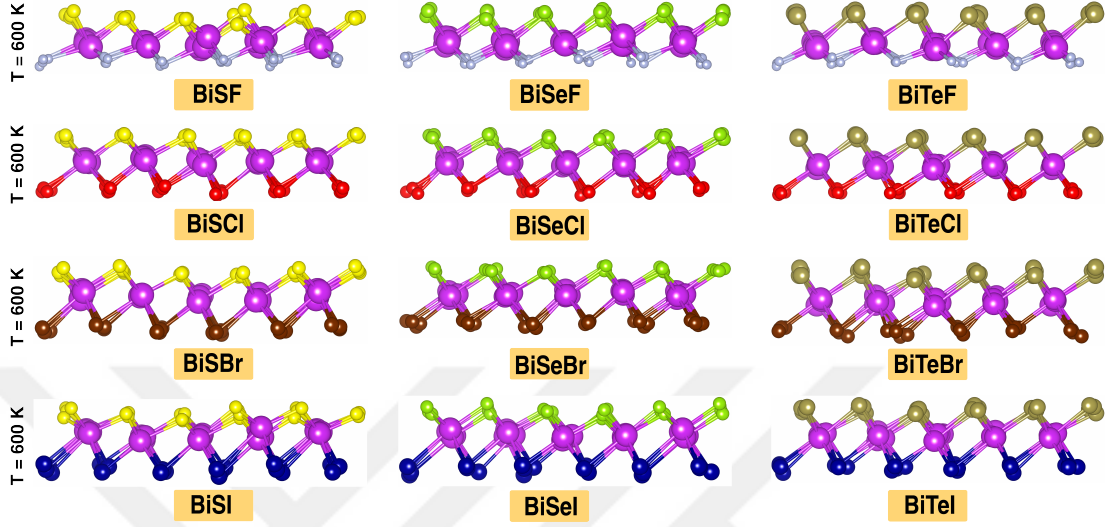


Figure 5.5: The snapshots of *ab initio* molecular dynamics (AIMD) simulations of BiXY Janus monolayers at 600 K.

technique to investigate the physical properties related to the lattice symmetries. Due to the C_{3v} symmetry, the six optical vibration modes are either non-degenerate or doubly degenerate at the Γ point. The irreducible representations of the corresponding optical phonons in the center of the BZ (Γ -point) for the Janus BiXY monolayers is given by $\Gamma^{C_{3v}} = 2A_1 + 2E$, where the E modes are assigned to the doubly degenerate in-plane displacements, whereas the non-degenerate A_1 modes are attributed to the vibration of the atoms along the z -direction. Both A_1 and E eigenmodes are Raman, and IR active modes since in the structures with C_{3v} symmetry, A_1 and E modes correspond to the linear and quadratic functions in the character table. Thus, the vibrational mode analysis of Janus BiXY monolayers reveals 4 peaks corresponding to the Raman and IR active modes. In a Raman experiment, the material is exposed to the light beams, and the scattered photons are immediately collected. The dispersion of the collected photons determines the Raman spectrum of the sample with respect to the frequency shift. According to the Raman theory, inelastically scattered photons originating from the oscillation of dipole moments of the crystal corresponds to the Raman active vibrational modes. The Raman intensity of a structure is mainly affected by incident light source wavelength and intensity, the concentration of the sample, and the scattering properties of the material [214]. The calculated Raman spectra of

Janus BiXY crystals are illustrated in Fig. 5.6(a-c). The atomic displacements of the Raman active modes are labeled on each spectrum to identify the origins of the Raman peaks. Depending on the atomic mass and bond strength, the Raman activity of the structures differs from each other. By going from the lightest (BiSF) to the heaviest (BiTeI) monolayer in the proposed systems, the Raman spectra shift towards lower frequencies mainly attributed to the increased mass and bond strength. In addition, for each subset of Y , the intensity of the $E^{(\text{Bi}-Y)}$ Raman peak increases down the chalcogen group. Our results point out that the most prominent Raman active mode in BiXF is $A_1^{(\text{Bi}-X)}$ while for BiTeY ($Y = \text{Br}$ and I) structures, $E^{(\text{Bi}-\text{Te})}$ mode is the most significant peak in the spectrum. For BiTeBr and BiTeI, the theoretical Raman spectra can be compared with the experimental data. Sklyadneva *et al.* demonstrated that the synthesized BiTeBr and BiTeI crystals possess four Raman active modes, the most prominent of which appear at the frequency of 98.5 and 99 cm^{-1} , respectively[215]. The highest calculated Raman active mode frequency is 108 cm^{-1} for BiTeBr and 103 cm^{-1} for BiTeI monolayer. The comparisons reveal that our results are in agreement with the experimental findings on synthesized bismuth tellurohalides. The intensity of the peaks in the spectrum is due to the contribution of macroscopic dielectric constants of vibrational modes to the Raman tensors. For BiSeF, BiTeF monolayer, $E^{(\text{Bi}-\text{F})}$ Raman mode and for BiTeI, $A_1^{(\text{Bi}-\text{I})}$ mode is vanished which indicates that their intensity is too weak to observe. To better explain the vibrational character of the BiXY monolayers, BiSeI monolayer is considered as a prototype to exemplify the four distinct atomic displacements in the optical spectrum, and the corresponding results are illustrated in Fig.5.7.

5.2.4 Mechanical and Piezoelectric Properties

After revealing the structural stability, the elastic strain tensor is computed to study the mechanical properties of the proposed structures, and the non-zero elastic constants (C_{ij}) are listed in Table 6.2. Firstly, it should be noted that all Janus BiXY monolayers satisfy the Born and Huang criteria[216, 217] ($C_{11} > |C_{12}|$ and

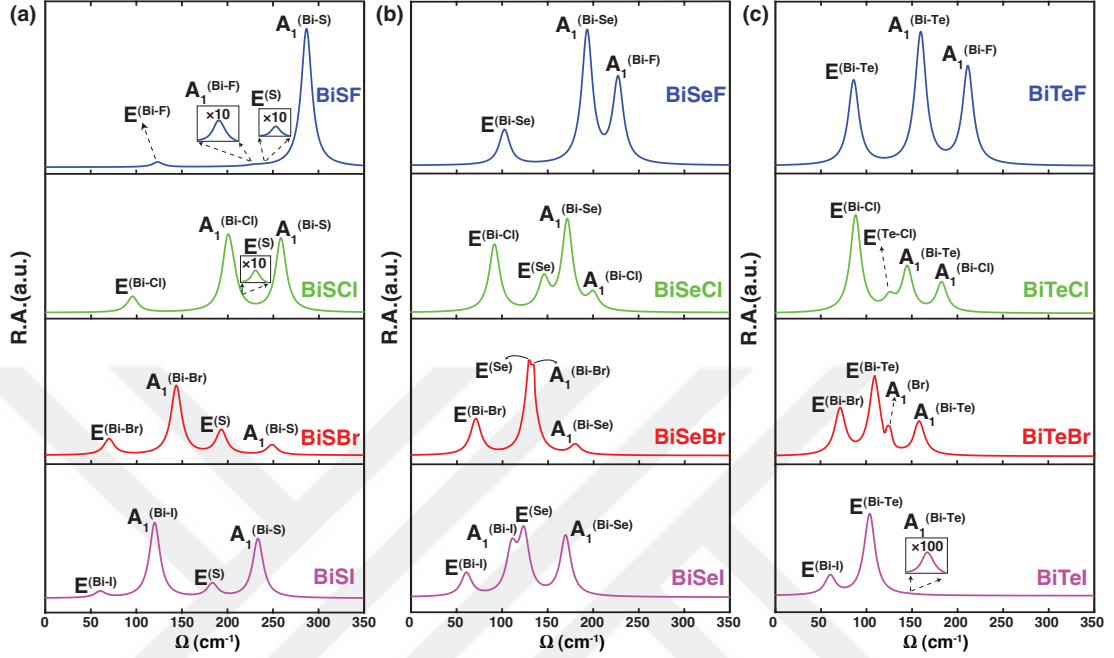


Figure 5.6: The normalized Raman activity spectra for (a) BiSY, (b) BiSeY, and (c) BiTeY monolayers.

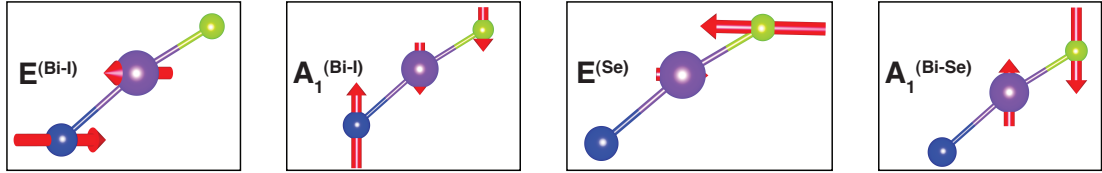


Figure 5.7: The atomic displacement of the Raman activity modes for BiSeI structure.

$C_{66} = (C_{11} - C_{12})/2 > 0$ for hexagonal lattice), indicating the mechanical stability. The elastic properties of the BiXY monolayers are examined in terms of two constants: the in-plane stiffness (Y_{2D}) and the Poisson's ratio (ν). The Y_{2D} , which is the 2D analogous to Young's modulus in 3D structures, is a measure of stiffness or flexibility of the materials. For the BiXY monolayers, the Y_{2D} is obtained by using the following relation, $Y_{2D} = (C_{11}^2 - C_{12}^2)/C_{11}$ and the results are summarized in the Table 6.2. For each subset of X (Y), Y_{2D} decreases down the chalcogen (halogen) group, which is related with the elongation of the bonds ($d_{\text{Bi-X}}$ and $d_{\text{Bi-Y}}$), i.e., weakening of the bonds between the atoms. Accordingly, the highest and lowest Y_{2D} is obtained for BiSF and BiTeI, respectively. A similar trend is also noticed in binary, and ternary TMDs [169]. The Y_{2D} values are in

between 25 - 42 N/m, indicating that BiXY monolayers are not stiff. While the obtained values are smaller than Y_{2D} of Janus TMDs, such as MoXY and WXY, they are within the same range of CrXY and VXY[169, 218]. Next, the Poisson's ratio ($\nu=C_{12}/C_{11}$), which is the ratio of the transverse contraction strain to the axial extension strain in the direction of the stretching force, is computed (Table 6.2). The calculated ν values are less than 1/3 (except BiSI), which implies that Janus BiXY monolayers are brittle based on the Frantsevich rule[129]. Additionally, in terms of bonding character, $\nu \approx 0.25$ marks a transition from ionicity to metallicity[219], therefore, for all the structures, the bonding nature is mainly ionic with a small metallic contribution.

Piezoelectricity is described as a coupling between electrical polarization and mechanical stress and can be produced when applied external stress generates electric dipole moments in the non-centrosymmetric materials (and vice versa)[171]. Due to the C_{3v} symmetry of the Janus BiXY monolayers, the piezoelectric tensor in these structures has two independent coefficients, i.e., e_{11}/d_{11} for in-plane piezoelectricity and e_{31}/d_{31} for out of plane piezoelectricity. The out-of-plane piezoelectric constants of the 2D materials are affected by out-of-plane asymmetry and charge density difference on two surfaces. The Voigt notation of Janus BiXY monolayers can be defined as;

$$e = \begin{pmatrix} e_{11} & -e_{11} & 0 \\ 0 & 0 & -e_{11} \\ e_{31} & e_{31} & 0 \end{pmatrix}, \quad d = \begin{pmatrix} d_{11} & -d_{11} & 0 \\ 0 & 0 & -2d_{11} \\ d_{31} & d_{31} & 0 \end{pmatrix}$$

The relation between the piezoelectric tensor coefficients for Janus BiXY monolayers are given by[86, 131, 21];

$$d_{11} = \frac{e_{11}}{c_{11} - c_{12}}, \quad d_{31} = \frac{e_{31}}{c_{11} + c_{12}} \quad (5.2)$$

The computed piezoelectric coefficients are summarized in Table 6.2. As can be seen, e_{ij} increases down the halogen and/or chalcogen group. As a comparison, for single layer MoS₂ and MoSSe structures, the e_{11} is reported to be 3.7×10^{-10} and 3.8×10^{-10} C/m, respectively[220]. The calculated values for BiSY and BiSeY

monolayers are in the range of $(1.22-5.09 \times 10^{-10} \text{ C/m})$, while for BiTeY structures, the e_{11} component is found to be smaller than most of the TMX_2 and Janus TMXY crystals. However, the obtained results of d_{11} for BiTeY monolayers are much larger than the predicted values for the TMX_2 and Janus TMXY crystals[86, 131]. The calculated piezoelectric coefficients, e_{11} (d_{11}), of SbTeI monolayer are reported as $2.69 \times 10^{-10} \text{ C/m}$ (12.95 pm/V), which are slightly larger than its Janus Bismuth counterpart[187]. In the case of 1T-TMDs, the piezoelectric coefficients are expected to be very small due to the central symmetry of the structures[22], while for BiXY crystal structures because of lack of inversion and mirror symmetry with respect to the Bi atoms, both in-plane and out-of-plane piezoelectric constants are significant. For ultra-thin materials, large values of out-of-plane piezoelectricity is desired for applications in electromechanical devices. The d_{31} coefficients are calculated to be -0.54, -0.57 and -0.56 pm/V for BiSI, BiSeI and BiTeI, respectively which are larger than that of 2D Janus TMD structures such as MoSSe(0.29 pm/V)[21], MoSTe(0.4 pm/V)[131] and 1H-WSO(0.4 pm/V)[221]. Such a large out-of-plane piezoelectricity makes Janus BiXI monolayers suitable candidates for applications in piezoelectric devices.

5.2.5 Electronic Properties

Lastly, the electronic properties of the Janus BiXY monolayers are analyzed. The electronic band structures are calculated initially at the level of GGA-PBE. As shown in Fig. 5.8, all structures are semiconductors, and except BiTeF, they have indirect bandgaps. Due to the presence of heavy elements such as Bi, Te, and I and the broken inversion symmetry of the structures, the inclusion of the spin-orbit coupling (SOC) effect is necessary. The inclusion of SOC reduces the bandgap ($E_g^{\text{PBE-SOC}}$), and the effect is more dramatic as the elements get heavier. When the calculations are repeated with HSE + SOC method, similar band profiles but widened band gaps ($E_g^{\text{HSE-SOC}}$) are obtained (Fig. 5.8). For a given subset, $E_g^{\text{HSE-SOC}}$ decreases moving down the chalcogen and halogen group, which correlated with the charge transfer ($\Delta\rho_{(\text{Bi-X})}$ and $\Delta\rho_{(\text{Bi-Y})}$). $E_g^{\text{HSE-SOC}}$ is between 1.07 eV to 2.42 eV and covers a range from infrared to visible parts of the optical

Table 5.2: For the BiXY Janus monolayers, relaxed-ion elastic coefficients, C_{ij} , in-plane stiffness, Y_{2D} , and Poisson's ratio, ν , piezoelectric stress coefficients, e_{ij} , and the corresponding piezoelectric strain coefficients, d_{ij} . Note that the values of e_{ij} are multiplied by 10^{-10} .

	$C_{11}=C_{22}$	C_{12}	Y_{2D}	ν	e_{11}	e_{31}	d_{11}	d_{31}
Structure	(N/m)	(N/m)	(N/m)	(-)	(C/m)	(C/m)	(pm/V)	(pm/V)
BiSF	45	12	42	0.26	3.06	-0.19	9.11	-0.33
BiSCl	35	10	32	0.29	4.12	-0.13	16.61	-0.29
BiSBr	34	11	31	0.32	4.41	-0.18	19.11	-0.41
BiSI	33	11	29	0.34	5.09	-0.24	23.11	-0.54
BiSeF	43	11	40	0.26	1.22	-0.11	3.81	-0.20
BiSeCl	33	9	30	0.27	2.68	-0.11	11.20	-0.26
BiSeBr	32	9	29	0.29	3.03	-0.16	13.51	-0.4
BiSeI	31	10	28	0.31	3.65	-0.23	17.12	-0.57
BiTeF	39	11	36	0.27	-2.45	0.04	-8.54	0.07
BiTeCl	30	7	28	0.24	0.75	-0.07	3.29	-0.18
BiTeBr	28	7	26	0.26	1.21	-0.11	5.78	-0.31
BiTeI	27	7	25	0.27	1.87	-0.19	9.53	-0.56

spectrum. The calculated partial density of states (PDOS) of the Janus BiXY monolayers are shown in Fig.5.10. It is seen that for the structures with the same halogen atom, the PDOS diagrams are similar to each-other. Our results indicate that the states near the valence band maximum (VBM) are mainly composed of X-p and Y-p orbitals. In contrast, the conduction band minimum (CBM) states are dominated by the Bi-p orbital in all structures which is in good agreement with the previous studies on BiTeX crystals[208, 209]. It is noticed that the spin-orbit splitting in energy bands is more significant in the structures with heavier elements and more distinct broken inversion symmetry. Since the electronic band structure profile of Janus BiXY monolayers are similar to each other, BiSI is chosen as a prototype to represent the band splitting near the Γ -point. As it is seen from Fig. 5.9, the degenerate conduction band minimum (CBM) is reduced to the lower energies and split into two branches following the inclusion

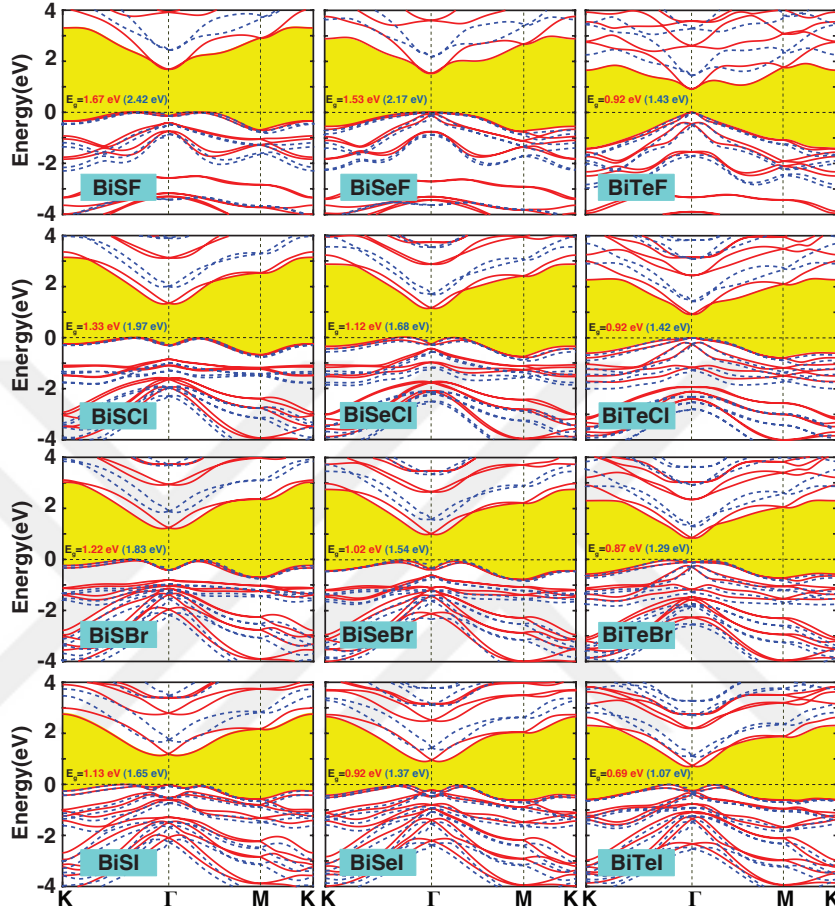


Figure 5.8: Calculated electronic band structures for Janus BiXY monolayers by using GGA-PBE + SOC and HSE06 + SOC are shown by red solid and dashed blue lines, respectively. The fundamental band gaps are shaded yellow. The Fermi level is set to zero.

of SOC. This can be considered as valid evidence of the Rashba splitting in the system. The strength of the Rashba splitting can be defined by two parameters; momentum offset (k_o) and the Rashba energy (E_R). The relation between these two terms and Rashba coefficient (α_R) is given by $\alpha_R = 2E_R/k_o$. The α_R of 2D materials should be large enough to be used in spintronic applications. E_R and α_R for the Janus BiXY monolayers are computed and listed in Table 5.3. It is noticed that, among the considered structures, BiXF (BiXI) monolayers have the lowest (highest) value of E_R and α_R . The obtained values of E_R and α_R are in for BiTeBr and BiTeI monolayers are in a good agreement with the previous theoretical calculations[186, 50].

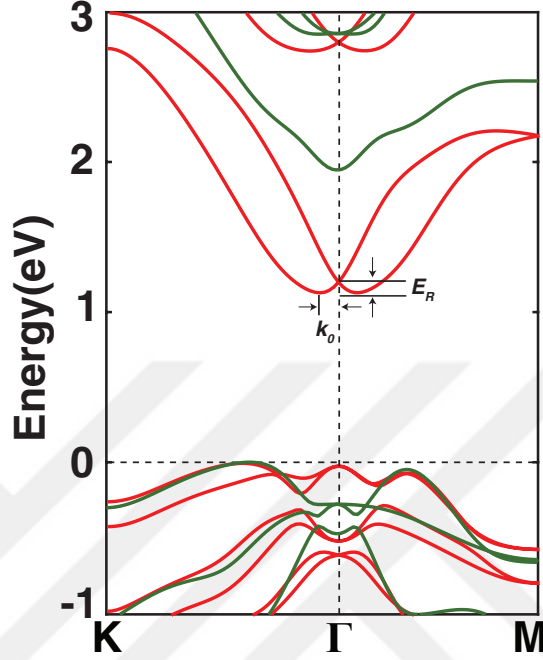


Figure 5.9: Closeup view of the electronic band structure of BiSI monolayer around the Γ -point and along the K - Γ - M points to exhibit the momentum offset k_o and the Rashba energy E_R . PBE and PBE-SOC results are shown by dark green and red lines, respectively.

5.3 Conclusion

In summary, we have systematically investigated structural, vibrational, elastic, piezoelectric, and electronic properties of the Janus BiXY ($X = \text{S, Se, Te}$ and $Y = \text{F, Cl, Br, I}$) monolayers. Our vibrational frequency analysis and *ab initio* molecular dynamics simulations up to 600 K reveal that all of the proposed Janus BiXY crystals are dynamically stable. The calculated Raman spectra exhibit that BiXY monolayers possess four typical Raman active modes. To characterize the mechanical response in the elastic regime, the in-plane stiffness and Poisson's ratio are calculated, and the results indicate that the considered systems are flexible and brittle. Following the calculation of the elastic tensors, the piezoelectric coefficients are computed, and large out-of-plane piezoelectric constants are obtained, especially for BiXI monolayers, which are greater than those of prominent TMDs. The electronic structure calculations show that except

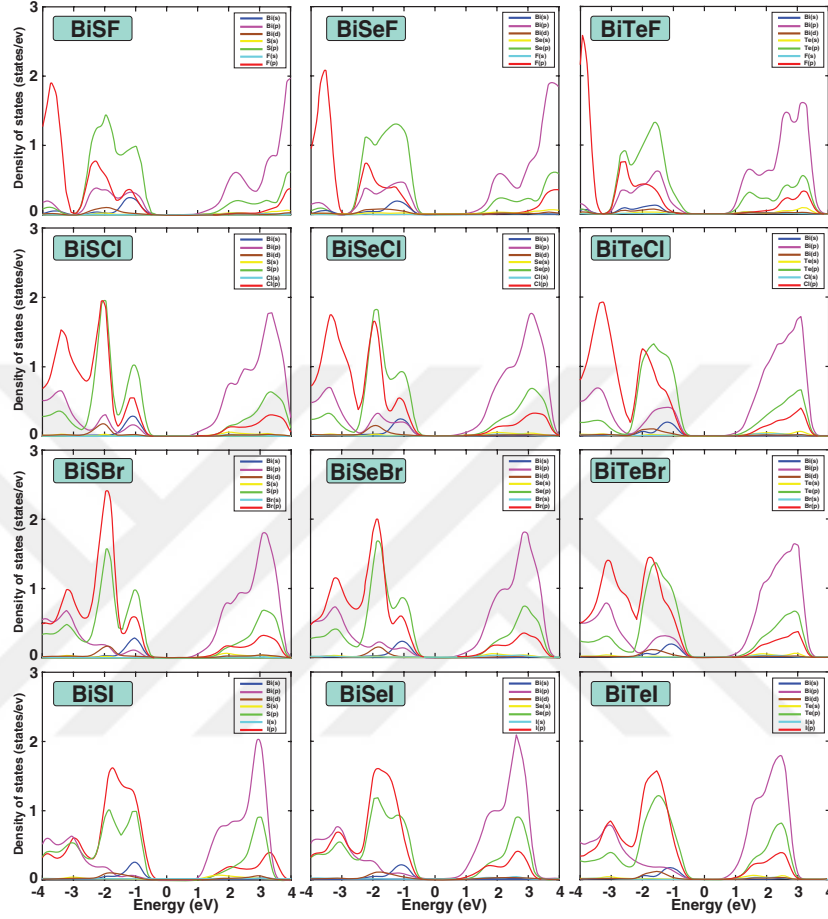


Figure 5.10: The projected density of states (PDOS) of Janus BiXY ($X = \text{S, Se, Te}$ and $Y = \text{F, Cl, Br, I}$) monolayers

BiTeF, which is a direct bandgap semiconductor, the rest of the monolayers are indirect bandgap semiconductors varying between 1.07 eV and 2.42 eV, which covers a range from infrared to visible spectrum. The inclusion of spin-orbit coupling results in large band splitting and momentum shift in conduction band minimum near Γ -point, which indicates the Rashba effect in these systems.

Table 5.3: Energy band gaps at the level of GGA-PBE, E_g^{PBE} ; GGA-PBE + SOC, $E_g^{\text{PBE-SOC}}$; HSE06 + SOC, $E_g^{\text{HSE-SOC}}$; the Rashba energy E_R and the Rashba coefficient, α_R for the BiXY Janus monolayers.

	E_g^{PBE}	$E_g^{\text{PBE-SOC}}$	$E_g^{\text{HSE-SOC}}$	E_R	α_R
Structure	(eV)	(eV)	(eV)	(meV)	(eV Å)
BiSF	1.98	1.67	2.42	2	0.19
BiSCl	1.80	1.33	1.97	29	1.20
BiSBr	1.77	1.22	1.83	40	1.37
BiSI	1.93	1.13	1.65	71	1.67
BiSeF	2.01	1.53	2.17	2	0.20
BiSeCl	1.65	1.12	1.68	25	1.30
BiSeBr	1.56	1.02	1.54	34	1.44
BiSeI	1.63	0.92	1.37	64	1.98
BiTeF	1.69	0.92	1.43	0	0.00
BiTeCl	1.77	0.92	1.42	12	1.25
BiTeBr	1.60	0.87	1.29	17	1.27
BiTeI	1.52	0.69	1.07	40	1.80

Chapter 6

Ternary, Pentagonal BNSi Monolayer

Recently, a new 2D metastable carbon allotrope composed of only pentagonal carbons (penta-graphene) has been proposed, and its dynamical stability has been verified by state-of-the-art theoretical calculations [56]. Unlike planar graphene, which is a semi-metal, penta-graphene is buckled and possesses a wide energy bandgap (3.25 eV) [56]. This indicates the effect of structural form on the physical properties of carbon allotropes [222]. Afterward, the 2D pentagonal configuration has been experimentally demonstrated following the fabrication of ultra-thin PdSe₂ flakes by micromechanical exfoliation technique [57, 58]. 2D penta-PdSe₂ is a semiconductor with high mobility and is also air-stable [57]. Later on, binary pentagonal structures including CN₂ [59], CB₂ [60], BN₂ [61], and SiC₂ [62] have been predicted and characterized. Similar to penta-graphene, the buckled nature of these materials facilitates their functionalization by chemical modifications [223]. Additionally, they exhibit remarkable physical properties, making them suitable materials for various applications, such as lithium-ion batteries [224]. By applying first-principles approaches, it has been shown that the penta-CN₂ sheet owns notable mechanical and thermal properties such as large in-plane stiffness (319 N/m) and high lattice thermal conductivity (661 W m⁻¹ K⁻¹) [59].

Li *et al.* have demonstrated that penta-CB₂ is a wide, indirect bandgap semiconductor and is dynamically stable [60]. Furthermore, the buckled structure of penta-CB₂ can be flattened by applying mechanical strain, and this results in semiconductor to semi-metal transition [60]. It has been reported that the monolayer penta-BN₂ possesses intriguing properties (e.g., high in-plane stiffness and negative Poisson's ratio), and its energy bandgap can be tuned by ionizing the structure [61]. In another study, it has been verified that the penta-SiC₂ monolayer is kinetically stable and possesses substantial features such as high carrier mobility, which make it a promising material for water splitting applications [62].

The design of pentagon-based 2D structures is no longer limited to unitary or binary forms. More recently, in parallel with the attempts to explore novel 2D pentagonal structures, the formation of ternary penta-sheets has been proposed [63, 225, 226]. It has already been shown in transition metal dichalcogenides (TMDs) that going from binary to ternary systems can offer additional degrees of freedom, which leads to distinct physical properties [19, 18, 221]. Computational studies reveal that a ternary pentagonal monolayer BCN (penta-BCN) is dynamically and mechanically stable and has remarkable physical properties such as wide, direct bandgap (2.81 eV) and significant piezoelectric coefficients, which are larger than those of functionalized penta-graphene [63]. Similar to penta-BCN, penta-CNP has also been found to be stable and is a direct bandgap semiconductor with a large spontaneous polarization [225]. Recently, binary and ternary 2D penta-XC₂ (X = Si, Ge, Sn) have been proposed, and their unique mechanical, electronic, and optical properties have been investigated [62]. In parallel with these advancements, recently, silicon nanoribbons composed of pentagon-rings have been grown on Ag(110) surfaces [227, 228, 229], which can be considered as a critical step for realizing 2D pentagonal structures. However, free-standing penta-silicene has been found to be unstable [230], it can be stabilized by surface decoration [231], stacking [230], and structural modification [232]. Inspired by the synthesis of penta-Si nanoribbons, advancements in 2D pentagonal systems, and recent developments on ternary structures, in this study, we propose and investigate a new ternary pentagon-based 2D monolayer, namely penta-BNSi and systematically study its basic physical properties and potential application

in photocatalytic water splitting applications.

6.1 Methodology

In the present work, all first-principles calculations were performed within the framework of density functional theory (DFT) [104, 105] which was implemented in Vienna *Ab initio* Simulation Package (VASP) [106, 107, 108, 109]. The projector augmented wave (PAW) [155] method was utilized to describe the pseudopotentials of B, N, and Si elements. The exchange-correlation term was treated by the generalized gradient approximation (GGA) as parameterized within the Perdew-Burke-Ernzerhof (PBE) form [80]. To acquire electronic properties and energy bandgap, the Heyd-Scuseria Ernzerhof (HSE06) hybrid functional approach was utilized [112, 113]. The HSE06 functional was constructed by mixing 0.25 of the nonlocal Fock exchange with 0.75 of PBE exchange and screening length of $\lambda = 0.2 \text{ \AA}^{-1}$. A plane-wave basis set with a cutoff energy value of 520 eV was taken for all calculations. The Brillouin Zone (BZ) was sampled by using $24 \times 24 \times 1$ uniform k -point meshes within Monkhorst-Pack scheme [114]. The convergence threshold for electronic relaxation between the successive steps in the total energy calculations was set to 10^{-5} eV. For optimization of lattice constants and the ionic positions in the unit cell, the pressure on the lattice was reduced below 1.0 kbar, and a conjugate-gradient (CG) algorithm was used until the Hellmann-Feynman force components on each atom were decreased below 0.01 eV/ $\text{\AA}$. A vacuum space of $\sim 20 \text{ \AA}$ was inserted perpendicular to the 2D plane to avoid any interaction in the non-periodic direction. To examine the dynamical stability and obtain the phonon density of states (PhDOS) of the system, phonon spectrum analysis was carried out for $5 \times 5 \times 1$ supercell using the finite displacement method with fine q-grid [115]. To test the thermal stability of the structure, *ab initio* molecular dynamics (AIMD) calculations were performed for $5 \times 5 \times 1$ supercell by implementing the constant volume and temperature (NVT ensemble) method where the temperature was controlled by employing the Nose-Hoover thermostat [233, 234]. The piezoelectric stress tensors were calculated by directly using the density functional perturbation theory (DFPT) method with a

$48 \times 48 \times 1$ k -point meshes, and the plane wave cutoff energy was increased to 700 eV. For the calculation of the optical properties, random phase approximation (RPA) [235, 236] on top of GW was employed with $8 \times 8 \times 1$ k -point mesh, 480 eV cutoff energy, and the number of bands was tripled. The complex dielectric function $[\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)]$ was computed by considering the light polarization along x - and y -directions. To examine the optical response of the system beyond the independent-particle approach, single-shot G_0W_0 approximation [237] was employed, and excitonic effects were treated by solving the Bethe-Salpeter equation (BSE) [238, 239] within the Tamm-Dancoff approximation. The Bader charge technique was employed to estimate the net charge transfer between the atoms [116].

6.2 Results and Discussion

6.2.1 Atomic structure and Energetics

For the construction of an initial penta-BNSi structure, we consider the atomic configuration of penta-graphene and replace B, N, and Si elements with 3-, 3-, and 4-fold coordinated carbon atoms, respectively. After that, the structure is optimized by relaxing lattice vectors and atomic positions. Top and side views of the optimized penta-BNSi monolayer are shown in Fig. 6.1. The primitive cell of penta-BNSi crystal contains six atoms with the ratio of 1:1:1 for B:N:Si and its geometry belongs to the C_2^2 symmetry (space group No.4) identical with penta-BCN [63]. The atomic bond lengths between the B-N, B-Si, and N-Si atoms (d_{B-N} , d_{B-Si} and d_{N-Si}) are 1.41, 2.04 and 1.81 Å, respectively. The optimized lattice constants of penta-BNSi structure are $\mathbf{a}=4.44$ Å and $\mathbf{b}=4.40$ Å and the layer thickness is $\mathbf{h}=1.60$ Å which is larger than those of penta-graphene [56] and penta-BCN [63] due to the longer bond length between the constituent elements. The Bader charge analysis shows that the net charge on B, N, and Si atoms are 0.03, -2.17, and 2.14 | e |, respectively. The average charge transfer among the atoms in the unit cell correlates with the electronegativity difference ($\Delta\chi$)

between the atoms. The anisotropic charge distribution combined with noncentrosymmetric geometry of penta-BNSi points out the emergence of spontaneous polarization in this system. To determine the strength of binding between the atoms, the cohesive energy per atom (E_C) is calculated by using the following expression;

$$E_C = \frac{[2E_T(\text{B}) + 2E_T(\text{N}) + 2E_T(\text{Si})] - [E_T(\text{BNSi})]}{6} \quad (6.1)$$

where $E_T(\text{B})$, $E_T(\text{N})$, and $E_T(\text{Si})$ are the single atom energies of B, N, and Si elements, respectively; $E_T(\text{BNSi})$ corresponds to the total energy of the penta-BNSi monolayer. The E_C is calculated as 5.43 eV/atom and indicates strong binding between constituent elements. When compared to similar configurations, E_C of penta-BNSi is higher than that of penta-silicene (3.84 eV/atom) [230] and slightly lower than that of penta-BCN (5.68 eV/atom) [63].

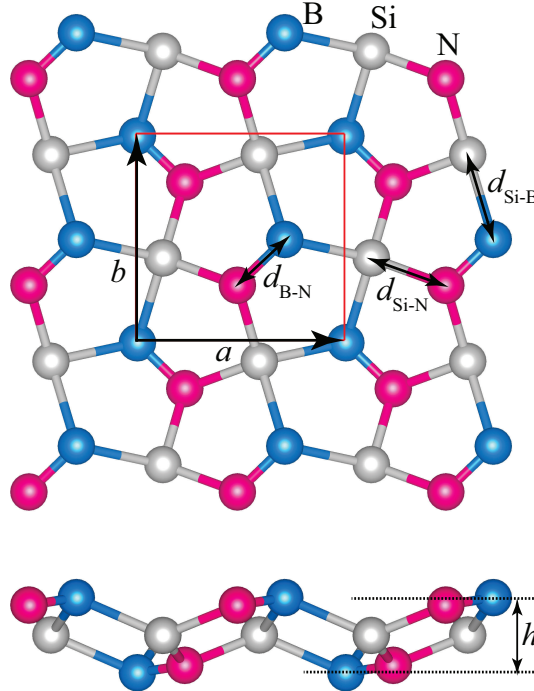


Figure 6.1: Top and side views of the optimized structure of penta-BNSi monolayer with the relevant structural parameters. The blue, purple, and gray spheres represent B, N, and Si atoms, respectively.

6.2.2 Dynamical, Thermal, and Mechanical Stability

To test the dynamical stability of the proposed structure, firstly, the phonon dispersion relations are calculated, and the corresponding phonon band structure calculated with the finite-displacement method is presented in Fig. 6.2(a) (The phonon band structure computed with DFPT is shown in Fig. 6.3). The phonon spectrum is free from any imaginary frequencies indicating dynamical stability of the penta-sheet. As mentioned above, the unit cell of the penta-BNSi monolayer consists of six atoms resulting in eighteen vibrational branches, including three acoustical and fifteen optical modes. The longitudinal and transverse acoustic (LA and TA) modes have linear dispersion near the Γ -point, whereas the flexural acoustic (ZA) eigenmode displays quadratic dispersion near the zone center as the force constants related to the transverse vibrations decay rapidly [240]. This mode also determines the bending rigidity of the monolayer [241].

In the phonon band structure, there is no phononic bandgap between the acoustic and optical phonon modes along M - Y symmetry points, leading to strong acoustic and optical scattering and consequently low thermal conductivity in the system [119, 120]. On the other hand, at the higher frequency ranges, bandgap among optical modes can be noticed. The presence of phonon bandgap in a material provides the ability to inhibit the propagation of mechanical waves in forbidden frequencies, which makes it an appropriate material for vibrational protection applications [242]. We also present the phonon density of states (PhDOS) of the penta-BNSi monolayer in Fig. 6.2(a). Analysis of the PhDOS results reveals that the high-frequency phonon modes are characterized by the vibrations of B and N atoms which are lighter elements than Si. On the other hand, the movement of Si atoms predominates the lower frequency phonon modes. Therefore, the gap in the higher frequency part of the phonon spectrum originates from the mass differences between constituent atoms.

To further investigate the structural stability of the penta-BNSi monolayer, AIMD simulation is performed at 1000 K for a total simulation time of 6 ps. To

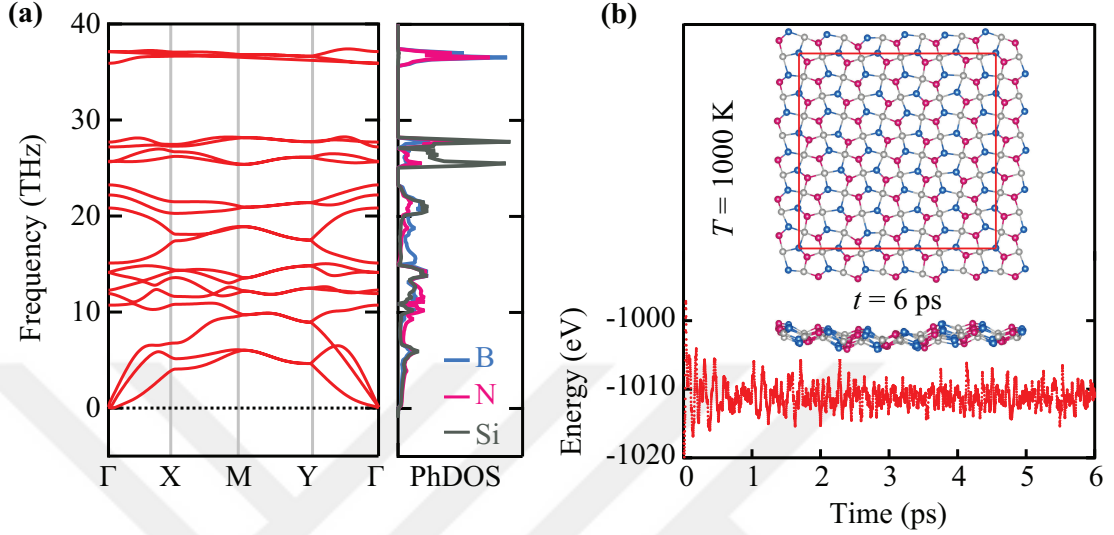


Figure 6.2: (a) Calculated phonon band dispersion and corresponding phonon density of states of penta-BNSi monolayer. (b) The variation of total energy with time during AIMD simulation at 1000 K for 6 ps. The insets represent the top and side views of atomic configurations at the end of the AIMD simulation.

remove the unit cell size constraint, a $5 \times 5 \times 1$ supercell is generated. As the total energy of the monolayer is sensitive to any bond breaking and bond-forming, the variation of the total energy with respect to the simulation time is plotted to monitor the alteration of crystalline morphology (Fig. 6.2(b)). The small fluctuations in total energy and the final snapshot of the atomic configuration at the end of the AIMD simulations indicate that penta-BNSi can withstand temperatures at and above room temperatures and preserve its atomic configuration without any significant distortion.

Finally, to ensure the mechanical stability of the penta-BNSi monolayer, the effect of strain on the structure is investigated. For a 2D crystal, the elastic energy change per unit area, $U_s(\epsilon)$, with respect to the small strain levels can be written as [243];

$$U_s(\epsilon) = \frac{1}{2}C_{11}\epsilon_x^2 + \frac{1}{2}C_{22}\epsilon_y^2 + C_{12}\epsilon_x\epsilon_y + 2C_{66}\epsilon_{xy}^2 \quad (6.2)$$

where ϵ_{ij} and C_{ij} refer to the strain and linear elastic constants, respectively,

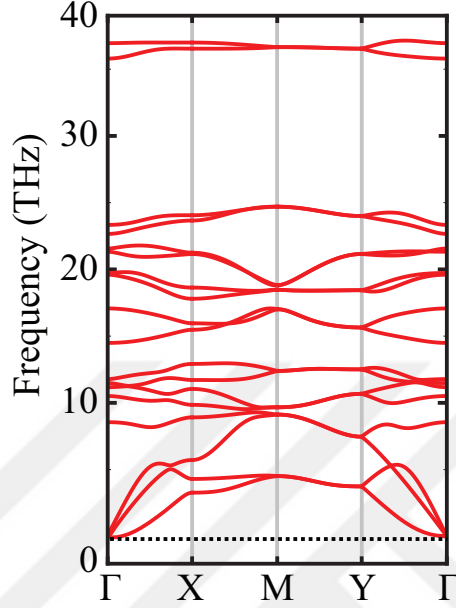


Figure 6.3: Phonon band structure of penta-BNSi monolayer calculated with density functional perturbation theory.

according to the standard Voigt notation (i.e. $1 \equiv xx$, $2 \equiv yy$, and $6 \equiv xy$). ϵ_{ij} can be described as $\epsilon_{ij} = \frac{L'_i - L_i}{L_i}$ where L'_i and L_i are the lattice constants of the strained and unstrained structures. The variation of elastic energy as a function of applied strain levels are shown in Fig. 6.6. The calculated elastic constants are $C_{11} = 114.46$ N/m, $C_{22} = 111.21$ N/m, $C_{12} = C_{21} = 12.76$ N/m and $C_{66} = 48.97$ N/m. $C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$ conditions according to the Born-Huang criteria [216] are satisfied, which further validates the mechanical stability of penta-BNSi monolayer.

6.2.3 Mechanical Properties

After revealing the stability of penta-BNSi monolayer, the mechanical properties within the elastic regime are studied by computing in-plane stiffness (or 2D Young's modulus, Y_{2D}), Poisson's ratio (ν), and ultimate tensile strength (UTS). The orientation-dependent Y_{2D} and ν can be calculated by using the following formulas;

$$Y_{2D}(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}s^4 + C_{22}c^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{66}} - 2C_{12}\right)s^2c^2} \quad (6.3)$$

$$\nu(\theta) = \frac{C_{12}(s^4 + c^4) - \left(C_{11} + C_{22} - \frac{C_{11}C_{22} - C_{12}^2}{C_{66}}\right)s^2c^2}{C_{11}s^4 + C_{22}c^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{66}} - 2C_{12}\right)s^2c^2} \quad (6.4)$$

where $s = \sin(\theta)$ and $c = \cos(\theta)$, respectively. The obtained results are shown in Fig. 6.4. Y_{2D} is a measure of the rigidity and depends on the crystalline structure and the bonding nature among the constituent elements. The computed Y_{2D} for penta-BNSi monolayer along the x and y directions are found to be $Y_{2D}^a = 113$ N/m and $Y_{2D}^b = 109$ N/m, respectively and indicates that penta-BNSi is a soft material. It can also be noticed from Fig. 6.4(a) that $Y_{2D}(\theta)$ is quasi-isotropic. As compared to similar pentagonal systems, while penta-BNSi is more flexible than penta-graphene ($Y_{2D}^a = Y_{2D}^b = 263$ N/m) [56] and penta-BCN monolayer ($Y_{2D}^a = 223$ N/m and $Y_{2D}^b = 189$ N/m) [63], is stiffer than multi-layered (52 - 88 N/m) [230] and hydrogenated penta-silicene (23 N/m) [231].

Next, $\nu(\theta)$, which is defined as the negative ratio of the transverse contraction to the longitudinal extension strain is obtained and shown in Fig. 6.4(b). Similar to $Y_{2D}(\theta)$, $\nu(\theta)$ is found to be quasi-isotropic. While $\nu_a = \nu_b = 0.11$, the highest value is estimated as 0.12 at $\theta = 45^\circ$. Small value of $\nu(\theta)$ is also obtained for penta-BCN ($\nu_a = 0.02$, $\nu_b = 0.03$) and is correlated with the high-buckled morphology that reduces extension/contraction along the transverse direction due to strain.

The UTS is also an essential inherent mechanical property of 2D materials, described as the maximum value of tensile stress that a material can resist before breaking. To estimate UTS, firstly $3 \times 3 \times 1$ supercell is constructed to reduce the artificial effect of small unit cell size, and then the variation of stress as a function of the uniaxial and equi-biaxial tensile strains (up to $\sim 25\%$) is computed. It can be seen from Fig. 6.5 that up to $\sim 10\%$, the stress-strain curve is linear and specifies the range of elastic regime. After this threshold, the plastic deformation starts, and in-plane stress monotonically increases until the breaking point. UTS is obtained at 20%, 18%, and 17% uniaxial- x , uniaxial- y , and biaxial strain levels,

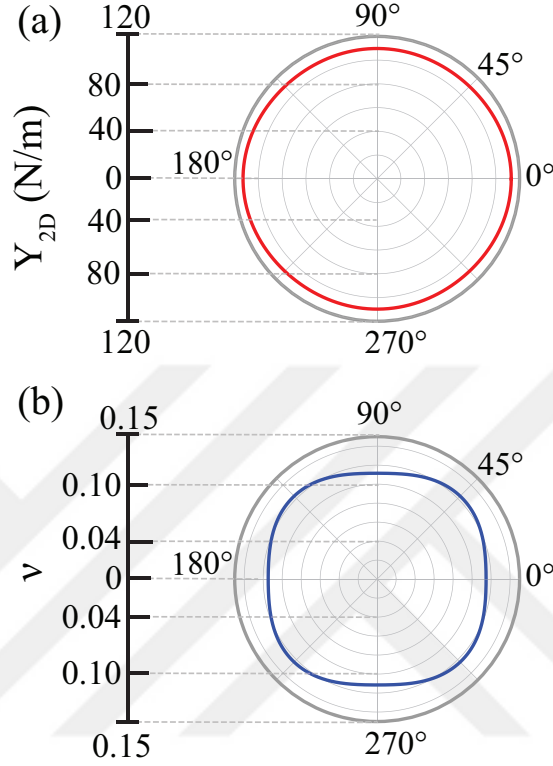


Figure 6.4: Schematic representation of the angle-dependent (a) in-plane stiffness (Y_{2D}) and (b) Poisson's ratio (ν) of penta-BNSi monolayer.

respectively. These strain levels are comparable to penta-graphene [56] and penta-SiC₂ ($\sim 21\%$) [62] and points out the ductility of penta-BNSi.

6.2.4 Electronic Properties

Next, the electronic and transport properties of the penta-BNSi monolayer are investigated. To obtain an accurate energy bandgap, the electronic band structure is calculated by HSE06 hybrid functional and illustrated in Fig. 6.7. The bandgap is equal to 2.21 eV, and valence band maximum (VBM) and conduction band minimum (CBM) reside along the $X - \Gamma$ path in the BZ. Due to the minimal momentum difference between the VBM and CBM, the penta-BNSi monolayer can be considered as a quasi-direct bandgap semiconductor. The bandgap of penta-BNSi is narrower than that of penta-BCN (2.81 eV) [63] and penta-SiC₂

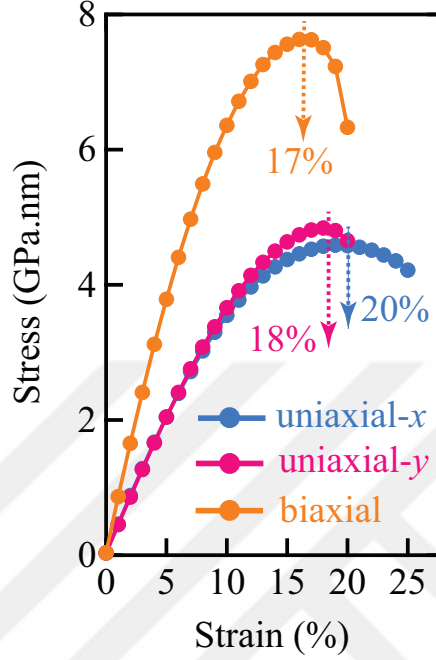


Figure 6.5: The variation of stress with respect to biaxial and uniaxial (x and y directions) strain for penta-BNSi monolayer.

(2.39 eV) [62], correlated with the reduced orbital overlapping due to elongation in bond lengths. To understand the electronic character of the penta-BNSi monolayer, the projected density of states (PDOS) is calculated and plotted in Fig. 6.7. Analysis of the PDOS reveals that VBM is mainly contributed from the B- p_x , B- p_y , and Si- p_z orbitals, and since Si and B atoms are bonded with N atoms, this results in the hybridization of p orbitals of B and Si atoms with the orbitals of N atoms and formation of flat bands near VBM. Moreover, the electronic states near CBM mainly belong to the p_z orbitals of B and N atoms.

To characterize the electronic transport features of penta-BNSi monolayer, effective mass (m_e^* , m_h^*) and mobility (μ_e , μ_h) of charge carriers (electron and hole) are also computed. The m^* values are estimated by the parabolic fitting of the energy band curvature around Γ -point using $m^* = \hbar^2 / (\frac{\partial^2 E(k)}{\partial k^2})$ formula; where $\hbar$ and k represent reduced Planck constant and the wave vector, respectively; $E(k)$ is the energy of the lowest conduction band (LCB) or highest valence band (HVB) for holes and electrons, respectively. The obtained results of effective masses along x - and y -directions and their average ($m_d = \sqrt{m_x^* m_y^*}$) are given

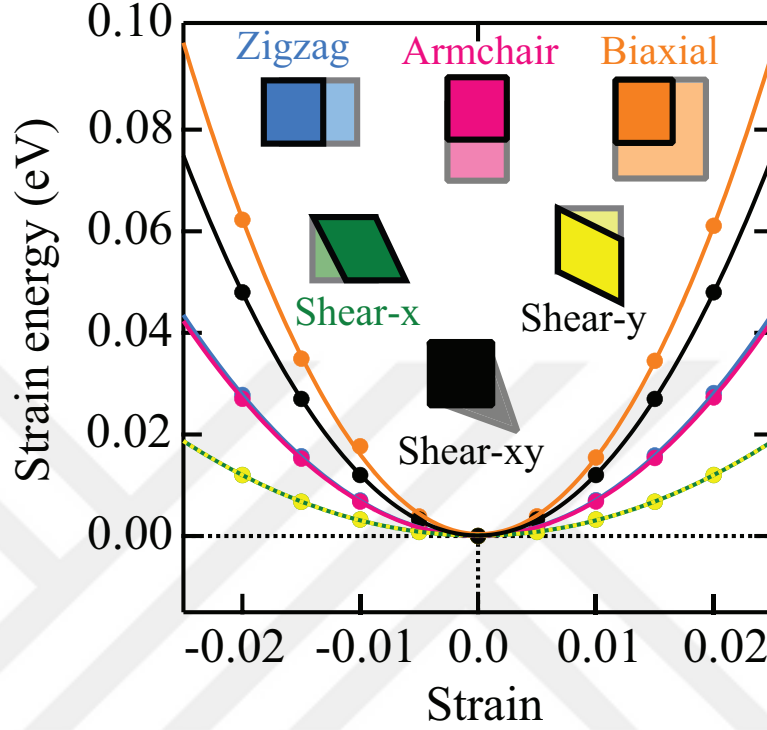


Figure 6.6: Calculated strain energy of penta-BNSi monolayer with respect to the applied strain.

in Table 7.1. m_e^* and m_h^* along the Γ -X (Γ -Y) direction are $0.44 m_0$ and $0.98 m_0$ ($0.44 m_0$ and $4.26 m_0$), respectively. Once the m^* is obtained, the mobility can be estimated by applying deformation potential theory; [244]

$$\mu_{2D} = \frac{e\hbar^3 C_i}{k_B T m_i^* m_d E_d^2} \quad (6.5)$$

where e , k_B , and T are the electron charge, Boltzmann constant, and temperature, respectively; C_i refers to the elastic constants and $E_d^2 = \Delta E / (\frac{\Delta l}{l_0})$ is the deformation potential of the HVB for a hole or the LCB for an electron in the transport direction, and ΔE is the energy change of the HVB or LCB under small lattice strain. The calculated band energies of the HVB or LCB with respect to the vacuum energy of the structure as a function of $\Delta x/x$ and $\Delta y/y$ are presented in Fig. 6.8.

Based on Eq. (6.5), the μ_e and μ_h of penta-BNSi monolayer are calculated

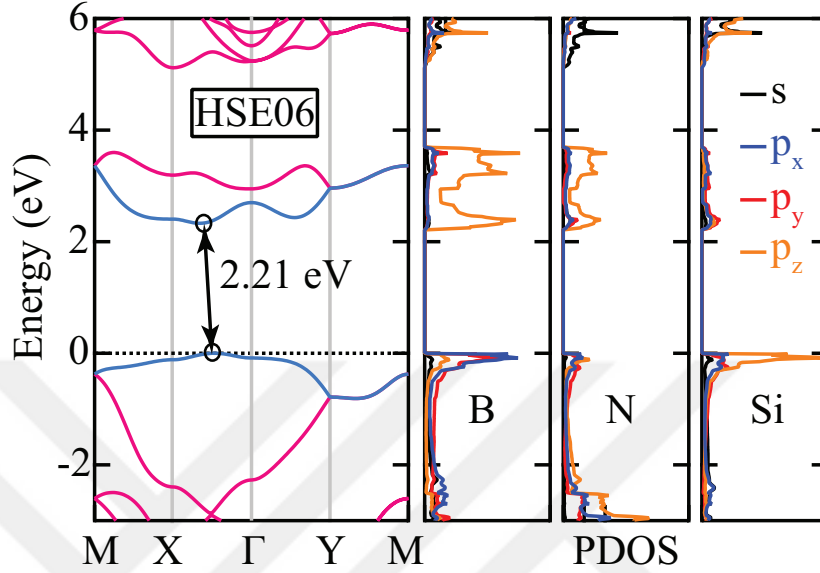


Figure 6.7: The electronic band structure and the corresponding projected density of states (PDOS) of penta-BNSi monolayer calculated at the level of HSE06. The Fermi level is set to 0 eV. The highest valence band (HVB) and the lowest conduction band (LCB) are shown with blue solid lines.

along x - and y -directions and listed in Table 7.1 together with relevant parameters. μ_e^x and μ_e^y are found to be 1.46 and 21.4 ($10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), respectively. The hole mobilities are also high but significantly lower than electron mobilities and calculated as 0.44 and 0.04, ($10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for μ_h^x and μ_h^y , respectively. The strong anisotropy of the carrier mobilities along the transport directions reduces the probability of recombination of the photo-generated electrons and holes, thus can enhance the efficiency and performance of the device (e.g., the photocatalytic activity) together with the high mobility. It should be noted that even though

Table 6.1: Calculated carrier effective masses, m^* , in-plane stiffness, Y_{2D} in N/m, deformation potential constant E_d , and carrier mobility, μ_{2D} ($\times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) along Γ -X and Γ -Y directions at 300K.

Carrier type	m_x^*/m_0	m_y^*/m_0	m_d/m_0	Y_{2D}^x	Y_{2D}^y	E_d^x	E_d^y	μ_x	μ_y
Electron	0.44	0.44	0.44	113.03	109.74	0.92	0.24	1.46	21.4
Hole	0.98	4.26	2.05	113.03	109.74	0.52	0.86	0.44	0.04

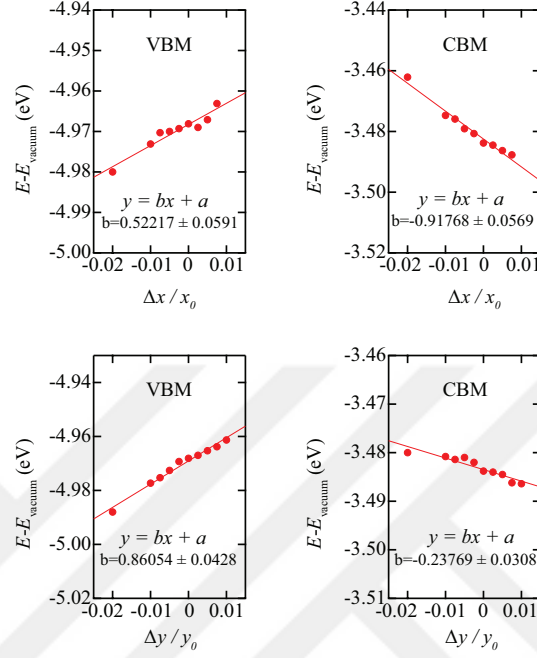


Figure 6.8: The variation of the energies of VBM and CBM with respect to the vacuum level as a function of lattice along x and y directions. The solid red lines are linear fitting to the data and the obtained slopes correspond to the deformation potential.

our results based on deformation potential theory suggest high electron mobilities, fully *ab initio* calculations that properly include scattering with all phonons are needed for more accurate estimations [245, 246, 247].

6.2.5 Piezoelectric Properties

Piezoelectricity is a unique material property that is described as the generating electric dipole moment from mechanical energy (or vice versa) in noncentrosymmetric structures [171]. Previous experiments have demonstrated that the piezoelectric response is enhanced in ultra-thin materials compared to their bulk counterparts [86, 248]. The piezoelectric stress tensor, e_{ijk} , can be defined as the coupling between electrical polarization (P_i) and strain (ε_{jk}) tensor. e_{ijk} is formulated as $e_{ijk} = \frac{\partial P_i}{\partial \varepsilon_{jk}}$, where i , j and k correspond to the x , y and z Cartesian directions, respectively. Due to the C_2^2 point group symmetry of penta-BNSi structure, the

piezoelectric stress tensors in the form of Voigt notation can be written as;

$$e_{ij} = \begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & e_{16} \\ e_{21} & e_{22} & e_{23} & 0 & e_{25} & 0 \\ 0 & 0 & 0 & e_{34} & 0 & e_{36} \end{pmatrix} \quad (6.6)$$

e_{ij} is related to the piezoelectric strain tensor d_{ij} and elastic stiffness constant C_{kj} through the equation below;

$$e_{ij} = d_{ik}C_{kj}. \quad (6.7)$$

Accordingly the relation among the elastic constants and piezoelectric strain and stress tensors can be defined as;

$$\begin{pmatrix} 0 & 0 & e_{16} \\ e_{21} & e_{22} & 0 \\ 0 & 0 & e_{36} \end{pmatrix} = \begin{pmatrix} 0 & 0 & d_{16} \\ d_{21} & d_{22} & 0 \\ 0 & 0 & d_{36} \end{pmatrix} \begin{pmatrix} C_{11} & C_{12} & C_{16} \\ C_{21} & C_{22} & C_{26} \\ C_{31} & C_{32} & C_{36} \end{pmatrix} \quad (6.8)$$

and corresponding piezoelectric strain coefficients are;

$$d_{16} = \frac{e_{16}}{C_{66}}, \quad d_{21} = \frac{C_{21}e_{22} - C_{22}e_{21}}{C_{21}C_{12} - C_{11}C_{22}}, \quad d_{22} = \frac{C_{12}e_{21} - C_{11}e_{22}}{C_{21}C_{12} - C_{11}C_{22}}, \quad d_{36} = \frac{e_{36}}{C_{66}} \quad (6.9)$$

The nonzero coefficients e_{16} and e_{36} represent the induced polarizations along the x and z directions (zx) when the strain is applied along these directions. On the other hand, e_{21} and e_{22} stand for the induced polarizations along the x and y directions, respectively, when the strain is induced along the y -direction. The calculated piezoelectric strain coefficient along x direction, d_{16} , for penta-BNSi monolayer is 1.71 pm/V which is found to be comparable to that of penta-BCN and penta-CNP nanosheets. On the other hand, penta-BNSi possesses a remarkable piezoelectric response in the y direction ($d_{21} = 3.59$ pm/V), superior than penta-BCN [63] and penta-CNP [225] and functionalized penta-graphene [249]

structures. This enhancement of piezoelectricity is highly desired and correlated with the more elastic character of penta-BNSi monolayer than other penta structures.

Table 6.2: The relaxed-ion piezoelectric stress, e_{ij} , and the corresponding piezoelectric strain coefficients, d_{ij} for 2D penta-BNSi, penta-BCN, and penta-CNP. Note that the values for e_{ij} are multiplied by 10^{-10} .

Crystal structure	e_{16} (C/m)	e_{21} (C/m)	e_{22} (C/m)	e_{36} (C/m)	d_{16} (pm/V)	d_{21} (pm/V)	d_{22} (pm/V)	d_{36} (pm/V)
penta-BNSi	0.84	3.78	-2.40	-0.26	1.71	3.59	-2.57	-0.53
penta-BCN [63]	1.80	1.93	-1.24	-0.08	1.72	0.87	-0.67	-0.076
penta-CNP [225]	1.78	2.37	-1.21	-0.11	1.80	1.39	-0.69	-0.1

6.2.6 Photocatalytic Properties

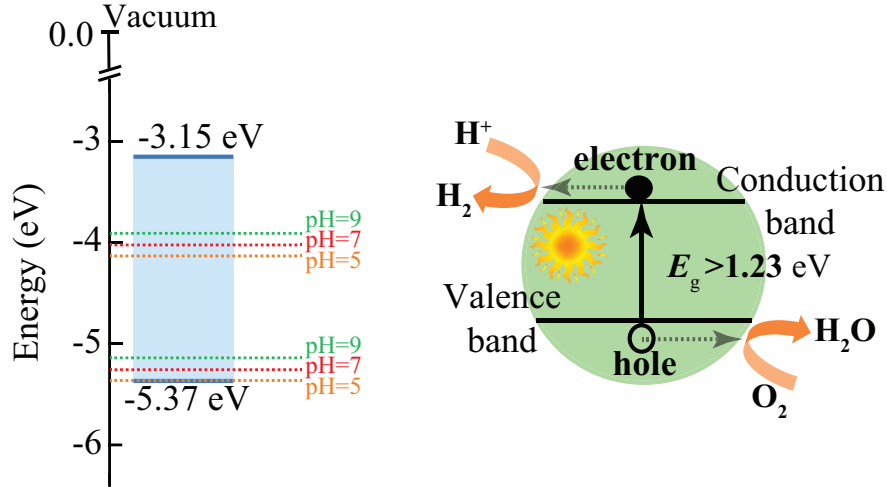


Figure 6.9: Schematic representation of the location of band edges with respect to the vacuum level calculated with HSE06 functional. The redox potential of water splitting at pH = 5, 7, and 9 are marked by orange, red, and green dashed lines, respectively.

Recent studies have shown that 2D semiconductors are among the best candidates for photocatalytic water splitting applications [250]. For a semiconducting

material, in order to be an efficient photocatalyst for water splitting (to split H_2O into H_2 and O_2), the following conditions must be fulfilled simultaneously. The energy bandgap of the system must exceed the free energy of water splitting (> 1.23 eV) and need to be smaller than 3 eV to assure effective solar light absorption [251]. Secondly, it should have suitable band edge positions so that the band edges cover the redox potentials of water, where the location of VBM must be lower than the oxidation level of $\text{O}_2/\text{H}_2\text{O}$ ($E_{\text{O}_2/\text{H}_2\text{O}} = -5.67 \text{ eV} + \text{pH} \times 0.059 \text{ eV}$) and the CBM should be higher than the reduction level of hydrogen ($E_{\text{H}^+/\text{H}_2} = -4.44 \text{ eV} + \text{pH} \times 0.059 \text{ eV}$). The proposed penta-BNSi monolayer satisfies the bandgap requirement of photocatalytic reaction with the bandgap of 2.21 eV. We further investigate the band edge positions of the structure by aligning them to the vacuum level and compared the results with the redox potentials for oxygen and hydrogen evolution reactions. The energy level of VBM and CBM for the penta-BNSi sheet is depicted in Fig. 6.9. As shown in the figure, the E_{CBM} of the structure is higher than the reduction potential of H^+/H_2 at $\text{pH} = 7$. Additionally, band edge positions satisfy the requirements for $9 \geq \text{pH} \geq 5$, indicating that penta-BNSi can also be functional in acidic and basic conditions. In other words, similar to other penta- and tetrahex-monolayers [62, 252, 253], penta-BNSi system possess the suitable bandgap and band edge positions to be used in photocatalytic water splitting.

As mechanical strain can significantly modify the electronic properties of 2D materials, the effect of uniaxial and biaxial strains on the electronic band structure of penta-BNSi is investigated. Fig. 6.10 illustrates the variation of the electronic bandgap and band edges with uniaxial (along x and y) and biaxial strains between -4% to 10%. At each strain point, the atomic positions are fully relaxed, and the band structures are calculated using the HSE06 hybrid functional. It is noticed that the energy levels of band edge positions do not significantly change under uniaxial strain. While bandgap remains almost constant for strain along x , it gradually decreases (increases) for tensile (compressive) strain along y . The effect of biaxial strain on band structure is more remarkable, and the trend is similar to uniaxial strain along y direction. The bandgap narrowing at $\sim -4\%$ is related to the onset of plastic deformation. Regarding the photocatalytic response, the

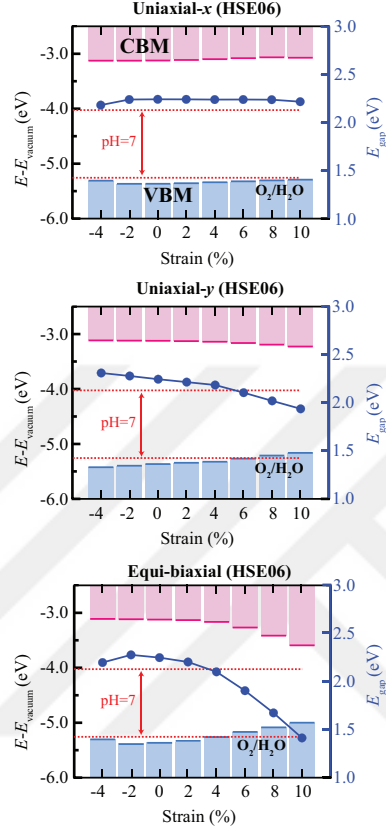


Figure 6.10: The variation of band edge positions of the VBM and CBM in penta-BNSi monolayer with respect to the vacuum level (computed with HSE06 functional) as a function of (a) uniaxial- x (b) uniaxial- y , and equi-biaxial strains. The light blue and pink bars illustrate the VBM and CBM energies, respectively. The variation of bandgap with strain is shown with dark blue, solid lines. The red dashed lines represent the redox potentials of water at $\text{pH} = 7$.

bandgap and band edge positions remain in the desired range, and penta-BNSi can be functional in photocatalytic water splitting applications under strain levels within the practical range. In addition, tunability of bandgap under strain is beneficial for optoelectronic applications.

6.2.7 Optical Properties

In addition to a suitable bandgap and proper band alignment, the optical absorption capability of 2D materials plays an essential factor in photocatalytic

applications. To study the optical response of penta-BNSi nanosheet, the optical absorption spectra along in-plane light polarization are investigated by considering the electron-hole (e-h) interactions. Based on the complex dielectric function ($\varepsilon(\omega)$), the absorbance ($A(\omega)$) can be determined by the following equation [254, 255, 256, 257];

$$A(\omega) = \frac{\omega}{c} L \varepsilon_2(\omega) \quad (6.10)$$

where c is the speed of light and L is the total size of the cell in layer-normal direction. The variation of $\varepsilon_2(\omega)$ and $A(\omega)$ with respect to the photon energy is shown in Fig. 6.12 (The frequency dependent absorption coefficient $\alpha(\omega)$ is presented in Fig. 6.12). The first prominent peaks are noticed in the visible and near-UV spectrum with high absorption and anisotropy in optical response is apparent [62, 252, 253]. When the e-h interactions are involved by solving the BSE, the optical transitions below the G_0W_0 bandgap (2.69 eV) arising from the excitonic effects are obtained. The exciton binding energy for the penta-BNSi monolayer is determined by the difference between the quasi-particle direct bandgap and the first peak and is found to be ~ 0.81 eV. The tightly bound excitons are correlated to quantum confinement and weak screening in low-dimensional systems and dominate the optical features [258]. The significant exciton binding energy and flat dispersion of the highest valence band and lowest conduction band suggest that excitons in penta-BNSi monolayer are Frenkel type [259], which can be ensured with analyzing the exciton wavefunction [260]. Consequently, in addition to charge carriers, excitons involved in the photoexcitation mechanism of penta-BNSi monolayer and significantly contribute to the photocatalytic features [261].

6.3 Conclusion

In conclusion, by using first-principles calculations, we design and characterize the ternary, pentagonal monolayer of BNSi. The phonon dispersion, *ab initio*

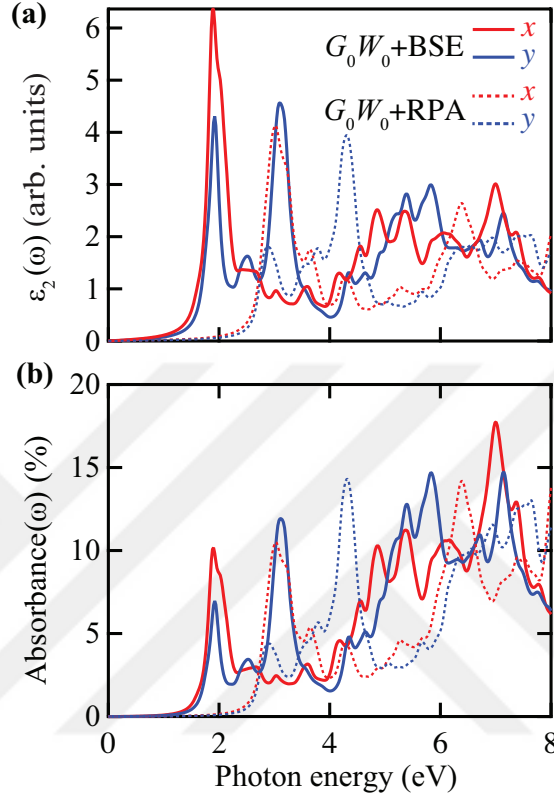


Figure 6.11: The variation of (a) imaginary part of the dielectric function ($\varepsilon_2(\omega)$) and (b) absorbance ($A(\omega)$) of penta-BNSi monolayer with respect to the photon energy for light polarized along x and y directions, calculated at the level of G_0W_0 -RPA and G_0W_0 -BSE.

molecular dynamics, and elastic tensor analysis reveal the structural, dynamical, and mechanical stability of the proposed system. The mechanical properties are found to be nearly isotropic. The computed in-plane stiffness, Poisson's ratio, and ultimate tensile strength indicate that penta-BNSi monolayer is a soft and ductile material. The calculated electronic band structure at the level of HSE06 shows that penta-BNSi is a quasi-direct semiconductor with a bandgap of 2.21 eV. In terms of electronic transport, the carrier mobilities of penta-BNSi sheet is found to be anisotropic, favorable for the separation of photo-generated carriers and electron mobilities of the structure are estimated to be potentially high (1.46 and $21.4 (\times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ along x - and y -directions, respectively). Non-centrosymmetric geometry of the penta-BNSi together with the semiconducting feature gives rise to the large intrinsic piezoelectric coefficients ($d_{16} = 1.71$ and d_{21}

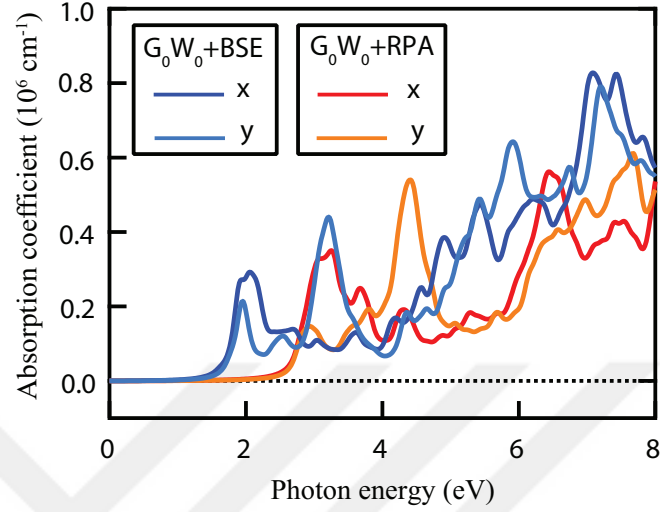


Figure 6.12: The optical absorption coefficient of penta-BNSi monolayer for light polarized along x and y directions, calculated at the level of G_0W_0 -RPA and G_0W_0 -BSE.

$= 3.59 \text{ pm/V}$), which are higher than those of other 2D penta-sheets. In addition, the penta-BNSi holds suitable bandgap and band edges, which ensure its redox ability for photocatalytic water splitting in practical pH ranges. It is also shown that the electronic properties can be modified by applied compressive/tensile strain within elastic regime. The analysis of optical properties demonstrated that penta-BNSi monolayer has high light absorption within the visible and near ultraviolet part of the spectrum and the inclusion of electron-hole interactions indicate strong exciton binding ($\sim 0.81 \text{ eV}$). Our results indicate that the proposed penta-BNSi ternary monolayer is an ideal material to be implemented in photocatalytic applications.

Chapter 7

$M\text{Si}_2\text{Z}_4$ (M : Pd and Pt, Z : N and P) Monolayers

Within the 2D dynasty, transition metal nitrides (TMNs) [262, 263] and transition metal dichalcogenides (TMDs) [264, 40] have gained considerable attention due to their diverse electrical and optical properties. The predominant structural phases of TMNs and TMDs with the general formula of MX_2 are labeled as hexagonal (H) and trigonal (T) based on coordination of constituent atoms [262, 264, 43]. Although they have similar structural profiles, the properties of TMNs differ significantly from TMDs [265]. For instance, the $1H$ - MoN_2 nanosheet is a ferromagnetic (FM) metal [266], whereas $1H$ - MoS_2 monolayer is a direct band gap semiconductor [43]. In addition to the regular phases, several different geometries (e.g., tetra- [267, 268], and ortho- [269]), which are energetically more favorable than H and T forms have been proposed for the pristine TMNs. In addition, several studies indicated that H - and T -TMNs are prone to instability related to the high reactivity of nitrogen atoms [270, 271]. Therefore, to maintain the H -TMN monolayers, chemical functionalization has been proposed [272, 273] and surface passivation of MoN_2 and WN_2 crystals with hydrogen, halogen or alkali metal atoms has been shown to improve structural stability [274, 275, 276].

In line with ongoing efforts to realize stable TMNs, Hong *et al.* have recently

synthesized a 2D septuple atomic layer of MoSi_2N_4 via chemical vapor deposition (CVD) technique [64]. The system consists of a $H\text{-MoN}_2$ monolayer inserted between two Si-N layers. Including Si atoms in the CVD process successfully passivates the dangling surface bonds of MoN_2 and enables the growth of large-scale 2D films. The obtained MoSi_2N_4 crystal is an indirect band gap (1.94 eV) semiconductor, exhibits high tensile strength, and good ambient stability [64]. The suggested technique can be applied to other TMNs, which can lead to the growth of similar materials [64]. Following the experimental progress, a variety of 2D materials with a general formula of MA_2Z_4 (which M : Cr, Mo, W, V, Nb, Ta, Ti, Zr or Hf, A : Si or Ge and Z : N, P or As) have been predicted by *ab initio* methods [64, 65] and these efforts have demonstrated the generality of the concept which opens up a new class of 2D materials [15]. As noted, the possible structures are not limited to the nitrides but can be extended to the other systems with different TM and pnictogen surface atoms. These investigated materials offer various properties and have the potential to be used in miscellaneous applications [277]. Recent theoretical studies have shown that MoSi_2N_4 and WSi_2N_4 monolayers possess high lattice thermal conductivities of 440 and 500 W/mK, respectively [65], superior to those of MoS_2 and WS_2 monolayers [119, 278]. In another study, the piezoelectric properties of MSi_2N_4 ($M = \text{Mo, W, Cr, Ti, Zr, and Hf}$) monolayers have been calculated, and large piezoelectric coefficients have been obtained [279]. The investigations on valleytronic properties of MoSi_2X_4 monolayers have revealed the presence of a pair of Dirac-type valleys, making them suitable materials for spintronic applications [280, 281]. Moreover, the van der Waals (vdW) heterostructure of MoSi_2N_4 with NbS_2 has been studied, and an ultra-low Schottky barrier height in $\text{MoSi}_2\text{N}_4/\text{NbS}_2$ contact which can be modulated by external electric field or inter-layer distance has been shown [282]. Nguyen *et al.* have demonstrated that the BP/ MoGe_2N_4 vdW heterostructure possesses a direct electronic band gap that can be tuned by a vertical strain and external electric field [283]. It has also been predicted that depending on the atomic composition, MA_2Z_4 monolayers show diverse electronic and magnetic features [65]. As an example, unlike MoSi_2N_4 and WSi_2N_4 which are non-magnetic semiconductors, VSi_2Z_4 monolayers are ferromagnetic spin-gapless

semiconductors [66, 67] and TaSi_2N_4 nanosheet is a type-I Ising superconductor [284]. A recent DFT study has shown that the optical absorption onset of MSi_2X_4 monolayers can fall into visible and near-infrared regions together with a significant light carrier coupling [285]. Furthermore, optical characterization of MoSi_2N_4 crystals by exciton resonance technique has revealed an exceptionally strong exciton–phonon coupling in the system [286]. In addition to MSi_2N_4 crystals, MSi_2P_4 ($M = \text{V}, \text{Nb}, \text{and Ta}$) crystals have been demonstrated to be dynamically stable, exhibit novel magnetic features [284, 287], and can possess suitable direct energy band gap, which is highly desirable for photoelectric applications [288, 65].

Similar to Mo and W, Pd and Pt belong to d -block transition metals (group X) and are considered noble and precious metals [289]. They are essential catalysts for various industrial activities [290], and their nanoparticles are extensively utilized in chemical catalytic applications [291]. Recently, 2D Pd- and Pt-based dichalcogenides such as PdSe_2 [57, 292] and PtSe_2 [293] have been synthesized and proposed for various applications including hydrogen evolution reactions (HER) catalysts [294], FETs [295], and photodetectors [292]. Additionally, stable PtN_2 and PdN_2 sheets with unique properties have been predicted recently by swarm optimization-based structure investigation methods [296, 277]. Furthermore, a stable form of layered transition metal phosphides, MP_2 (M : Pd and Pt) has been theoretically explored [297], and they are identified as direct band gap semiconductors with good carrier transport properties and high thermoelectric efficiency [298]. Up to date, the investigations on MA_2Z_4 monolayers are mainly concentrated on the systems where their core atom (M) is an early TM from group IVB, VB, and VIB of the periodic table. With this motivation, in this study, we extend the investigation on MA_2Z_4 family to the late TM atoms (namely Pd and Pt) and provide a comprehensive study on physical properties of MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers and highlight their intriguing features.

7.1 Methodology

In this study, all first-principles calculations were performed on the framework of density functional theory (DFT) [104, 105] by using projector-augmented wave (PAW) [155] pseudopotentials, as implemented in the Vienna *ab initio* simulation package (VASP) [106, 107, 108, 109]. The exchange-correlation interactions were parameterized by Perdew-Burke-Ernzerhof (PBE) [80] functional of the generalized gradient approximation (GGA). In addition, the hybrid Heyd-Scuseria-Ernzerhof (HSE06) [112, 113] functional was adopted to obtain more accurate electronic band gaps. The HSE06 functional was constructed by mixing 25% of the exact Hartree-Fock (HF) exchange potential with 75% of PBE exchange and 100% of PBE correlation energy. The kinetic cutoff energy for the plane-wave basis set was taken as 520 eV, and the vacuum space 15 Å was inserted in the non-periodic direction to hinder the unrealistic interactions between the neighboring images. The total energy convergence criterion for electronic relaxation between the consecutive steps was taken to be 10^{-5} eV. For the optimization of the ionic positions and lattice constants, the maximum allowed force on each atom was less than 0.01 eV/Å, and the maximum pressure on the lattice was reduced below 1 kbar. To sample the Brillouin zone (BZ) in reciprocal space, a set of Γ -centered $16 \times 16 \times 1$ uniform k -point meshes were utilized for the primitive cells [114]. To understand the bond characteristics of the structures and charge transfer between the constituents atoms, Bader analysis was employed [116]. The phonon spectrum analyses were carried out by $4 \times 4 \times 1$ supercells, using the finite-displacement method as implemented in PHONOPY [115]. The Raman activity of each phonon mode was obtained by derivation of the macroscopic dielectric tensor using the small difference method at the Γ -point [299]. The infrared (IR) intensities of each of the vibrational modes were attained by calculating the Born effective charge (BEC) tensor using the density functional perturbation theory (DFPT) method. BEC matrix is correlated to the variation of atomic polarizability with respect to an applied electric field, and it is a key parameter to compute the vibrational intensities [300, 301]. The Raman and IR curves were generated by a suitable Gaussian broadening based on Raman and IR calculations. To examine the thermal stability of the structures, *ab initio*

molecular dynamic (AIMD) simulations were performed by using a microcanonical ensemble method at constant temperatures (300 K and 600 K) with a total simulation time of 3 ps with 1 fs time steps. To calculate the optical properties, the random-phase approximation [235, 236] (RPA) on top of single-shot GW (G_0W_0) was adopted [237]. For the GW calculation, Omega integration was used with $8 \times 8 \times 1$ k -point mesh, 480 eV cutoff energy, and 160 total number of bands, which were shown to yield accurate results[302]. Regarding the optical response beyond the independent particle approach, the Bethe-Salpeter equation (BSE) [238, 239] was solved within the Tamm–Dancoff approximation and RPA screening following G_0W_0 step.

7.2 Results and Discussion

7.2.1 Atomic Structure and Energetics

In accordance with the geometry of synthesized 2D MoSi_2N_4 and WSi_2N_4 crystals, the structure of the MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers is designed. Based on the geometric structure of the MN_2 layer, H - or T -phase structures can be designed for these systems. Initial analyses indicate that the H -phase is neither energetically favorable nor dynamically stable (Fig. 7.1 and Fig. 7.2).

In this regard, we focus only on the T -phase. The schematic representation of the MSi_2Z_4 nanosheets in T -phase is depicted in Fig. 8.2(a)-(b), where the stacking order of the atomic layers is $Z-\text{Si}-Z-M-Z-\text{Si}-Z$. The crystal exhibits a sandwiched structure, where a MZ_2 layer is between two $\text{Si}-Z$ plates. The MSi_2Z_4 monolayer possesses a hexagonal lattice with the symmetry of D_{3d} and belongs to the space group of $\text{P}\bar{3}\text{m1}$ (No. 164). The structure holds an inversion symmetry with respect to the M atoms, whereas the horizontal mirror symmetry corresponding to the plane of the M layer is broken. The calculated structural parameters including in-plane lattice constants ($\mathbf{a} = \mathbf{b}$), bond lengths between M - Z (d_{M-Z}) and Si - Z atoms ($d_{\text{Si}-Z}$), and thickness (h) are listed in Table 7.1.

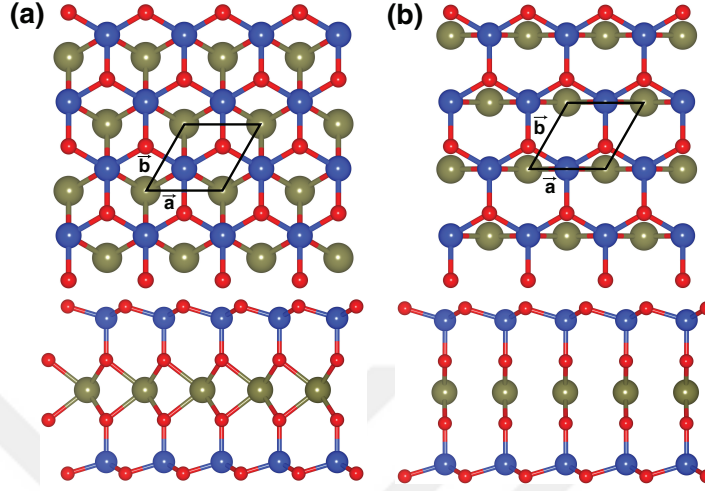


Figure 7.1: (a) The initial (b) final (relaxed) structures of MSi_2N_4 monolayers in H -phase. H -PdSi₂N₄ and H -PtSi₂N₄ monolayers transform into another geometry following the ionic relaxation.

The optimized lattice constants ($\mathbf{a}$) for PdSi₂N₄, PtSi₂N₄, PdSi₂P₄, and PtSi₂P₄ are 2.98, 3.02, 3.66, and 3.67 Å, respectively and the elongation of $\mathbf{a}$ is following the variation atomic radius (r) of constituent atoms (i.e., $r_{Pt} > r_{Pd}$ and $r_P > r_N$). In the MSi_2Z_4 structures, two types of Si– Z bonds are formed in inner and outer layers. The vertical bond between the Si atom and the inner Z atom is smaller than the bond with the outer Z atom. In addition, the bond length between M and inner Z atom for the structures with the same pnictogen atoms does not alter with the type of TM, since r_{Pt} is only slightly larger than r_{Pd} . Furthermore, h , which is defined as the normal distance between two boundary Z atoms thickens with elongation of d_{M-Z} and d_{Si-Z} .

To analyze the bonding characteristics in MSi_2Z_4 monolayers, electron localization functions (ELF) are calculated. It is found that the ELF profile can be grouped into MSi_2N_4 and MSi_2P_4 as displayed in Fig. 8.2(c)-(d). The red and blue regions around the constituent elements represent the maximum and the minimum probability of electron localization, respectively. The negatively charged Z atoms are surrounded by positively charged Si atoms due to the charge transfer from Si to neighboring pnictogen atoms. Fig. 7.4 illustrates the net charge transfer among the atoms in the MSi_2Z_4 structures. According to the Bader

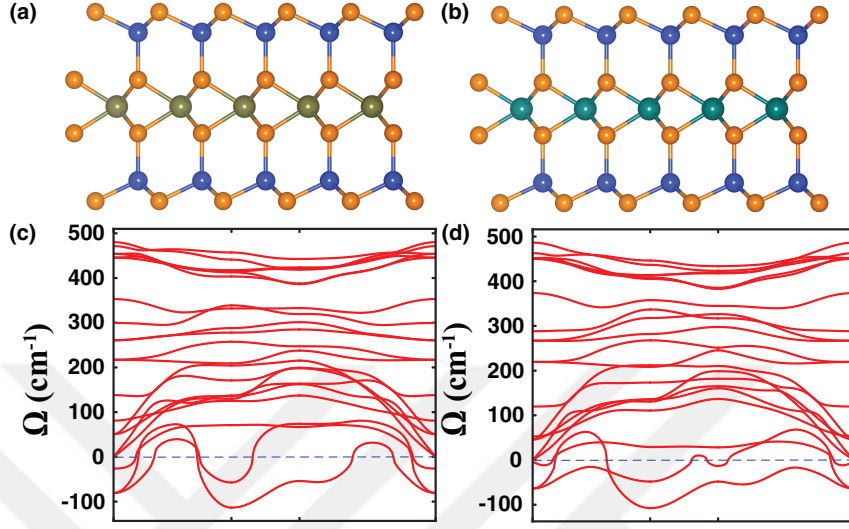


Figure 7.2: The optimized structures and phonon dispersion diagrams for (a)-(c) $H\text{-PdSi}_2\text{P}_4$ and (b)-(d) $H\text{-PtSi}_2\text{P}_4$.

charge analyses, in PdSi_2N_4 (PtSi_2N_4) monolayer, the charge donation from Pd (Pt) to its adjacent N atoms is 1.07 (1.13) e^- . In contrast, in PdSi_2P_4 (PtSi_2P_4) monolayer 0.04 (0.23) e^- charge is transferred from neighboring P atoms to Pd (Pt). This elucidates that the $M\text{-N}$ bonds possess more ionic character than the $M\text{-P}$ bonds [65].

Additionally, the planar averaged electrostatic potentials of the MSi_2Z_4 are computed, and their variations along the z -axis are plotted in Fig. 7.5. From these graphs, the work function (Φ) of the MSi_2Z_4 nanosheets can be calculated by $\Phi = E_{\text{Vacuum}} - E_{\text{Fermi}}$, where E_{Vacuum} is the energy of the vacuum on both sides and E_{Fermi} is the Fermi energy. Knowledge of a material's work function is essential for device applications, especially where the energy level discontinuity between different materials greatly impacts the performance of electronic devices such as Schottky diodes. The calculated results are listed in Table 7.1, and they are found to be smaller than reported values for MoSi_2N_4 (5.12 eV) [303] and MoSi_2P_4 (5.06 eV) [304] monolayers. In general, a lower work function is desired since many electron emission applications require high emitted current densities from the electron source [305].

To determine the strength of the binding between the atoms, the cohesive

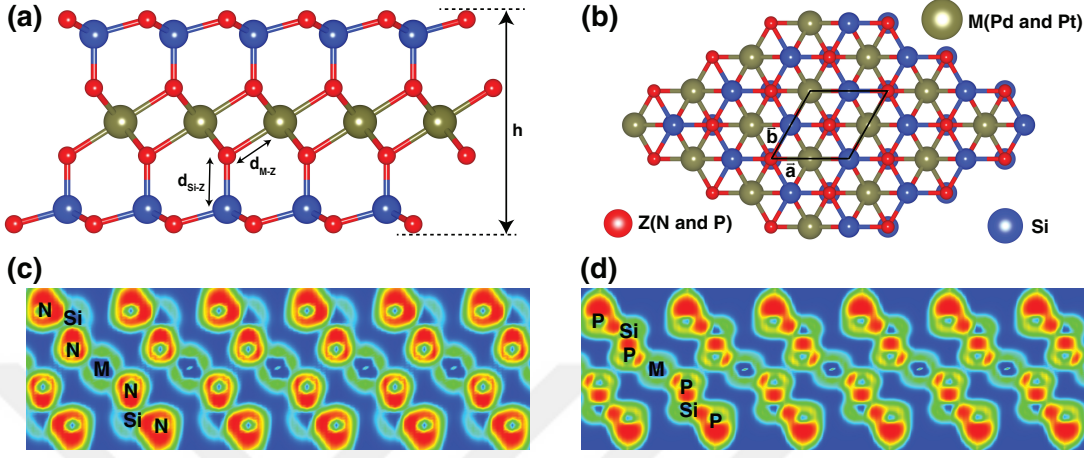


Figure 7.3: (a) Side and (b) top views for the MSi_2Z_4 monolayers in T -phase and the corresponding electron localization function (ELF) for (c) MSi_2N_4 and (d) MSi_2P_4 monolayers, respectively. A color scheme with linear scaling from blue (low) to red (high) indicates probability of electron localization around the atoms. The relevant structural parameters are displayed.

energy per atom (E_C) for the proposed structures are computed by using the following expression;

$$E_C = \frac{[E_T(M) + 2E_T(\text{Si}) + 4E_T(Z)] - [E_T(MSi_2Z_4)]}{7} \quad (7.1)$$

where $E_T(M)$, $E_T(\text{Si})$, and $E_T(Z)$ are the single atom energies of M , Si, and Z elements, respectively; $E_T(MSi_2Z_4)$ is the total energy of the MSi_2Z_4 monolayers. The denominator corresponds to the total number of atoms (7) in the primitive cell.

The E_C for PdSi_2N_4 , PtSi_2N_4 , PdSi_2P_4 , and PtSi_2P_4 are found to be 5.13, 5.43, 4.00, and 4.35 eV/atom. In accordance with the variation of $\mathbf{a}$ (and also the bond lengths), $E_C(MSi_2N_4)$ is larger than $E_C(MSi_2P_4)$ suggesting that M -N and Si-N bonds are stronger than M -P and Si-P bonds. The trend within MSi_2N_4 (MSi_2P_4) is correlated with the amount of charge transferred from M to N (P to M) atoms. The similar variation of E_C is also found in MoSi_2N_4 (7.34 eV/atom) and MoSi_2P_4 (6.08 eV/atom) monolayers[280, 65] as listed in Table 7.1. The

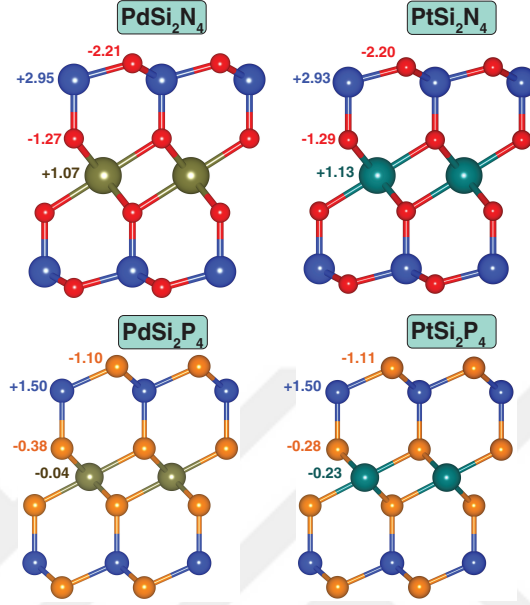


Figure 7.4: Net charge transfer between the atoms in the structures are shown in the unit of $|e|$. Negative (positive) values indicate electron accumulation (donation).

decrease in E_C among MoSi_2Z_4 and PdSi_2Z_4 (or PtSi_2Z_4) monolayers can be correlated with the partially-filled d -electrons of constituent TM elements[306] and electronegativity differences between Mo and Pd/Pt atoms (i.e., electronegativity increases along the d -block elements), which is also observed in 2D TMDs[40].

7.2.2 Dynamical Stability

Following the structural optimization, the dynamical stability of the MSi_2Z_4 monolayers is first investigated by analyzing their vibrational frequencies. The corresponding phonon dispersion spectra are represented in Fig. 7.6. All phonon band structures are free from any imaginary eigenfrequencies indicating the dynamical stability of the proposed systems. The overall characteristics of phonon band dispersions in structures with common pnictogen atoms are nearly identical, whereas the frequency ranges of vibrations in the systems containing the same metal atoms but different pnictogen atoms are dissimilar. The three acoustic vibrational modes are the longitudinal acoustic (LA), the transverse acoustic (TA),

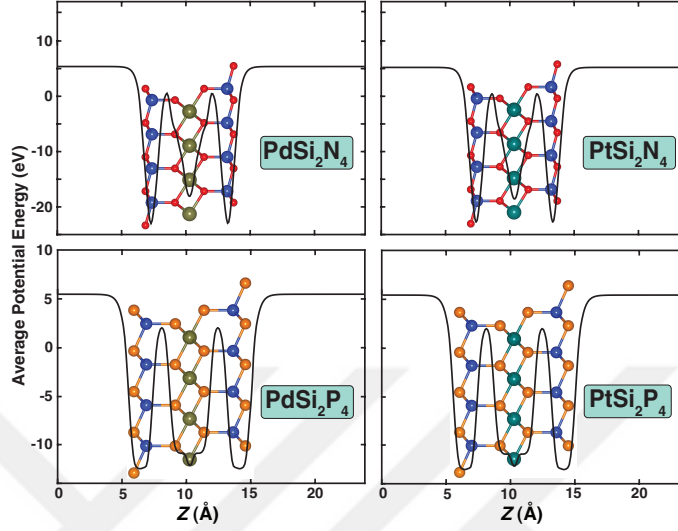


Figure 7.5: Planar average of the electrostatic potential along the non-periodic direction for the MSi_2Z_4 monolayers.

and the flexural acoustic (ZA) branches. The LA and TA phonon modes have linear dispersion near Γ -point while the ZA branch has quadratic dispersion, as the force constants associated with the transverse vibrations of atoms decay rapidly [240, 241]. Additionally, in all structures, there is a phononic band gap between low and high-frequency ranges of the optical phonon modes. The frequency gap for MSi_2N_4 monolayers are in the range of $430 - 580 \text{ cm}^{-1}$ whilst the gap appears around $210 - 290 \text{ cm}^{-1}$ for MSi_2P_4 monolayers. The existence of the phononic band gap can suppress the propagation of mechanical waves at forbidden frequencies, making them suitable materials for vibrational protection applications [242]. To interpret the phonon spectra of the MSi_2Z_4 monolayers, phonon density of states (PhDOS) calculations were performed. The PhDOS diagrams indicate that for MSi_2N_4 monolayers, the high-frequency phonon modes are mainly attributed to the vibrations of N atoms and, to a lesser extent, Si atoms. On the other hand, in MSi_2P_4 structures, the high-frequency modes are mainly determined by the vibration of Si and P elements since their atomic masses are close to each other. Moreover, the low-frequency lattice vibrations are dominated by M ions due to their heavier atomic masses; however, Si and Z atoms also play considerable roles. The larger mass difference and stronger M -N bonds in MSi_2N_4 monolayers than M -P bonds in MSi_2P_4 structures leads to wider frequency gap between

Table 7.1: The optimized lattice constants, $\mathbf{a}$; atomic bond lengths, d_{M-Z} and d_{Si-Z} ; thickness, h ; cohesive energy per atom, E_C ; the calculated work function, Φ ; the relaxed-ion elastic coefficients, C_{ij} ; in-plane stiffness, Y_{2D} ; Poisson's ratio, ν ; energy band gaps at the level of GGA-PBE, E_g^{PBE} ; HSE06, E_g^{HSE} ; and the locations of VBM and CBM edges in the BZ for MSi_2Z_4 (M : Pd, Pt, and Mo Z : N and P) monolayers.

Crystal structure	$\mathbf{a}$ (Å)	d_{M-Z} (Å)	d_{Si-Z} (Å)	h (Å)	E_C (eV/atom)	Φ (eV)	$C_{11}=C_{22}$ (N/m)	C_{12} (N/m)	Y_{2D} (N/m)	ν (-)	E_g^{PBE} (eV)	E_g^{HSE} (eV)	VBM/CBM (-)
PdSi ₂ N ₄	2.98	2.04	1.74/1.79	6.64	5.13	4.82	392	117	357	0.30	2.14	3.25	K- Γ / Γ -M
PtSi ₂ N ₄	3.02	2.05	1.75/1.80	6.58	5.43	4.36	386	116	351	0.30	2.54	3.77	Γ -M/ Γ -M
MoSi ₂ N ₄	2.91	2.09	1.74/1.75	10.11	7.34	5.12	-	-	491	0.28	1.79	2.23	Γ /K
PdSi ₂ P ₄	3.66	2.38	2.23/2.31	8.58	4.00	4.73	167	59	146	0.35	0.04	0.39	Γ /M
PtSi ₂ P ₄	3.67	2.38	2.24/2.31	8.55	4.35	4.55	204	61	185	0.30	0.69	1.24	Γ /M
MoSi ₂ P ₄	3.47	2.46	2.24/2.25	12.96	6.08	5.06	-	-	203	0.26	0.70	0.99	K/K

low and high-frequency optical modes. In addition, associated with the analysis of the phonon band dispersions, several thermal properties, e.g., isovolume heat capacity (C_V) of the MSi_2Z_4 monolayers (Fig. 7.7) can also be obtained.

We further examined the thermal stability of the crystals at elevated temperatures via AIMD simulations. The calculated results for AIMD simulations at 300 and 600 K are displayed in Fig. 7.8 and Fig. 7.9, respectively. Apart from small oscillations of atoms in the vicinity of their thermal equilibrium positions, no significant distortions are observed during the simulations. Since any bond breaking or geometry reconstruction at a higher temperature shifts the overall energy of the system, we plotted the variation of the potential energy of the structures as a function of simulation time to trace their crystalline morphology. The calculated results show that the gradient values of total energies of the systems oscillate without any considerable deviation during the whole simulation, which represents the dynamical and thermal stability of the MSi_2Z_4 monolayers.

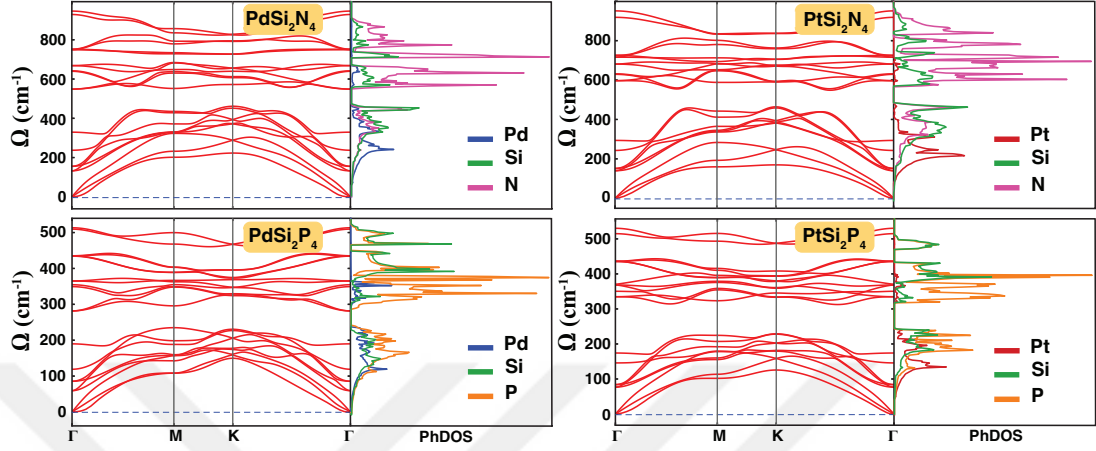


Figure 7.6: Phonon dispersion diagrams for the MSi_2Z_4 structures and the corresponding phonon density of states (PhDOS).

7.2.3 Vibrational Properties

Raman spectroscopy and infrared spectroscopy analysis are the most common techniques for characterizing a material, providing information about the crystallographic symmetry and bonding between constituent elements in materials. As mentioned above, the symmetry of the MSi_2Z_4 structures is described by $P\bar{3}m1$ (No. 164) space group and D_{3d} point group. The group theory analysis reveals that the irreducible representation for the optical phonon modes at the Γ point can be described by $\Gamma = 3E_g + 3E_u + 3A_{1g} + 3A_{2u}$, where $E_g(n)$ and $E_u(n)$ phonon modes are attributed to the doubly degenerate in-plane vibrations whereas $A_{1g}(n)$ and $A_{2u}(n)$ modes represent vibrations along the out-of-plane direction (n corresponds to the first, second, or third peak). Among the vibrational modes, the E_g and A_{1g} are Raman active (RA) and E_u and A_{2u} are infrared active (IRA) modes. Therefore, the examined monolayers should exhibit 6 peaks at Raman and 6 peaks at the infrared spectrum. The Raman spectra of the structures are illustrated in Fig. 7.10(a). RA vibrational modes correspond to the inelastically scattered photons generated by the oscillation of a crystal's dipoles [307]. As noticed from Fig. 7.10(a), the Raman activity and the position of the Raman peaks in the structures with the same pnictogen are within the same frequency intervals. The most prominent RA peaks for MSi_2N_4 and MSi_2P_4 monolayers are $E_g(2)$ and $A_{1g}(3)$ vibrational modes. The intensity of each peak in the Raman

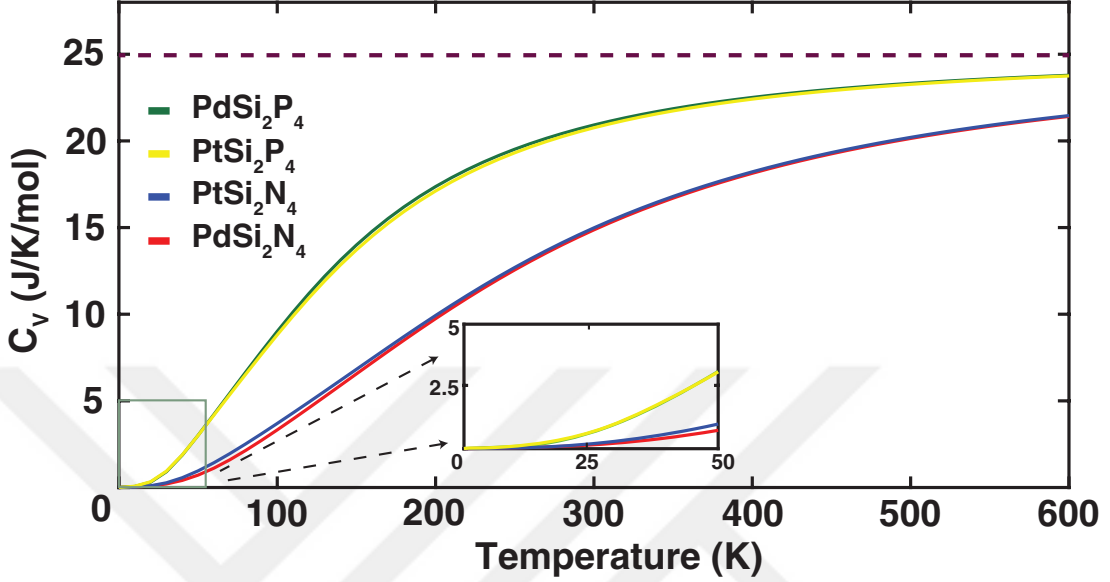


Figure 7.7: Variation of isovolume heat capacity (C_V) for the MSi_2Z_4 structures with temperature. The low temperature limit is shown as inset.

spectrum depends on the contribution of macroscopic dielectric constants of vibrational modes to the Raman tensors. The IR spectra of the MSi_2Z_4 monolayers are shown in Fig. 7.10(b). The atomic shift of each IRA mode is labeled on the corresponding spectrum to identify the origin of the IR peaks. Theoretically, infrared absorption intensities are described in terms of dynamical (Hessian) matrix and Born effective charges, which are also known as atomic polarizability tensors [300]. The concept of IR spectroscopy is the analysis of infrared light interacting with a material. Here, the IR spectra are simulated to better characterize the vibrational modes and atomic displacements in the structures. In general, the most important factors determining where (at what frequency) a chemical bond would exhibit IR absorption are the bond order and the types of atoms forming bonds. The intensity of an absorption peak depends on the polarity of the bond, and the bond with greater polarity exhibits a more intense absorption peak. In MSi_2Z_4 monolayers, the IR spectra of the structures with the same M but different Z atoms exhibit different IR response whereas the crystals with the same Z but different M atoms show common features in their spectrum. In all structures, the $E_u(2)$ and $E_u(3)$ vibrational modes are the most intense peaks. For $PdSi_2N_4$ ($PtSi_2N_4$) monolayer, the most prominent peaks appear at

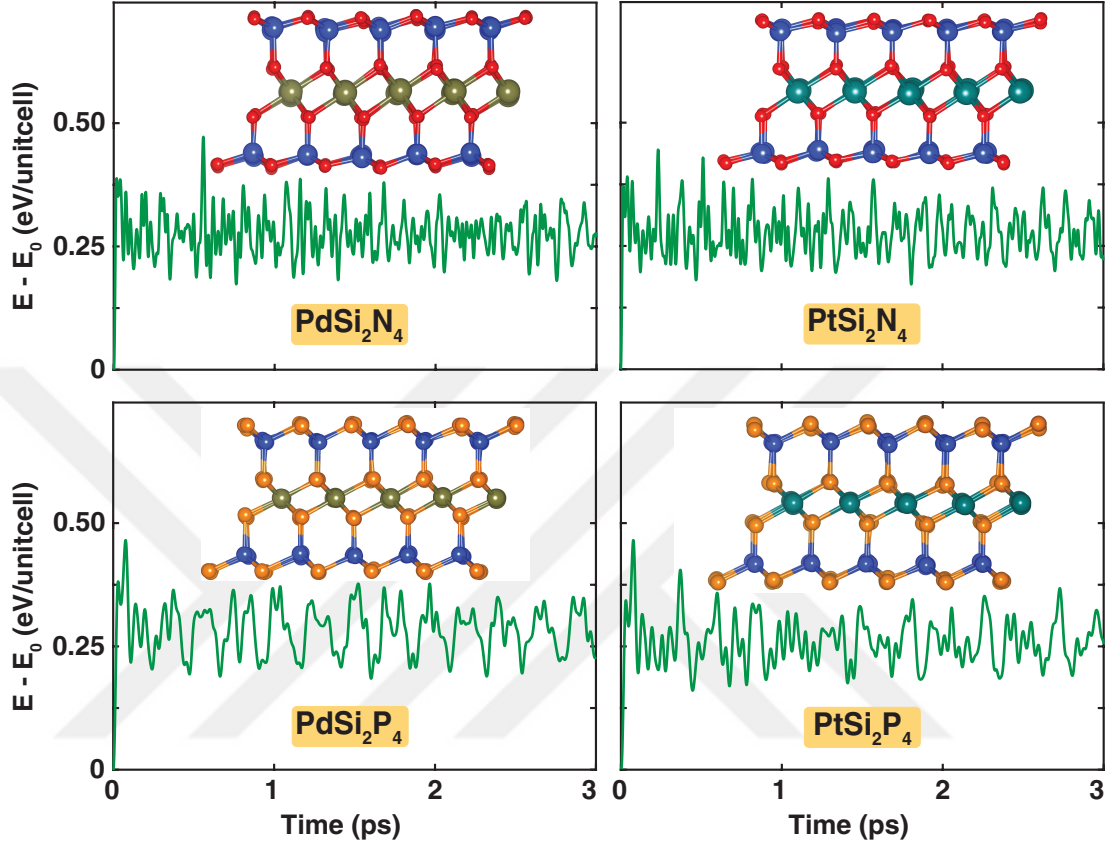


Figure 7.8: The total energy fluctuations of the MSi_2Z_4 monolayers with respect to the simulation time at 300 K. The insets represent the final snapshot of the atomic configurations at the end of simulation.

668 and 751 cm^{-1} (681, 725 cm^{-1}), while for $PdSi_2P_4$ ($PtSi_2P_4$) monolayer, the most prominent peaks are observed at 361 and 435 cm^{-1} (368, 435 cm^{-1}). The shared vibrational motion of optical phonon modes of the MSi_2Z_4 nanosheets are depicted in Fig. 7.10(c). The $E_g(1)$ phonon mode arises from the in-plane shear vibration of buckled Si-Z sublayers. The E_g mode is followed by E_u mode, which represents the asymmetric in-plane vibrations of Si-Z/ M atoms with respect to the M atoms. The $A_{1g}(1)$ mode is attributed to the vibrations of Z-Si-Z sub-layers in the opposite out-of-plane direction. The $A_{2u}(1)$ mode mostly arises from the mixed vibration of M and outer Si-Z sublayer along the vertical direction. The $E_g(2)$ mode corresponds to the dominant opposing in-plane vibration of the inner Z atoms in the unit cell, and the $A_{1g}(2)$ mode originates from the opposing out-of-plane vibrations of the Z-Si-Z sublayers against each other. In

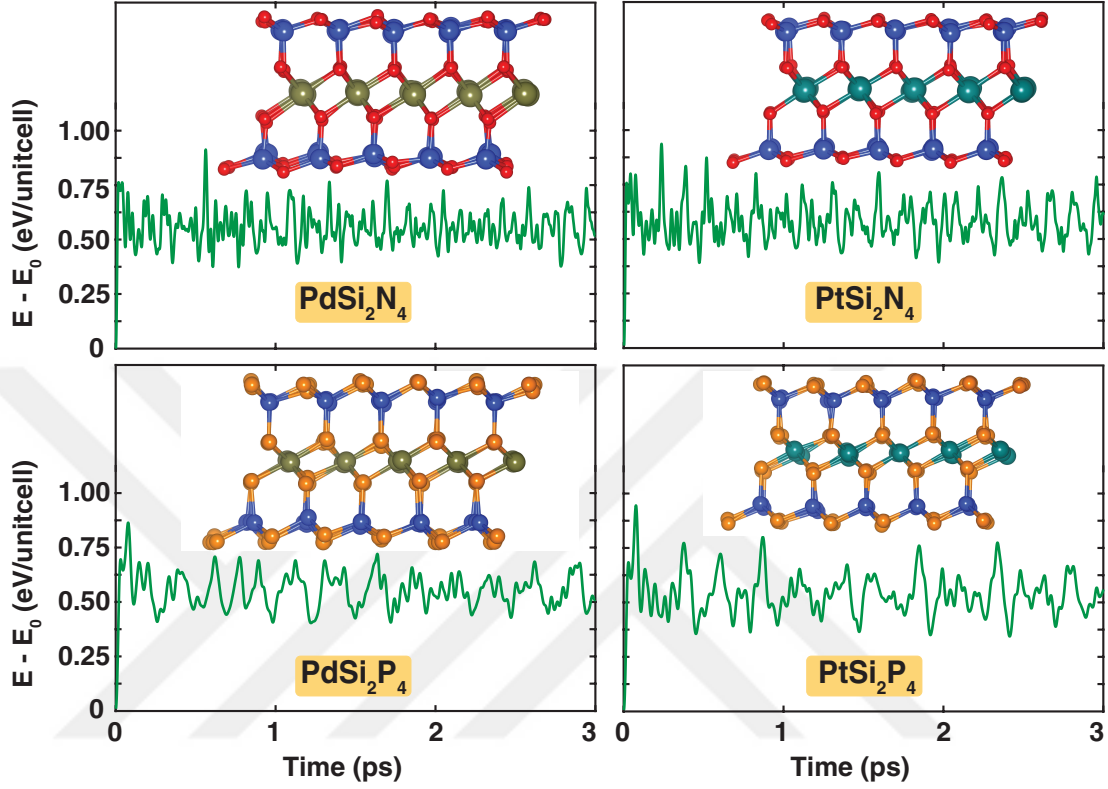


Figure 7.9: The total energy fluctuations of the MSi_2Z_4 monolayers as a function of simulation time at 600 K. The insets represent the final snapshots of the atomic configurations at the end (AIMD) simulations.

contrast, the inner Z atoms have small contributions to the vibration. Another coupled phonon mode, $A_{2u}(2)$, originates mainly from the asymmetric out-of-plane vibration of the two Z -Si- Z sublayers with respect to the M atoms. For the $E_u(2)$ mode, the in-plane vibration of the inner Z atoms against the M atoms is significantly larger. The $E_g(3)$ and $E_u(3)$ phonon modes are attributed to the symmetric and asymmetric in-plane vibration of buckled Si- Z sublayers around M atoms, respectively. Furthermore, the $A_{2u}(3)$ and $A_{1g}(3)$ phonon modes arise from the asymmetric and symmetric vibration of Si and inner Z atoms, while the vibration of Z atoms is more dominant.

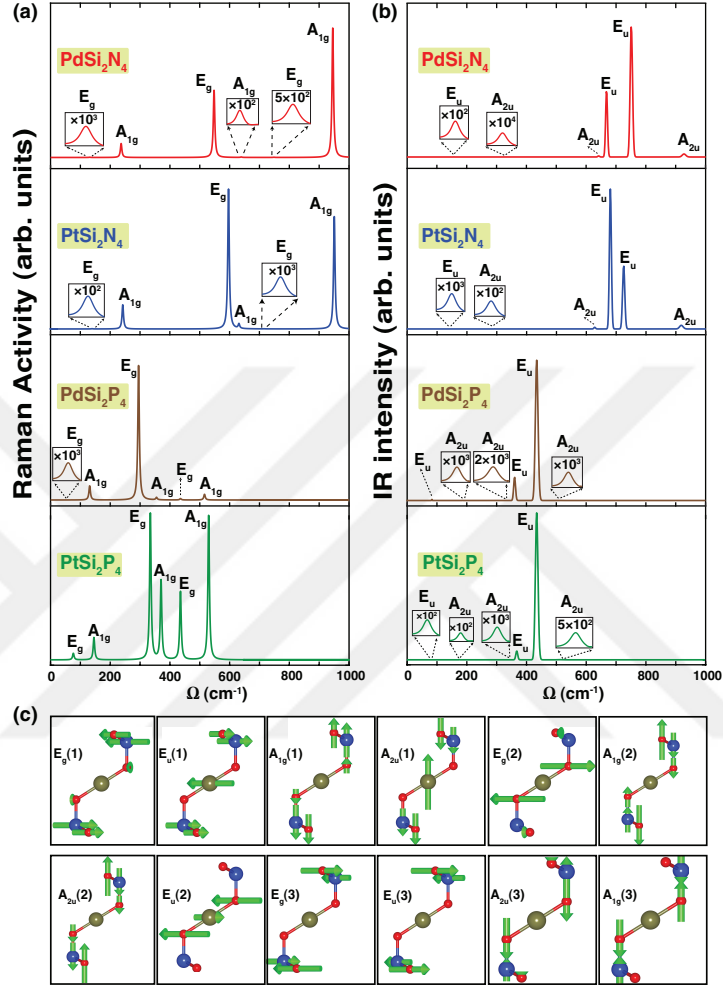


Figure 7.10: Calculated (a) Raman and (b) infrared (IR) spectra of the MSi_2Z_4 monolayers and (c) the corresponding atomic displacements of the optical phonon modes in the structures.

7.2.4 Mechanical Properties

After revealing the dynamical stability, the elastic tensors of the MSi_2Z_4 structures are computed to evaluate their mechanical stability and elastic properties. The obtained non-zero elements of elastic tensors (C_{ij}) are listed in Table 7.1. Firstly, it should be noted that all of the MSi_2Z_4 nanosheets satisfy the Born-Huang criteria [216, 217] [$C_{11} > |C_{12}|$ and $C_{66} = (C_{11} - C_{12})/2 > 0$] for 2D hexagonal plane, verifying the mechanical stability. The linear elastic response of homogeneous 2D materials in the elastic regime can be defined in terms of

in-plane stiffness (Y_{2D}) and Poisson's ratio (ν). The Y_{2D} is defined as the measure of rigidity (or flexibility) of a material in a 2D limit analogous to Young's modulus in 3D structures. For a 2D hexagonal system, the Y_{2D} can be calculated with the following formula; $Y_{2D} = (C_{11}^2 - C_{12}^2)/C_{11}$. The computed Y_{2D} 's are 357, 351, 146 and 185 N/m for PdSi_2N_4 , PtSi_2N_4 , PdSi_2P_4 , and PtSi_2P_4 monolayers, respectively. Due to the geometrical symmetry, Y_{2D} is found to be isotropic for all structures. It is noticed that while the effect of the type of core metal is not drastic, replacing N with P significantly reduces Y_{2D} . As discussed above, the M -P and P-Si bonds in the MSi_2P_4 structures are longer and weaker than M -N and N-Si bonds in MSi_2N_4 monolayers. This results in lower Y_{2D} values of MSi_2P_4 crystals than those of MSi_2N_4 structures. A similar trend is also observed in 2D MoSi_2Z_4 systems. The Y_{2D} of MoSi_2N_4 and MoSi_2P_4 are estimated as 491 and 203 N/m, respectively[65]. For the same pnictogen atom (N or P), Y_{2D} decreases from MoSi_2Z_4 to PdSi_2Z_4 (or PtSi_2Z_4) in accordance with the decrease in E_C [306, 40]. We further analyze the Poisson's ratio (ν) of the MSi_2Z_4 monolayers. ν is defined as the negative ratio of the transverse contraction strain to the longitudinal extension strain in the direction of the tensile force and can be calculated using the following relationship; $\nu = C_{12}/C_{11}$. Similar to Y_{2D} , ν is also isotropic and has the values 0.30, 0.30, 0.35, and 0.30 for PdSi_2N_4 , PtSi_2N_4 , PdSi_2P_4 and PtSi_2P_4 monolayers, respectively, which are larger than those reported for MoSi_2N_4 monolayer (0.28)[65]. The obtained values for ν are slightly larger than 2/7 (except for PdSi_2P_4), which is the threshold for the ductile/brittle transition in the materials according to the Christensen criterion [84]. The MSi_2N_4 monolayers exhibit prominent mechanical properties, including large elastic constants and in-plane stiffness, that make them promising for elastic energy storage. On the other hand, in terms of the calculated mechanical response of MSi_2P_4 , it can be concluded that these materials are flexible and stretchable, suggesting the possibility of their use in flexible electronic devices[308].

7.2.5 Electronic Properties

Next, we investigate the electronic properties of the MSi_2Z_4 monolayers. The electronic band structures and the orbital projected density of states (PDOS) of the designed structures are shown in Fig. 7.11 and Fig. 7.12, respectively. The computed energy band gaps by GGA-PBE and HSE06 functionals and the locations of the valence band maximum (VBM) and conduction band minimum (CBM) are listed in Table 7.1. The electronic band structures calculated at the level of GGA-PBE show that all the structures (except $PdSi_2P_4$ monolayer, which is a semimetal) are semiconductors. When the calculations are repeated with HSE06, similar trends with wider band gaps (E_g^{HSE}) are obtained; however, the band structure profiles are not modified. The E_g^{HSE} of $PdSi_2N_4$, $PtSi_2N_4$, $PdSi_2P_4$, and $PtSi_2P_4$ monolayers are calculated to be 3.25, 3.77, 0.39, and 1.24 eV, respectively. Compared to MSi_2N_4 , MSi_2P_4 monolayers have a narrower energy band gap. The reduction in E_g^{HSE} of MSi_2P_4 crystals can be correlated with the increase in the bond length (due to the larger atomic radius of P than N), which is caused by the reduced orbital overlap in the structures. Recent studies have shown that the small band gap materials are promising for applications in infrared sensing devices [309, 310]. The VBM (CBM) in MSi_2P_4 monolayers are located at Γ (M) point, while VBM (CBM) for MSi_2N_4 structures occur between Γ -M (Γ -M) points. Additionally, the highest valence band (HVB) for $PdSi_2N_4$ and $PtSi_2N_4$ monolayers is dispersive with two maximum levels between Γ -M and K- Γ points, whose energy levels are very close to each other. Accordingly, MSi_2N_4 structures can be considered as quasi-direct wide band gap semiconductors. It has been reported that 2D wide band gap materials can be utilized in many applications such as solar cells, photoelectrochemical catalysts, and field effect transistors (FETs) [311, 312]. To understand the nature of band edges in the proposed structures, we analyzed the results of orbital projected density of states (PDOS). The PDOS results indicate that in MSi_2N_4 monolayers, VBM and CBM are mainly derived from the d orbitals of M atoms and p orbitals of N atoms while for MSi_2P_4 nanosheets, the contribution of the p orbitals of P atoms are more dominant in VBM. Due to the shorter bond length of d_{M-N} than d_{M-P} in the MSi_2Z_4 monolayers, and also the similar contribution of $M-d$ and $N-p$ orbitals in

VBM of MSi_2N_4 monolayers, the orbital hybridization of $M-d$ and N- p orbitals is more plausible in MSi_2N_4 than $M-d$ and P- p orbitals in MSi_2P_4 .

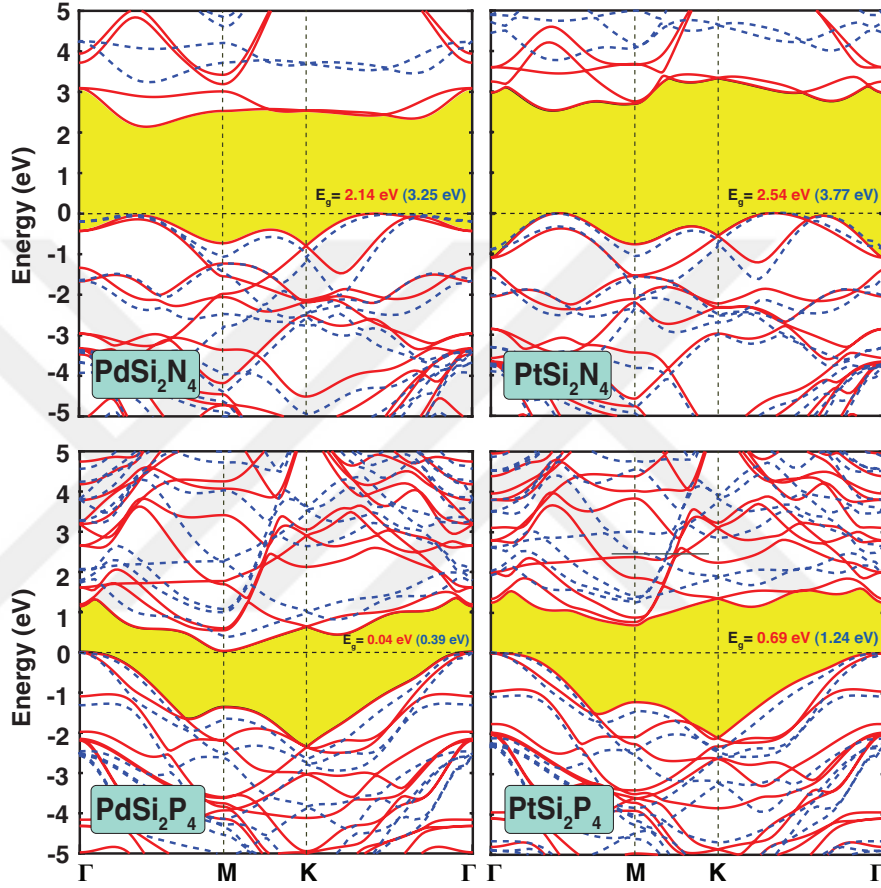


Figure 7.11: The electronic band structures (calculated within the level of GGA-PBE (red solid lines) and HSE06 (dashed blue lines)) of the MSi_2Z_4 monolayers. The Fermi level is set to zero.

7.2.6 Optical Properties

Finally, the in-plane optical responses of the MSi_2Z_4 monolayers are analyzed via calculating the frequency-dependent complex dielectric function $[\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)]$, where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ correspond to the real and imaginary parts, respectively. Acquiring the dielectric function allows the calculation of variety of optical properties such as absorbance, $A(\omega)$ and absorption coefficient, $\alpha(\omega)$ [313]. The variation of $A(\omega)$, $\alpha(\omega)$, and $\varepsilon_2(\omega)$ with respect to the photon energy

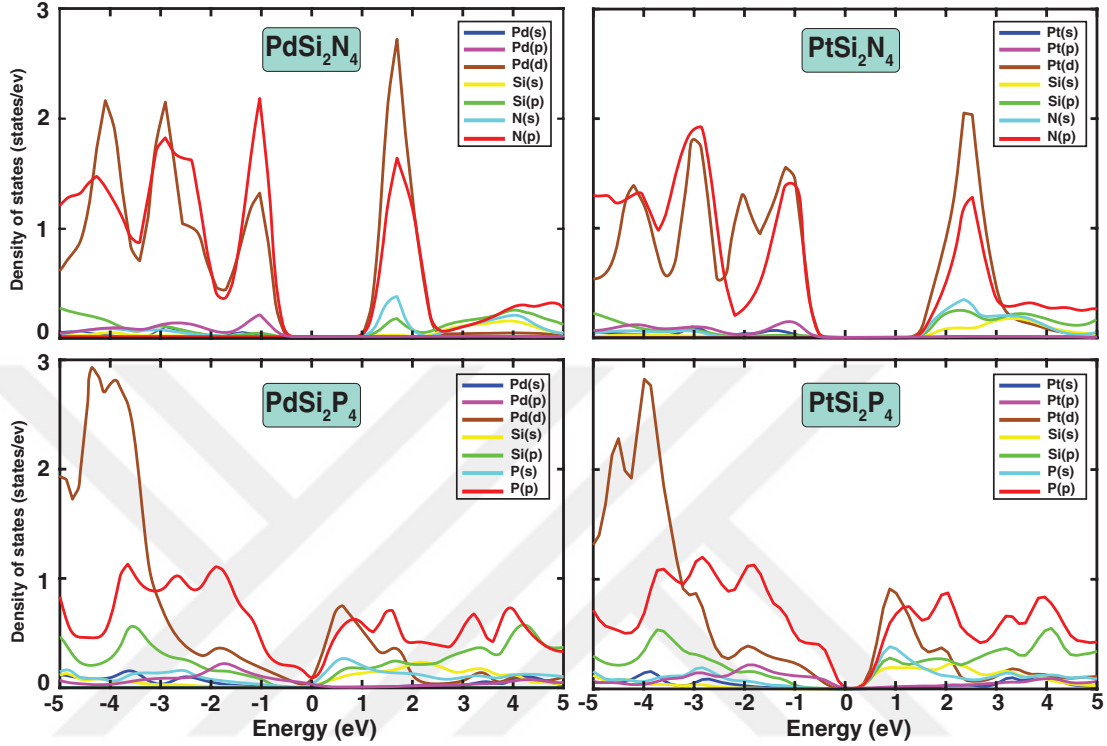


Figure 7.12: The projected density of states (PDOS) of MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers.

for in-plane light polarization of the designed systems are presented in Fig. 7.13, and Fig. 7.14, and Fig. 7.15, respectively. The following equation can be used to determine $A(\omega)$ of the 2D materials[313, 255]:

$$A(\omega) = \frac{\omega}{c} L \varepsilon_2(\omega) \quad (7.2)$$

where L is the length of the supercell along the non-periodic (z) direction, and c is the speed of light. Due to the symmetry along the x - and y - directions, the optical spectra in the MSi_2Z_4 are found to be isotropic. The G_0W_0 (quasi-particle) band gap (E_g^{GW}) of $PdSi_2N_4$, $PtSi_2N_4$, $PdSi_2P_4$ and $PtSi_2P_4$ monolayers are computed as 3.21, 3.83, 0.55 and 1.25 eV, respectively, which are in agreement with E_g^{HSE} . (Hence, the full band structure is not calculated with G_0W_0 in addition to HSE06). In addition, the electron-hole (e - h) interactions are included by employing the BSE approach on top of G_0W_0 (G_0W_0 -BSE). Going

beyond independent-particle methodology mainly results in a red shift in the optical spectrum, and the alternation is more significant in MSi_2N_4 systems indicating the dominance of excitonic effects. When the optical spectra for MSi_2N_4 monolayers are examined, in addition to optical absorption features in UV-region, three intense absorption peaks that fall behind E_g^{GW} are noticed. Since the exciton binding energy (for bound excitons) can be defined as the difference between the GW band gap and the exciton peaks, the corresponding exciton binding energies for $PdSi_2N_4$ ($PtSi_2N_4$) monolayer are 0.60, 0.29, and 0.02 eV (0.62, 0.38, and 0.13 eV), respectively. A strong exciton binding energy (0.95 eV) and multiple excitonic peaks are also reported in $MoSi_2N_4$ monolayer [314]. The first and prominent peak also sets the optical band gap, which narrows to 2.61 eV (3.21 eV) for $PdSi_2N_4$ ($PtSi_2N_4$) monolayer. This results in 23% (14%) of the incident light's absorbance in the visible (near UV) spectrum for $PdSi_2N_4$ ($PtSi_2N_4$) systems as shown in Fig. 7.13. On the other hand, for MSi_2P_4 systems, absorption peaks are beyond the GW band gap, and no bound excitons are obtained. The prominent peaks fall in the infrared region of the solar spectrum with $\sim 8\%$ absorption capability. The reduced excitonic effects in MSi_2P_4 with respect to MSi_2N_4 can be attributed to the weakening of Coulomb interactions, increase in dielectric screening[315, 258], and the narrowing of the band gap[316]. Similar effects (to a lesser extent) are also observed in $MoSi_2Z_4$ (Z : N, P, As) monolayers[285]. The MSi_2N_4 monolayers have a suitable band gap for potential optical applications in the near UV region of optical spectrum such as UV detectors[317]. The MSi_2P_4 structures, on the other hand, cover a range in the near visible and deep IR spectrums, making them promising materials for application in visible-light solar harvesting/utilization techniques or application in IR sensing devices[281].

7.3 Conclusion

In summary, inspired by the recent synthesis of high-quality $MoSi_2N_4$ and WSi_2N_4 crystals, we design and investigate the physical properties of MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers based on first-principles calculations. The phonon spectrum analysis and *ab initio* molecular dynamics simulations indicate that all

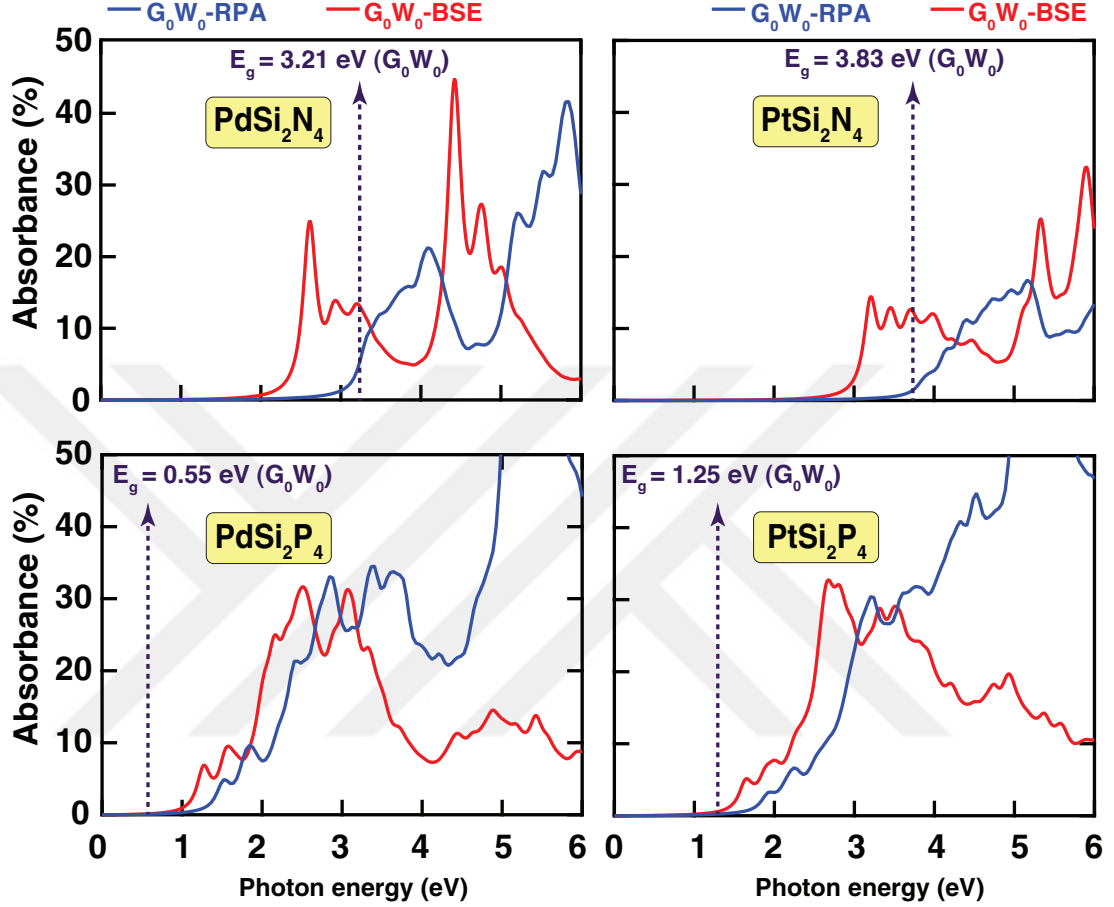


Figure 7.13: The optical absorbance in MSi_2Z_4 crystals for light polarized along symmetry directions, calculated at the level of G_0W_0 -RPA (blue) and G_0W_0 -BSE (red).

the proposed structures are dynamically stable. Our vibrational analysis reveals six characteristic Raman active and six infrared modes for MSi_2Z_4 monolayers, which can be considered as their spectral fingerprints. The mechanical response of these nanosheets within the elastic regime is found to be isotropic, and the calculated in-plane stiffness values are 357, 351, 146, and 185 N/m for $PdSi_2N_4$, $PtSi_2N_4$, $PdSi_2P_4$, and $PtSi_2P_4$ monolayers, respectively. These results demonstrate that while the systems containing N atoms are stiff due to strong M -N and Si-N bonds, the incorporation of P atoms makes nanosheets more flexible. The Poisson's ratios are estimated as ~ 0.30 , which are within the threshold for the ductile/brittle transition. The electronic structure results indicate that, although all MSi_2Z_4 systems are semiconductors, MSi_2N_4 monolayers possess a

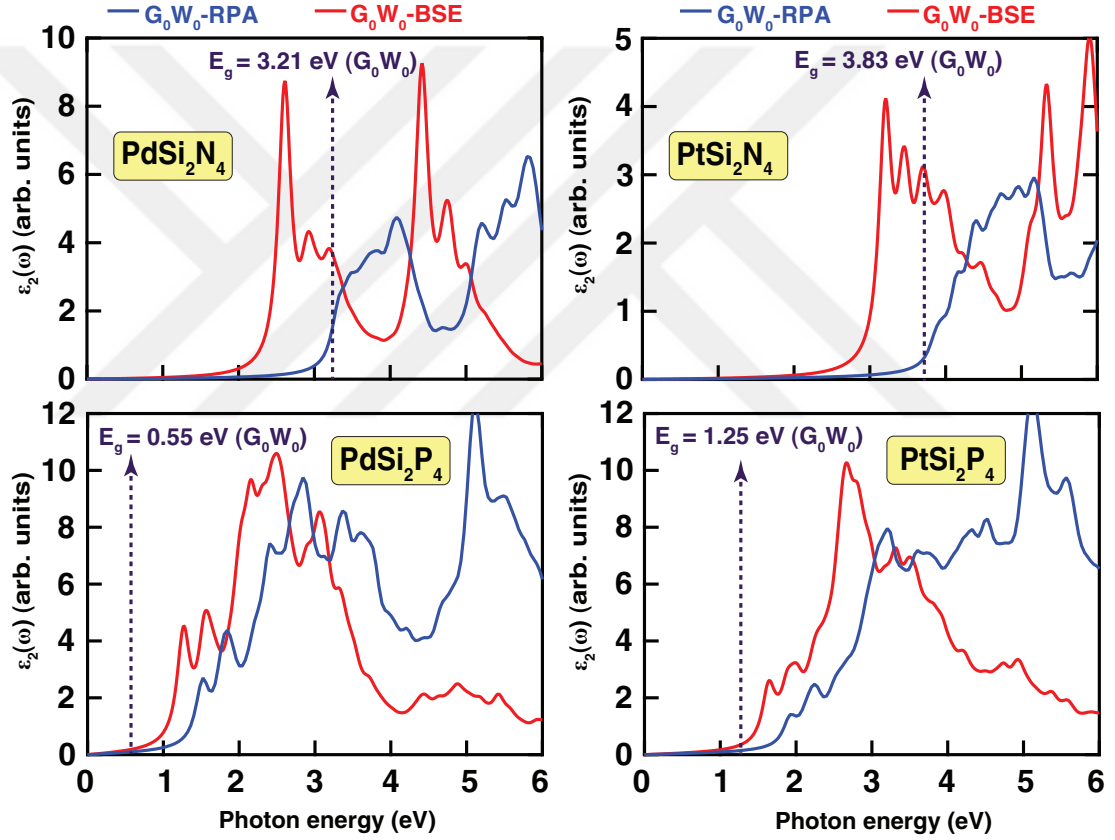


Figure 7.14: The variation of the imaginary part [$\epsilon_2(\omega)$] of the dielectric function with respect to the photon energy for the MSi_2Z_4 monolayers (in-plane light polarization). The blue and red lines represent the calculated optical response at the level of G_0W_0 -RPA and G_0W_0 -BSE, respectively.

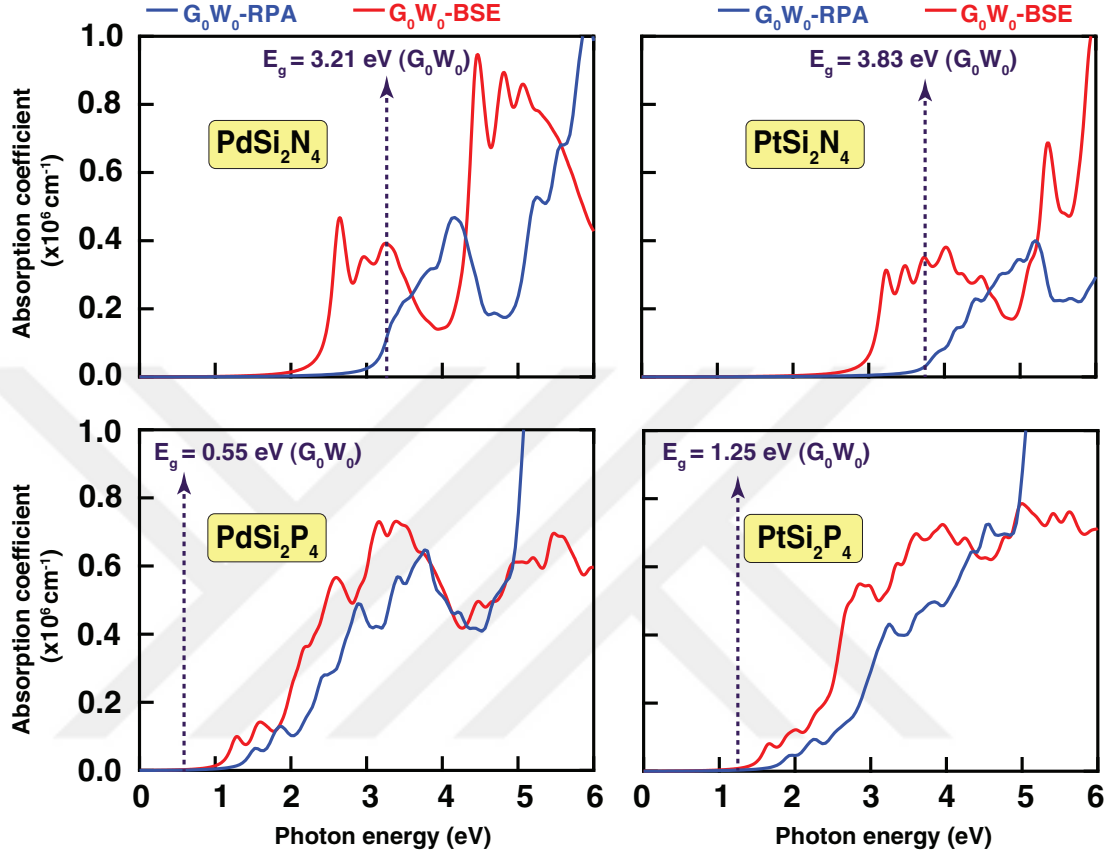


Figure 7.15: The optical absorption coefficient of the MSi_2Z_4 monolayers for light polarized along symmetry directions, computed at the level of G_0W_0 -RPA (blue) and G_0W_0 -BSE (red).

wide, quasi-direct energy band gap and MSi_2P_4 monolayers have narrow, indirect band gap. The analysis of optical properties demonstrates that the MSi_2N_4 monolayers exhibit significant absorption peaks in the visible and near-UV part of the solar spectrum in accordance with their electronic band profile while in the MSi_2P_4 structures the onset of prominent optical peaks emerge in the IR and visible part of the optical spectrum. The optical response of the considered crystals is modified by taking into account the electron-hole interactions and strong exciton binding energy, and multiple excitonic peaks are noticed in MSi_2N_4 monolayers. Our results indicate that MSi_2Z_4 monolayers are stable materials with intriguing electronic and optical properties, making them suitable candidates for a wide range of optoelectronic applications.

Chapter 8

InSiN₂ monolayer

The successful synthesis of 2D MoSi₂N₄ crystal [64] via chemical vapor deposition (CVD) technique has received considerable attention both from experimental and theoretical viewpoints [318, 65]. Hong *et al.* showed that the addition of silicon atoms during CVD growth of molybdenum nitride (MoN₂) passivates the surface dangling bonds of the MoN₂ layer with Si-N tetrahedrons and enables the synthesis of large scale 2D MoSi₂N₄ nanosheet[64]. Consecutive to the growth of MoSi₂N₄ nanosheet, the same fabrication technique has been applied to other 2D transition metal nitrides (TMNs) [64]. The MoSi₂N₄ and WSi₂N₄ crystals are bottom-up synthesized nanostructures which do not have any known natural 3D van der Waals (vdW) layered parent. The MoSi₂N₄ crystal is septuple-atomic-layer structure of N-Si-N-Mo-N-Si-N, which a MoS₂-like MoN₂ layer is sandwiched between two SiN plates[64]. Despite of that the pristine MoN₂ monolayer exhibits a ferromagnetic (FM) metal behavior[266], the MoSi₂N₄ crystal has been found to be an indirect bandgap non-magnetic semiconductor with high tensile strength and excellent ambient stability[64, 319]. Following this accomplishment, a large family of 2D materials with a general formula of MA_2Z_4 where M represents a transition metal (TM), A is C, Si or Ge and Z can be a pnictogen atom, have been predicted and characterized by density functional theory methods[15, 65, 280]. Recent theoretical calculations demonstrated that MoSi₂N₄ and WSi₂N₄ nanosheets possess remarkable lattice thermal

conductivity and stiffness[320, 321], exceptional piezoelectricity[65, 279], good photocatalytic hydrogen evolution performance[322, 319] and high electron and hole mobility[303]. Furthermore, a vdW heterostructure of MoSi_2N_4 with NbS_2 has been proposed and its tunable interfacial electronic properties by means of external electric field or inter-layer distance are investigated and an ultra-low Schottky barrier height has been detected in $\text{MoSi}_2\text{N}_4/\text{NbS}_2$ contact[282]. Furthermore, the investigations on valleytronic properties of MoSi_2X_4 monolayers have revealed the presence of a pair of Dirac-type valleys in the material, which makes them promising materials for spintronics applications [323, 280]. It has been found that the variation of the TM in the MA_2Z_4 systems significantly influences on the electronic and magnetic properties of the structures[324, 65]. For instance, unlike MoSi_2N_4 and WSi_2N_4 nanosheets which are nonmagnetic semiconductors[325], VSi_2N_4 is a ferromagnetic semiconductor with a considerable valley polarization[66] and TaSi_2N_4 monolayer is a metal with intriguing electronic properties which make it promising candidate for application as a type-I Ising superconductor[284]. In addition, for bilayer MSi_2N_4 ($M = \text{Ti}$, Cr or Mo) systems, it has been reported that under a certain amount of strain a semiconducting-to-metallic phase transition occurs which is attributed to the asymmetric charge transfer of the proposed crystals[326]. In another theoretical study, it has been shown that MoSi_2N_4 sustain mechanically and dynamically stable up to 18% of tensile strain and the light absorption coefficient of the system can be increased by 70% under 8% of the strain[327]. Also, MSi_2Z_4 (M : Pd and Pt, Z : N and P) monolayers have been investigated by using density functional theory and have been reported that they are thermodynamically stable and their bandgap ranges from infrared to ultraviolet region of the optical spectrum [328]. So far, researches on MA_2Z_4 family are mainly focused on the structures in which the core atom is a TM and the studies on alternative core atoms from other groups are limited. The element indium is a post-transition metal which belongs to the group IIIA of the periodic table. It is a ductile metal that can be used for various applications, such as a protective plate for other metal surfaces [329]. As an important family of metal nitrides, Indium nitride (InN) crystal has received great deal of interest due to its unique optical response and electronic properties that make it a key material for optical and high temperature device

applications[330, 331]. Until now, various phases of InN such as cubic zinc blende (zb-InN)[332] and wurtzite phase(w-InN)[333] have been synthesized. In a recent theoretical work, possible hexagonal monolayer phases of InN (h-InN) has been proposed and its electronic properties thoroughly investigated[334]. Additionally, studies on thermoelectric efficiency of InN monolayer indicated that electrical conductivity of the system can be increased threefold, and lattice thermal conductivity can be reduced by half at 1% compressive strain[335]. Recent studies have proved that the chemical functionalization of InN surface can effectively tune and enhance the electronic and optical response of the material[336]. In the present work, inspired by recent synthesise of large area MoSi_2N_4 and WSi_2N_4 2D crystals, which paves the path for experimental realization of new 2D materials with a general formula of $M_xA_2Z_4$, we suggested InSiN_2 ($\text{In}_2\text{Si}_2\text{N}_4$) nanosheet and explored its intrinsic fundamental properties through the *ab initio* methods. In this regard, we first design single layer InSiN_2 and relaxed the structure without any constraint to obtain the ground state configuration. Then the system's stability is examined via phonon spectrum analysis and *ab initio* molecular dynamics (AIMD) simulations. Revealing the stability of the material, vibrational properties, and Raman activity of each phonon mode is investigated. Next, the electronic and optical properties are studied, and the corresponding electronic and optical bandgaps are calculated. Moreover, we study the mechanical response in the elastic regime and evaluate the in-plane piezoelectric coefficients of the proposed crystal. Finally, the effect of an external biaxial strain on the electronic and vibrational properties of the InSiN_2 nanosheet is investigated.

8.1 Methodology

All first principles calculations were carried out on the basis of density functional theory (DFT)[104, 105] as implemented in the Vienna *Ab initio* Simulation Package (VASP)[106, 107, 108, 109]. The exchange-correlation potential was formulated by the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE)[80] scheme. The projector-augmented wave (PAW)[155] method was used to portray the pseudopotentials of the elements. The kinetic

cutoff energy for the plane wave basis set was taken to 520 eV. A vacuum space ~ 15 Å was considered in the non-periodic direction to hinder artificial interactions between the neighboring images. The Brillouin zone (BZ) was sampled with a Γ -centered $16 \times 16 \times 1$ uniform k -point meshes within Monkhorst-Pack scheme[114]. The convergence criterion of total energy for electronic relaxation between the sequential steps was set to 10^{-5} eV. For the structural optimization, the Hellmann-Feynman forces on each atom were reduced below 0.01 eV/Å, while the pressure on the lattice was less than 1.0 kbar. To analyze the charge attributed to each atom and the bonding nature between the constituents elements in the suggested system, the Bader technique was conducted[116]. The band structure were further computed by using the Heyd-Scuseria Ernzerhorf (HSE06)[112, 113] hybrid functional to obtain more accurate electronic bandgaps. The phonon dispersion spectra were calculated by using the finite displacement method as implemented in PHONOPY[115] code, by considering a $4 \times 4 \times 1$ supercell. To examine the thermal stability of the proposed system, AIMD simulations were performed using the microcanonical ensemble simulation at constant temperatures (300K and 600K) for a total simulation time of 6 ps, with a time step of 1 fs. The off-resonant Raman activities were calculated at the Γ -point of the BZ by utilizing finite displacement method. To construct dynamical matrix, each atom in the unit cell was initially distorted by 0.01 Å. Then, the vibrational modes were determined via a direct diagonalization of the dynamical matrix. After that, the corresponding Raman activity of each vibrational mode was attained from the derivative of the macroscopic dielectric tensor by employing the small difference method. Both elastic constants and piezoelectric stress coefficients were obtained by employing density functional perturbation theory (DFPT) with a $48 \times 48 \times 1$ k -point meshes and the plane wave cutoff energy of 700 eV. To obtain optical properties of the designed system, random phase approximation (RPA)[235, 236] on top of single-shot GW (G_0W_0) was with $8 \times 8 \times 1$ k -point mesh, 480 eV cut-off energy was employed while the number of bands was tripled with respect to GGA step. For the optical responses beyond the independent-particle approach, we computed the frequency dependent dielectric function including excitonic effects by solving the Bethe-Salpeter equation (BSE) following G_0W_0 step[237].

8.2 Results and Discussion

8.2.1 Atomic structure and stability

Initially, in accordance with the atomic configuration of synthesized 2D MoSi_2N_4 crystal, the structure of InSi_2N_4 is designed by substituting the Mo atom with In atom. The optimized crystal structure of single-layer InSi_2N_4 is depicted in Fig. 8.1 (a). The stability analysis according to phonon dispersion calculations reveals that InSi_2N_4 is prone to instability (See Fig. 8.1 (b)). Indeed, it is expected due to the existence of unsaturated In bonds in the system (Our calculated magnetic moment for InSi_2N_4 monolayer is $1 \mu_B$).

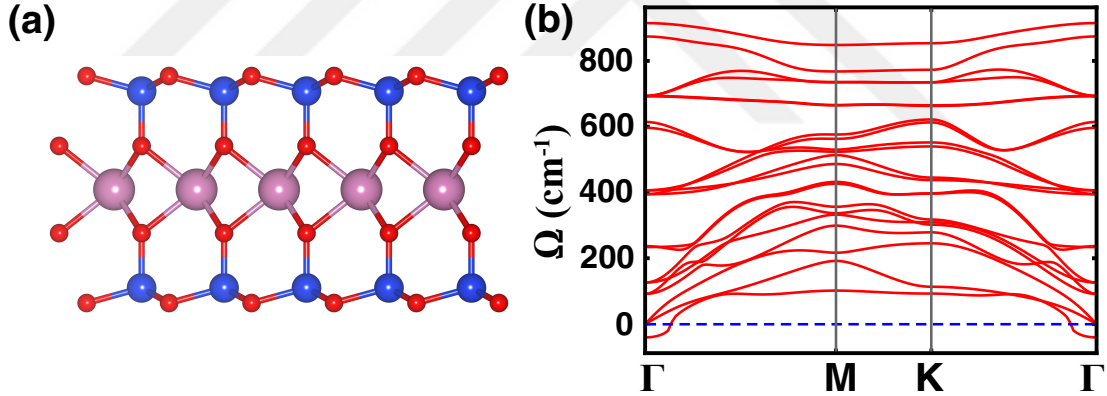


Figure 8.1: For InSi_2N_4 monolayer, (a) side view of the structure and (b) the corresponding phonon band dispersion.

Thereafter, we considered replacing the Mo atom in MoSi_2N_4 monolayer with two vertically bonded In atoms to form the geometry similar to the previously synthesized 2D InSe. [337]. The top and side view of the optimized crystal structure of InSiN_2 ($\text{In}_2\text{Si}_2\text{N}_4$) monolayer are shown in Figs. 8.2(a)-(b). The structure of the material can be regarded as an InSe-like InN layer sandwiched in between two buckled honeycomb SiN layers. The suggested system is built from octuple atomic layers of N–Si–N–In–In–N–Si–N, which are held together with strong covalent bonds. The symmetry of the monolayer belongs to the $D_{3h}(\bar{P}6m2)$ space group. The monolayer is formed by two pairs of InSiN_2 (upper P and lower P') and holds a mirror symmetry paralleling the horizontal plane

between two In atoms. The structural optimization calculations reveal that the InSiN₂ monolayer has hexagonal geometry similar to InSe and MoSi₂N₄ crystals and, possesses a nonmagnetic ground state. The fully optimized in-plane lattice constant for the material is $\mathbf{a} = \mathbf{b} = 3.16$ Å. In the InSiN₂ nanosheet two types of Si–N bonds can be seen; in inner and outer layers. The atomic bond lengths between In–In, In–N, inner N–Si and outer Si–N ($d_{\text{In–In}}$, $d_{\text{In–N}}$, $d_{\text{N–Si}}$ and $d_{\text{Si–N}}$) are 2.80, 2.13, 1.74 and 1.87 Å, respectively, and the thickness of the structure (which is defined as the normal distance between two boundary N atoms) is found to be 9.40 Å. The charge partition analysis via Bader method reveals that the net charge on In, inner N, Si and outer N atoms are +0.82, -1.57, +2.88, -2.13 | e |, respectively. This large charge depletion from In and Si atoms to their adjacent N atoms demonstrate the strong interaction between the constituent elements in the unit cell which mainly depends on the electronegativity difference ($\Delta\chi$) of the atoms. The charge depletion in Si atoms is larger than that in In atoms in the system since Si atoms are bonded to two N atoms (i.e., the electronegativity of the N atoms is greater than that of Si and In atoms) whereas In atoms are only bonded to one N atom. To analyze the strength of cohesion between the atoms in the primitive cell, we calculate the cohesive energy per atom (E_C) for the proposed system via using the following relation;

$$E_C = \frac{[2E_T(\text{In}) + 2E_T(\text{Si}) + 4E_T(\text{N})] - [E_T(\text{InSiN}_2)]}{8} \quad (8.1)$$

where $E_T(\text{In})$, $E_T(\text{Si})$, and $E_T(\text{N})$ are the single atom energies of In, Si, and N elements, respectively; $E_T(\text{InSiN}_2)$ corresponds to the total energy of InSiN₂ structure and the denominator is the total number of atoms (8) in the unit cell. The calculated E_C (4.55 eV/atom) is larger than double layer hexagonal InN (3.73 eV/atom)[338], indicating strong binding energy between the constituent elements in the structure but smaller than planar InN monolayer (5.49 eV/atom) [339] and MoSi₂N₄ monolayer (7.34 eV/atom)[327].

To check the dynamical stability of the InSiN₂ nanosheet, we performed the vibrational frequency analysis and the corresponding phonon band diagram is represented in Fig. 8.3(a). The real values of all phonon modes frequencies through the whole BZ indicates the dynamical stability of the structure. The three acoustic phonon modes are the longitudinal acoustic (LA), the transverse

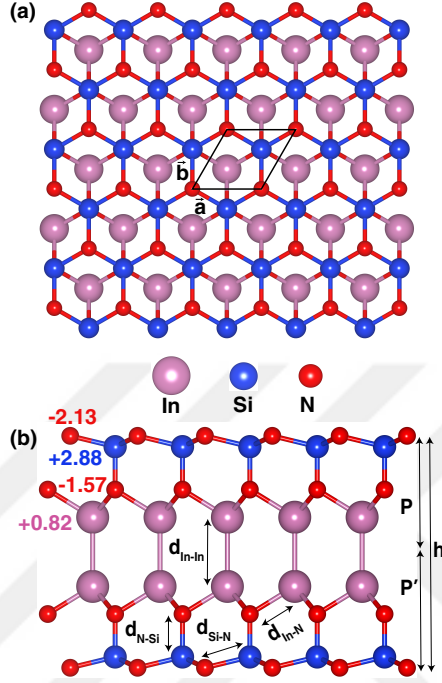


Figure 8.2: For single layer InSiN₂; (a) Top and (b) side views and the corresponding net charge transfer on the individual elements.

acoustic (TA), and the flexural acoustic (ZA) branches. LA and TA modes have linear dispersion near Γ point while ZA mode has quadratic dispersion in the wavevectors near the zone center as the force constants associated with transverse vibration of atoms decay rapidly which is a distinguishing property of 2D materials[240]. According to the phonon spectrum of the InSiN₂ nanosheet, there are frequency ranges in which the acoustic and optical vibrational modes intersect each other, leading to robust acoustic-optical phonon scattering and, consequently, a low thermal conductivity. Beside phonon band dispersion, we also present the phonon density of states (PhDOS) of the proposed system to interpret the corresponding phonon spectrum. The PhDOS diagram indicates that the low frequency vibrational modes are mainly characterized by In atoms which is heavier than Si and N atom, whereas the main contribution to the high frequency phonon modes are attributed by the vibrations of Si and N atoms. In addition, two phononic gap in the optical segment are noticed in the frequency ranges of $(450 - 480 \text{ cm}^{-1})$ and $(700 - 810 \text{ cm}^{-1})$ which is due to the bond strength and the mass differences between the constitute elements in the structure. To further

examine the structural stability of the InSiN₂ monolayer at elevated temperatures, AIMD simulations are performed. To this purpose, initially, the structure is kept at 300 K, and then the temperature is increased to 600 K for total simulation time of 6 ps with a time step of 1 fs. To remove the size constraint, a $4 \times 4 \times 1$ supercell was used. As the total energy of the 2D ultra-thin materials is sensitive to any bond breaking and/or bond forming at elevated temperatures, the variation of the total energy of InSiN₂ monolayer as a function of the simulation time is displayed to monitor the crystalline morphology of the structure. The total energy fluctuation of InSiN₂ nanosheet during the AIMD simulation and the final snapshots of the resulting structure at the end of 300 K and 600 K are illustrated in Fig. 8.3(b). The results of AIMD simulations indicate that no significant distortions occur in the examined system, and the basic crystalline integrity of the material remains unchanged, confirming its dynamical stability at and above ambient temperatures.

8.2.2 Vibrational properties

Vibrational characteristics and Raman activities of phonon modes at the Γ point are closely related to the geometrical structure of a material and their analysis could be a suitable technique to investigate the physical properties correlated with its lattice symmetries. As mentioned in the previous section, the symmetry of SL-InSiN₂ belongs to the D_{3h} space group. By analyzing the symmetry of the eigenvectors in each optical eigenmode in the phonon spectrum, the corresponding irreducible representation can be assigned by $\Gamma = 4E' + 3E'' + 4A'_1 + 3A''_2$, where E' and E'' phonon modes are attributed to the doubly degenerate in-plane vibrations whereas A'_1 and A''_2 modes represent non-degenerate out-of-plane vibrations. E' , E'' and A'_1 vibrational modes are Raman active modes as they correspond to quadratic functions in the character table of D_{3h} symmetry. Therefore, InSiN₂ crystal should exhibit 11 peaks in Raman spectrum. Raman spectroscopy analysis is one of the most common techniques for the characterization of a material which provides information about the nature of the material by monitoring the distinctive vibrational levels of the structure. The predicted Raman spectrum of

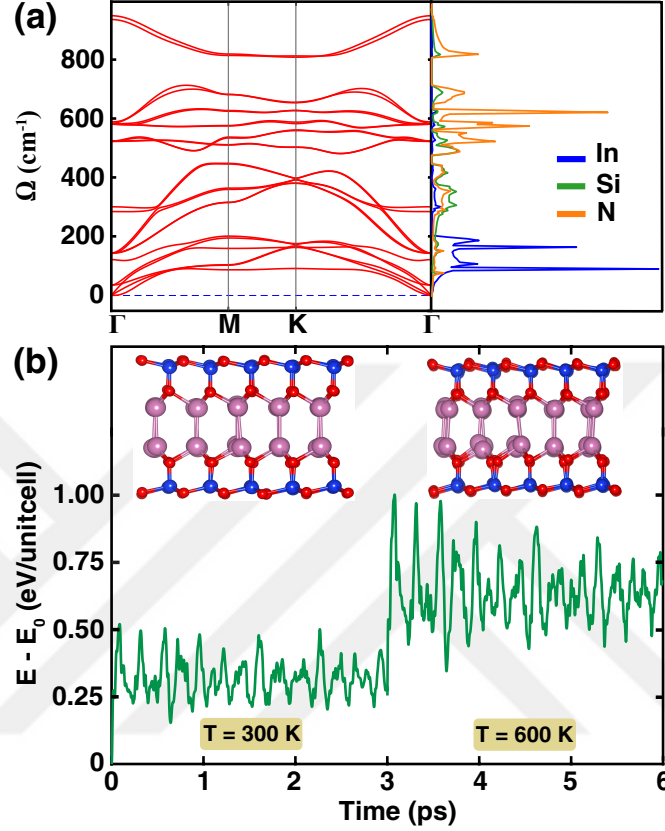


Figure 8.3: (a) Phonon dispersion diagram and the corresponding phonon density of states (PhDOS) and (b) the variation of total energy of InSiN₂ nanosheet during the AIMD simulation .

the InSiN₂ monolayer is illustrated in Figs. 8.4(a). As can be seen, the Raman activity of A'_1 phonon mode at 949 cm^{-1} is very robust, which is due to the relatively higher contribution of the out-of-plane macroscopic dielectric coefficients to the Raman tensors. To identify the origins of each Raman peaks, the atomic displacements of the Raman active modes are labeled on the spectrum. As mentioned above, the designed system is constructed by upper and lower InSiN₂ pairs, denoted by the letters P and P', respectively. The vibrational motion of optical phonon modes are displayed in Figs. 8.4(b). The first vibrational mode, $E''(1)$, appears at 34 cm^{-1} frequency and arises from the opposite vibrations of P and P' pairs against each-other. The $A'_1(1)$ eignemode at frequency of 121 cm^{-1} is attributed to the vibration of P and P' pairs along the z direction while the vibration of In atoms are more dominant. The $E''(2)$ and $E'(1)$ modes have very close

energies (142 and 143 cm^{-1}) and are mostly dominated by the displacement of the Si atoms, while they are attributed to the symmetric and asymmetric in-plane vibration of P and P' pairs, respectively. The frequency of $A_2''(1)$ and $A_1'(2)$ with asymmetric and symmetric out-of-plane vibrational character of P and P' pairs appear at 284 and 300 cm^{-1} , respectively. The $E''(3)$ and $E'(2)$ at frequencies of 522 and 523 cm^{-1} are mainly originated from the symmetric and asymmetric in-plane vibration of inner N atoms. Furthermore, the $E'(3)$ and $E'(4)$ Raman active modes at 580 and 581 cm^{-1} frequencies correspond to the coupled vibrations of Si and outer N atoms. The $A_2''(2)$ and $A_1'(3)$ peaks at 584 and 588 cm^{-1} are attributed to the asymmetric and symmetric out-of-plane vibration of N-Si-N sublayers in the P and P' pairs, respectively, while the displacement of boundary N atoms are dominant. The same trend can be found for $A_2''(3)$ and $A_1'(4)$ phonon modes (with the frequencies of 935 and 949 cm^{-1}). However, these two modes are mostly arises from the intense vibration of inner N atoms along the z axis. Herewith, the calculated Raman spectrum and the peak position of the Raman active modes can be used to characterize the InSiN₂ monolayer effectively.

8.2.3 Electronic and optical Properties

We further investigate the electronic properties of InSiN₂ monolayer via calculating its electronic band structure and projected density of states (PDOS). The corresponding results are depicted in Fig. 8.5(a-b). The electronic band structure is initially calculated based on the GGA-PBE functional. According to our results, the material is a semiconductor with a direct bandgap of 1.32 eV at the Γ point. When the calculation is repeated with the hybrid HSE06 functional, the energy bandgap increases to 2.38 eV, but the band profile remains the same. In terms of electronic features of MoSi₂N₄ and InSe monolayers, they also exhibit semiconducting character with the indirect energy bandgaps of 2.29 eV and 2.82 eV at the level of HSE06, respectively. To understand the nature of band edges, we analyzed the PDOS diagram of the structure. It is seen that the states near VBM are relatively flat, resulting a high density of states and mainly composed of the p orbitals of In and N atoms. Since the In and inner N atoms are bonded

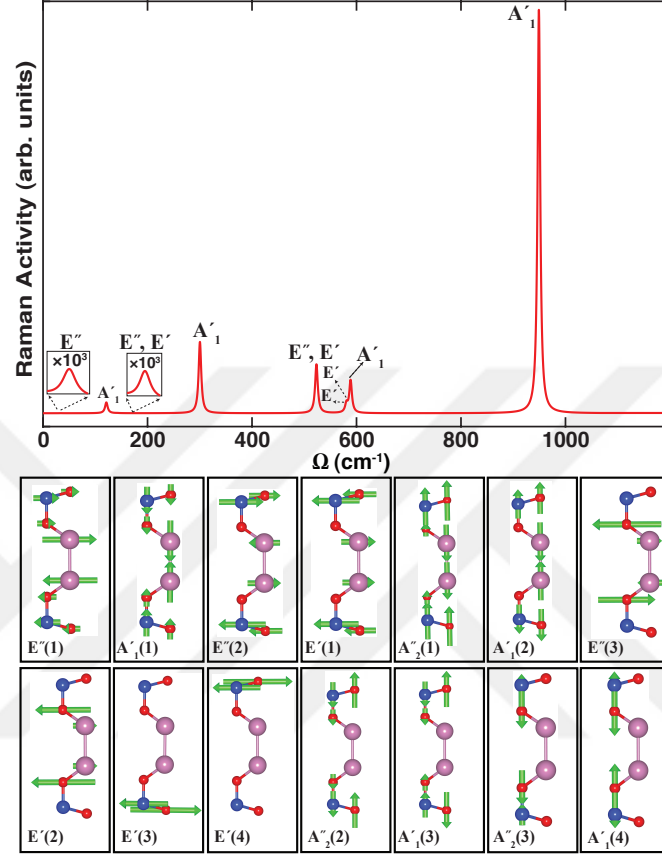


Figure 8.4: (a) Calculated Raman spectrum of InSiN₂ monolayer and (b) the corresponding atomic displacements of the optical phonon modes in the structure.

together and considerable contribution of VBM originates from their p orbitals, hybridization of In- p and N- p is expected in the proposed system. Moreover, the electronic states near CMB are mainly attributed to the In- s , In- p and N- p orbitals. The sharp valley of the CMB near Γ point is an indication for the light electron effective mass and consequently high electron carrier mobility.

In the following, we study the optical properties of InSiN₂ nanosheet. The investigation of the optical response of the proposed system would be beneficial, since it possesses a direct electronic bandgap in visible light region which plays an essential role in photo-catalytic application of 2D materials. The in-plane optical responses of InSiN₂ monolayer is analyzed by calculating the frequency dependent complex dielectric function [$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$], which enables computation of the optical properties such as optical conductivity, absorbance, absorption

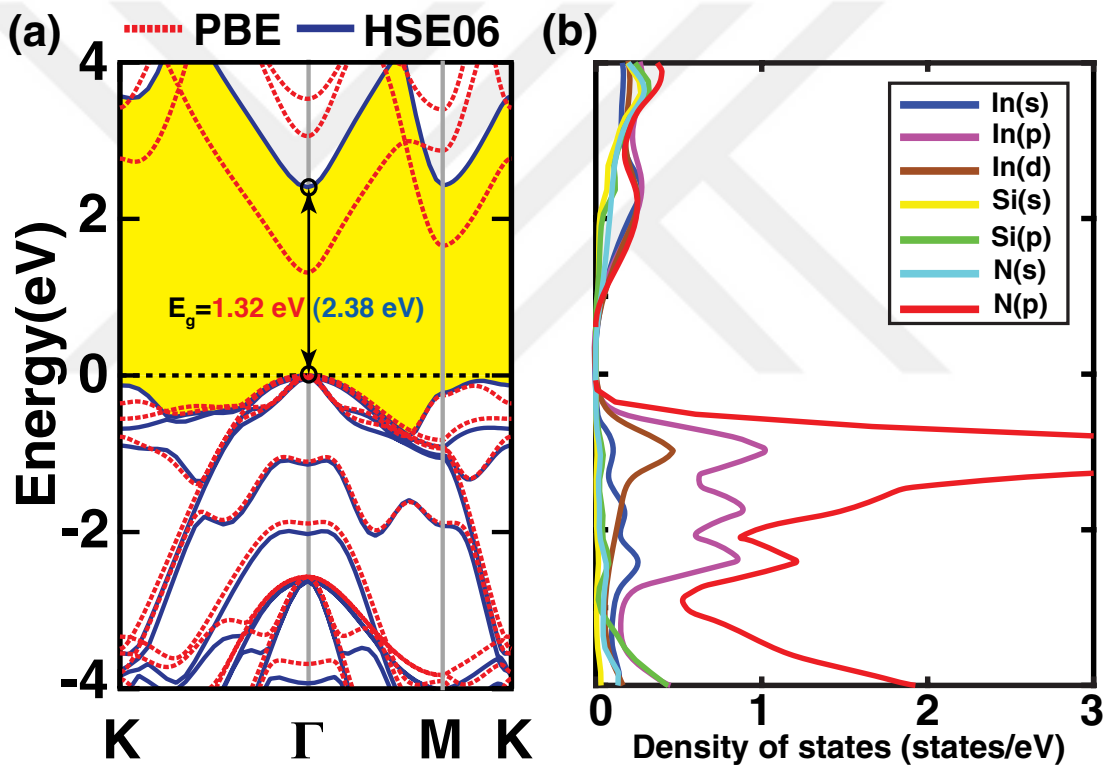


Figure 8.5: (a) The electronic band structures calculated within the level of GGA-PBE (dashed red lines) and HSE06 (blue solid lines) for and (b) the projected density of states (PDOS) of InSiN₂ monolayer. The Fermi level is set to zero.

coefficient, and reflectively [313]. The $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of dielectric function. The variation of $[\varepsilon_2(\omega)]$ as a function of photon energy for in-plane light polarization of the suggested structure is presented in Fig.8.6. Due to the inherent structural isotropy, the optical spectrum along the x - and y -directions is found to be the same. The G_0W_0 (quasi-particle) band gap (E_g^{GW}) of the examined monolayer appears at the visible light region (2.16 eV). For 2D materials with wide energy bandgap, the electron (e) and hole (h) interactions can be sizeable and such interactions are involved in solving BSE approach on top of G_0W_0 (G_0W_0 -BSE). Thus, the results of G_0W_0 -BSE can be utilized to determine the main optical features of the system by including e-e and e-h interactions. The exciton binding energy for the InSiN₂ monolayer is determined by the difference between the E_g^{GW} and the first peak of the spectrum. Since the first absorption peak of the system is located beyond the E_g^{GW} , no bound exciton is acquired, which implies a low coulombic force between quasiparticles of electron-hole pairs.

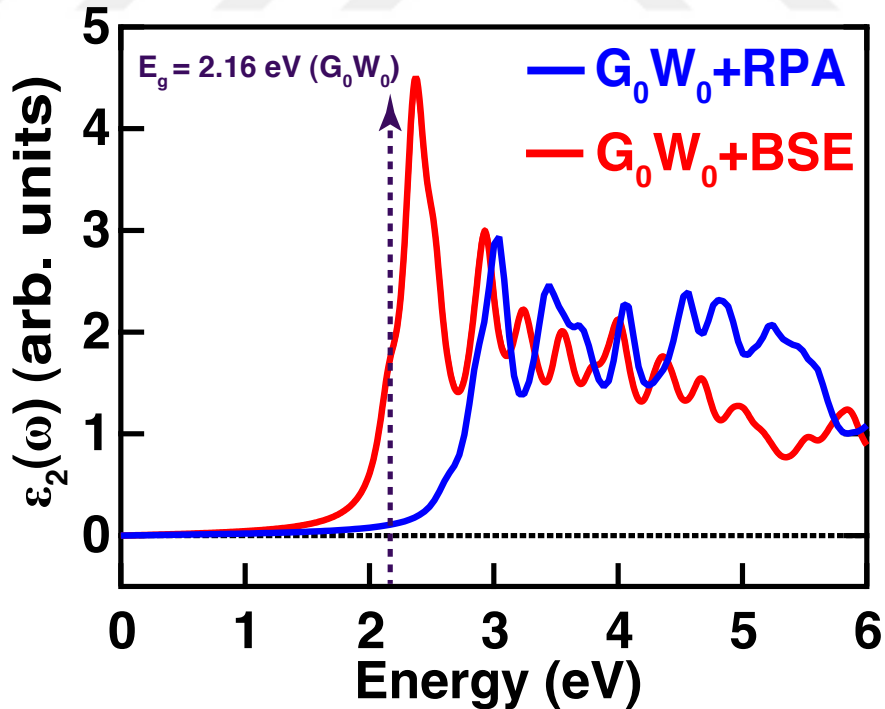


Figure 8.6: The variation of the imaginary part ($\varepsilon_2(\omega)$) of the dielectric function with respect to photon energy for the InSiN₂ nanosheet. The blue and red lines represent optical response at the level of G_0W_0 -RPA and G_0W_0 -BSE.

8.2.4 Mechanical and piezoelectric properties

Next, the mechanical tensors of the structure is computed and the corresponding C_{11} and C_{12} values are found to be 338 and 117 N/m, respectively. The calculated elastic coefficients satisfy the Born-Huang criteria of a 2D hexagonal lattice [$C_{11} > |C_{12}|$ and $C_{66} = (C_{11} - C_{12})/2 > 0$] indicating the mechanical stability of the material. Having demonstrated the mechanical stability of the InSiN₂ monolayer, we further study its mechanical properties. The mechanical properties of 2D crystals can be represented by in-plane stiffness (Y_{2D}), Poisson's ratio (ν), and ultimate tensile strength (UTS). The Y_{2D} , which is the 2D analog to Young's modulus in the 3D bulk structures, is a measure of rigidity of a material under applied load. For a 2D ultra-thin material, a larger Y_{2D} represents higher material's resistance against applied force. Since the SL-InSiN₂ is an isotropic 2D crystal, no orientational dependent mechanical properties is expected. For a hexagonal plane, the Y_{2D} can be obtained with the following expression; $Y_{2D} = (C_{11}^2 - C_{12}^2)/C_{11}$. The attained Y_{2D} value for InSiN₂ monolayer is 298 N/m which is smaller than the theoretical (491 N/m) [303] value for elastic modulus of MoSi₂N₄ crystal and larger than obtained value for InSe (42 N/m) [92] monolayer. It is clear that the replacement of the Mo atom with two vertically covalent bonded In-In atoms affects the mechanical properties of the material and decrease the value of Y_{2D} . We further computed the Poisson's ratio ($\nu = C_{12}/C_{11}$) which is defined as the transverse contraction strain to the longitudinal extension strain in the direction applied force. The calculated ν is found to be 0.34 which is larger than the predicted values for MoSi₂N₄ (0.28) [303] and InSe (0.29)[92], implying the ductile character of the structure. This indicates that SL-InSiN₂ is more effective towards the induced uniaxial strain and compared with MoSi₂N₄ and InSe 2D crystals, for the same applied uniaxial strain, a longer contraction is found in the perpendicular direction. Another essential inherent mechanical feature of 2D materials is UTS. During the strain engineering, extreme strains can be induced into the 2D system. In this regard, a suitable material for strain engineering should preserve it's integrity while strain is applied to the crystal. The UTS is described as the maximum amount of tensile stress that a material can withstand before breaking. To investigate the UTS of the examined system,

firstly a $3 \times 3 \times 1$ supercell was generated to reduce the unit cell size constraint, and then the variation of stress as function of applied equibiaxial tensile strain is calculated. As can be seen from Fig. 8.7, up to 9% the stress-strain curve appears linear, which specifies the elastic regime in the system. After this point, the plastic deformation of the system begins and stress gradually increases to the maxima. Our results indicate that UTS of monolayer InSiN₂ is obtained at 15% biaxial strain which is lower than obtained ultimate strains for MoSi₂N₄ (19.5%)[321] and InSe (26%) monolayers[340].

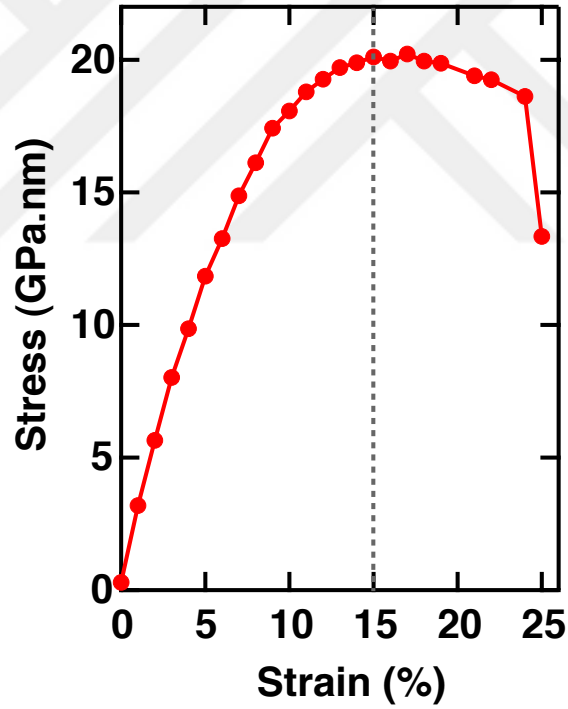


Figure 8.7: The variation of stress as a function of biaxial strain for InSiN₂ monolayer.

Piezoelectric effect is a unique material property which is described as the creation of electric dipole moment as a result of applied external stress (and vice versa) in noncentrosymmetric materials. Theoretical studies and experimental observations have demonstrated the enhancement of piezoelectric coefficients in 2D limit compared to their 3D counterparts[85, 86]. Due to the D_{3h} symmetry of SL-InSiN₂, the piezoelectric tensor in the structure has only in-plane piezoelectric

constant e_{11}/d_{11} . By employing the Voigt notation for the proposed system e_{ij} and d_{ij} become;

$$e = \begin{pmatrix} e_{11} & -e_{11} & 0 \\ 0 & 0 & -e_{11} \\ 0 & 0 & 0 \end{pmatrix}, \quad d = \begin{pmatrix} d_{11} & -d_{11} & 0 \\ 0 & 0 & -2d_{11} \\ 0 & 0 & 0 \end{pmatrix}$$

and the relation between e_{11} and d_{11} is given by

$$d_{11} = \frac{e_{11}}{C_{11} - C_{12}} \quad (8.2)$$

The computed piezoelectric coefficients, e_{11} and d_{11} , of the InSiN₂ nanosheet are 2.59×10^{-10} C/m and 1.72 pm/V, respectively. As a comparison, the computed $e_{11}(d_{11})$ values for single layer MoSi₂N₄ and InSe are 4.39×10^{-10} C/m (1.14 pm/V) [279] and 0.57×10^{-10} (1.46 pm/V) [24], respectively. Such a large in-plane piezoelectricity makes SL-InSiN₂ suitable candidate for applications in piezoelectric devices.

8.2.5 Biaxial strained InSiN₂ monolayer

Many studies have reported that the mechanical strain can significantly modify the electronic and vibrational properties of the materials [341, 342, 150]. Several experimental techniques are available to induce tensile and compressive strains to the ultra-thin materials. One approach is to apply a precise electronic potential to a piezoelectric material and make both tensile and compressive strains achievable [343, 344]. Another technique is to use thermal expansion mismatch between the monolayer and substrate to create a uniform biaxial strain [345]. In the case of Raman spectrum of the materials, the position of Raman peaks and their intensities are strongly dependent on the strain effect [346, 347]. In addition, the stretching and compression of the crystal usually leads to phonon mode softening and hardening, respectively. For a 2D material, an applied strain can be expressed by the following relation; $\epsilon_{ij} = \frac{L'_i - L_i}{L_i}$ where L'_i and L_i are the lattice parameters of the strained and unstrained structures along the strain direction.

For many 2D materials, the phonon instability occurs before mechanical failure. Studies show that in graphene phonon softening happens before the stress reaches its maximum in the unit cell[348]. Therefore, for InSiN₂ nanosheet, in addition to studying stress-strain relation, we investigated the strain dependent phononic instability. Fig.8.8 illustrates the phonon dispersion curve of the structure under 5 % and 8 % compressive and tensile strain, respectively. At 5 % of biaxial compressive strain, the ZA phonon mode softens and small imaginary frequencies around the Γ point appear. On the other hand, the InSiN₂ lattice remains stable under 7% tensile strain without any imaginary modes. As the tensile strain increases to 8%, imaginary frequencies emerge in the phonon spectrum, indicating the dynamical instability of the structure which is less than the strain of mechanical failure. The dynamical instability is arisen by both in-plane (TA) and out-of-plane (ZA) soft modes at K high symmetry points. This phenomena is refereed as the finite wave vector instability, which is likely to happen in 2D ultra-thin materials [348, 349]. When compared to other 2D materials with similar geometry, our computed critical strain value is lower than those reported for MoSi₂N₄ [321, 327]. To explore the phononic softening in the monolayer, we investigate its geometrical structure at the critical strain. The obtained values of $d_{\text{In-In}}$, $d_{\text{In-N}}$, $d_{\text{N-Si}}$, $d_{\text{Si-N}}$ and h are 2.81, 2.20, 1.75, 2.00, and 8.99 Å, respectively. When a biaxial strain is applied to the system, $d_{\text{In-In}}$ and $d_{\text{N-Si}}$ are perpendicular to the direction of the tension. Because of that, the variation of $d_{\text{In-In}}$ and $d_{\text{N-Si}}$ remains almost constant. On the other hand, the bond length between In and N atoms ($d_{\text{In-N}}$) and Si atoms with boundary N atoms ($d_{\text{Si-N}}$) are parallel to the direction of strain, therefore their value dramatically enlarges by the tensile strain, which can be the reason for phonon instability in the structure. We next investigate the effect of strain on the Raman activities of the Raman active modes.

According to Fig.8.9, tensile (compressive) biaxial strain shifts the spectrum towards lower (higher) frequencies, which is associated with the softening (hardening) of the phonon modes. However, due to the fact that induced biaxial strain to the system is in-plane, the response of different phonon modes to the strain and the corresponding frequency shifts of Raman peaks are anticipated to be different. This is correlated with the distinct mode Grüneisen parameters of each phonon

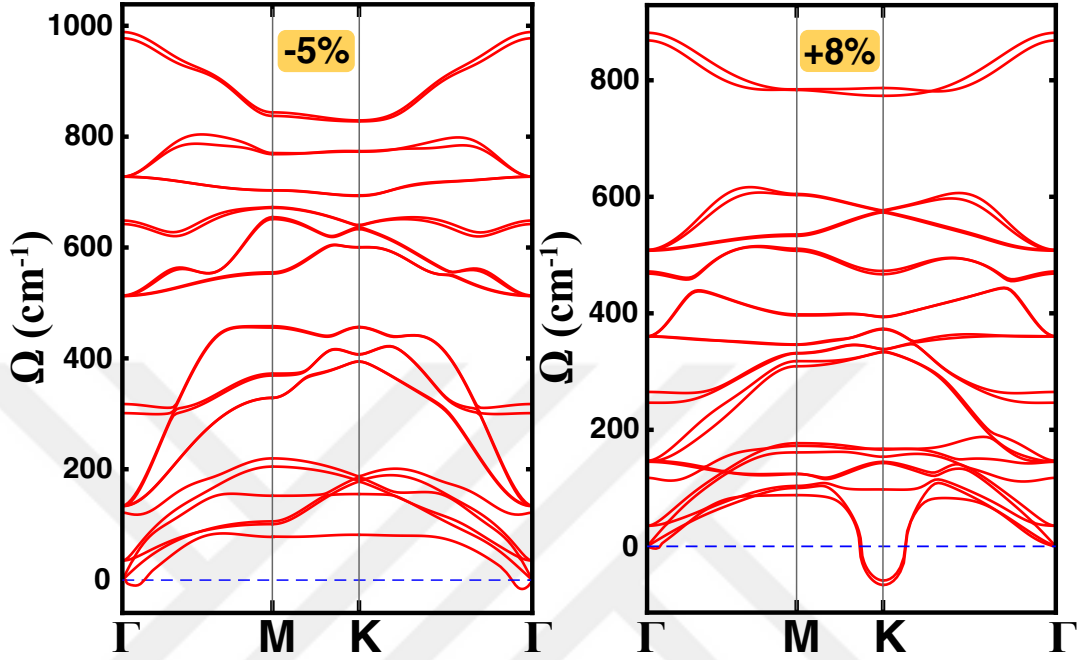


Figure 8.8: Phonon spectra of InSiN₂ monolayer under the biaxial tensile and compressive strains of 8% and 5%, respectively. Imaginary frequencies are displayed as negative frequencies.

mode. For a Raman active vibrational mode, the mode Grüneisen parameter at any wave vector q can be calculated via using the following relation;

$$\gamma(q) = -\frac{a_0}{2\omega_0(q)} \left[\frac{\omega_+(q) - \omega_-(q)}{a_+ - a_-} \right] \quad (8.3)$$

where the a_0 is the relaxed unstrained lattice constant, $\omega_0(q)$ is the frequency of unstrained phonon mode at wave vector q , $\omega_+(q)$ and $\omega_-(q)$ are the frequencies of phonon mode under tensile and compressive strain, respectively, and $a_+ - a_-$ is the difference of the lattice when SL-InSiN₂ is under strain. In our study, the phonon frequencies are computed in $q=0$, at Γ point. The obtained values of mode Grüneisen parameter for the most prominent peak in Raman spectrum, $A'_1(1)$, $A'_1(2)$, $A'_1(3)$, $A'_1(4)$, $E'(2)$ and $E'(3)$, are 0.21, 0.58, 1.10, 0.45, 0.03 and 2.41 respectively. All vibrational modes exhibit phonon softening (hardening) when tensile (compressive) strain is applied. This can be due to the changing of atomic bonding and electron distribution in the system with applied strain which is expected since all phonon modes possess positive mode Gruneissen parameter.

As the Grüneisen parameter of the $A'_1(1)$ and $E'(2)$ have lowest values, their shift of frequency is the smallest among all the phonon modes.

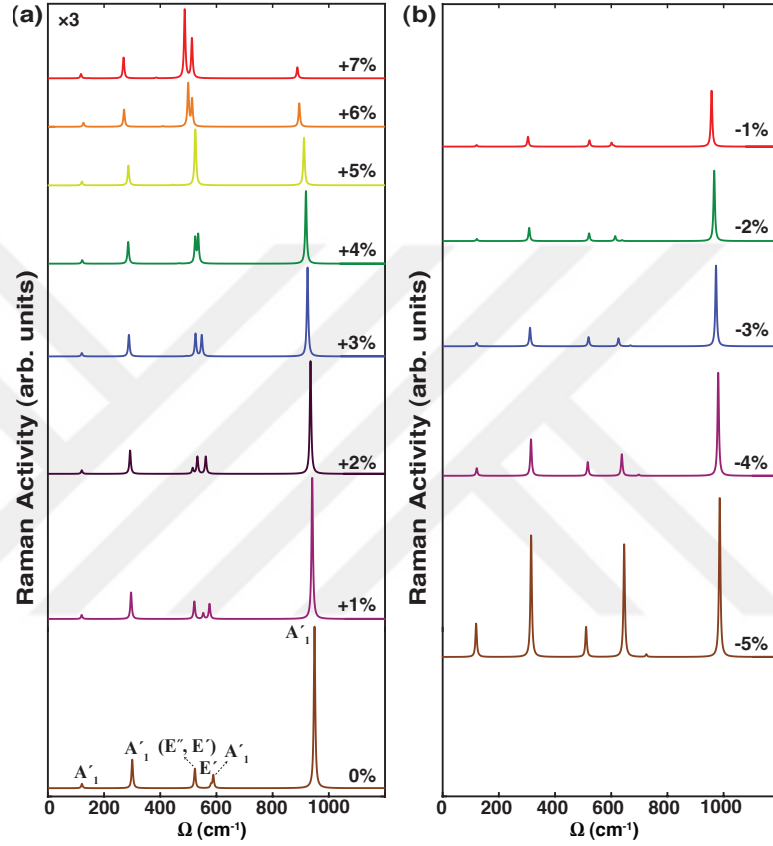


Figure 8.9: The evolution of the Raman spectrum of InSiN₂ nanosheet under (a) tensile and (b) compressive strains.

We next analyzed the effect of strain on the electronic properties of the proposed structure. Fig.8.10 represent the strain engineered electronic band structure at the level of HSE06 functional between the two limits of dynamical instability ($\epsilon = -5\%$ and $\epsilon = +7\%$) with the increment of 2 %. The atomic positions were fully relaxed at each strain point and then the corresponding electronic band profile was obtained from the optimized structures. Three observations can be generalized from the obtained results . First, the semiconducting nature of InSiN₂ monolayer can be tuned via application of biaxial strain. However, for the both tensile and compressive strains, the energy bandgap narrows with increased applied strain, as also seen in InSe monolayers[340]. The effect of compressive strain is more significant than the tensile strain on the energy bandgap. The second

main result is the direct to indirect bandgap transition under the biaxial tensile strains, which is because the induced tensile strain dramatically impacts the valence band edges. As the results of this effect, the VBM of the monolayer shifts from the Γ point to a point between K and Γ points. The shift of VBM can be correlated with the atomic orbital character of the structure at zone center of BZ (Γ point). Thirdly, under biaxial compressive strain the location of conduction band edge swings between Γ and M high symmetry points, whereas the position of VBM remains intact. For compression strain up to 3%, the CBM switches from the Γ to M point but further applying of strain until 5% makes CBM to return to the Γ point. In addition, the variation of band edge positions of VBM and CBM in InSiN₂ monolayer with respect to the vacuum level (calculated with HSE06 functional) as a functional of biaxial strains is represented in Fig. 8.11. Our findings indicate that SL-InSiN₂ is a suitable candidate for strain engineering of its vibrational and electronic properties.

8.3 Conclusion

In conclusion, by using first-principles calculations, we design and analyze the InSiN₂ monolayer which is the Indium based analogous of the MoSi₂N₄ system. Our phonon dispersion calculations and AIMD simulations up to 600 K verified the dynamical stability of the considered system. The electronic structure calculations exhibit that SL-InSiN₂ is a direct bandgap semiconductor with a energy bandgap of 2.38 eV at the level of HSE06 hybrid functional. The computed optical spectrum of the system shows strong light absorption within the visible and near ultra-violet region. Furthermore, the elastic properties of the InSiN₂ monolayer are investigated in terms of in-plane stiffness, Poisson's ratio, and ultimate tensile strength, and the estimated results indicate that the monolayer is a rigid and ductile material. Following the calculation of elastic constants, the piezoelectric coefficients are calculated and large in-plane piezoelectricity ($d_{11} = 1.72$ pm/V) is obtained which is even greater than that of MoSi₂N₄ monolayer. In addition, the effect of biaxial strain on the vibrational and electronic properties of the system is analyzed. Our analysis show that the InSiN₂ nanosheet

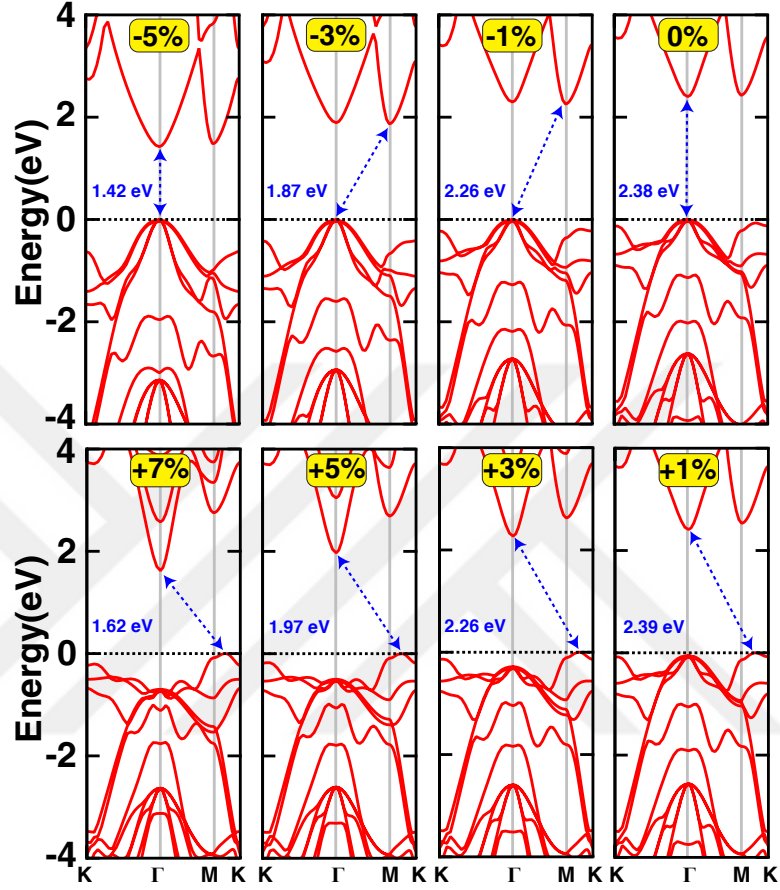


Figure 8.10: The variation of electronic band structures with in-plane biaxial strain for single layer InSiN_2 . The Fermi level is set to zero energy.

can preserve its dynamical stability until 7% tensile and 5% compression strain with large phonon mode shifts and frequencies of Raman active phonon modes soften (harden) under tensile (compressive) strains. In addition, via strain engineering (tensile and compressive), the energy bandgap decreases and direct to indirect bandgap transition occur in the system. Our results indicate that InSiN_2 monolayer with a suitable direct bandgap (lying within the visible spectrum) and proper strain tolerance range can be an ideal material for optoelectronic and nanoelastic applications.

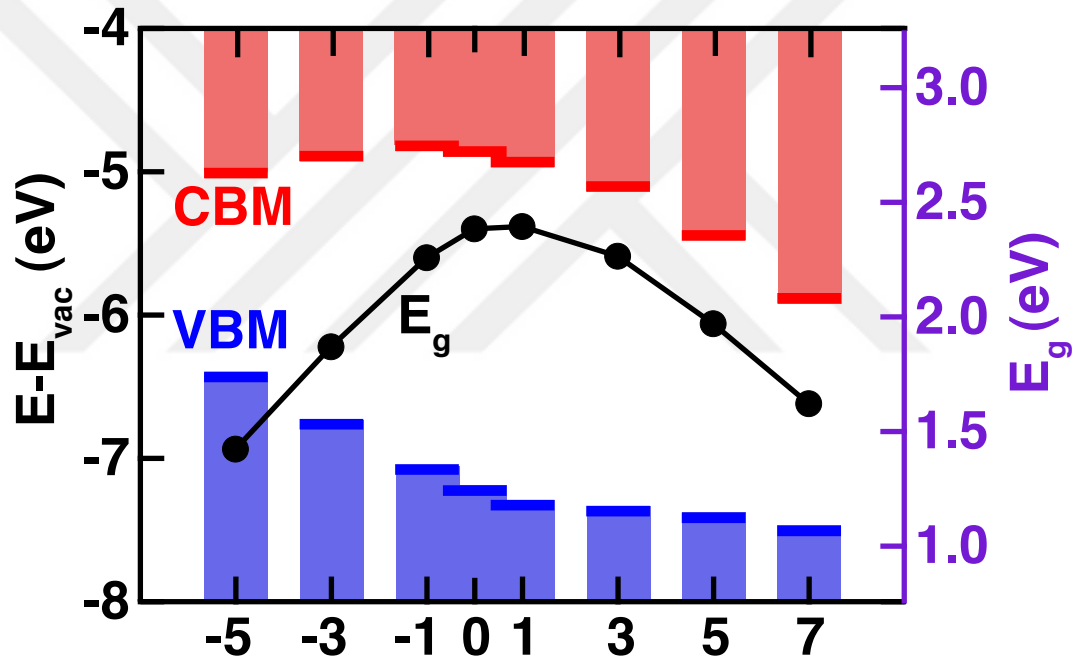


Figure 8.11: The variation of band edge locations of the VBM and CBM in InSiN₂ monolayer with respect to the vacuum level (calculated with HSE06 functional) as a function of equi-biaxial strains. The blue and red bars illustrate the VBM and CBM energies, respectively. The variation of bandgap with strain is shown with black, solid lines.

Chapter 9

CONCLUSION

In the present dissertation, structural, vibrational, thermal, mechanical, piezo-electric, electronic, and optical properties of novel 2D ternary monolayers such as Janus Al-monochalcogenide ($\text{Al}_2\text{XX}'$), Janus W-dichalcogenide oxides (WXO), Janus Bi-chalcohalide (BiXY), ternary pentagonal BNSi , and ternary MSi_2Z_4 systems were studied by means of *ab initio* technique based on DFT. Accordingly, we showed that theoretical investigations on 2D ternary crystals by first-principle methods are a reliable and inexpensive approach for elucidating the physical insights of these materials.

In the first study, we design and investigate Janus aluminum monochalcogenide monolayers, $\text{Al}_2\text{XX}'$ ($X/X' = \text{O, S, Se, and Te}$). Starting from binary constituents, the ternary structures of these nanosheets are obtained and their stability test confirm that except AlTeO all $\text{Al}_2\text{XX}'$ monolayers are dynamically stable. Mechanical properties examination of the proposed structures shows that they have a brittle character, but oxygenation makes them less stiff. Additionally, the electronic structure is also examined revealing their semiconducting nature. It is found that different from their binary counterparts, Al_2XO monolayers are direct band gap semiconductors. Modification of the electronic structure in the presence of biaxial compressive/tensile strain is investigated by taking into account possible indirect-direct band gap transitions.

In the second study, following the realization of WSSe, we propose three structural phases ($1H$, $1T$, and $1T'$) of Janus WXO ($X = S, Se, \text{ and } Te$) monolayers and investigate their basic physical properties. Stability analysis reveals that while $1H$ phase is dynamically stable, $1T$ phase exhibits imaginary frequencies and transforms to the distorted $1T'$ phase. Different from binary systems, additional Raman active modes appear upon the formation of Janus monolayers. Although the mechanical properties of $1H$ - WXO are found to be isotropic, they are orientation-dependent for $1T'$ - WXO . It is also shown that $1H$ - WXO monolayers are indirect band gap semiconductors and the band gap narrows down the chalcogen group. Except $1T'$ -WSO, $1T'$ - WXO monolayers have a narrow band gap correlated with the Peierls distortion.

As the third work, we concentrated on the Janus $BiXY$ ($X = S, Se, Te, \text{ and } Y = F, Cl, Br, I$) monolayers. The structural optimization and vibrational frequency analysis reveal that all of the proposed structures are dynamically stable. The mechanical response of the Janus $BiXY$ crystals in the elastic regime is investigated and the obtained results ascertain their mechanical flexibility. The piezoelectric stress and strain coefficients analysis demonstrates the appearance of strong out-of-plane piezoelectricity in $BiXI$ systems. The calculated electronic band structures reveal that except $BiTeF$, all Janus $BiXY$ monolayers are indirect bandgap semiconductors, and their energy bandgaps span from the infrared to the visible part of the optical spectrum. Subsequently, large Rashba spin splitting is observed in electronic band structures when the spin-orbit coupling is included.

In the fourth study, we performed a comprehensive investigation on 2D ternary pentagonal monolayer of $BNSi$ (penta- $BNSi$). The stability of the examined system is verified from the dynamical, thermal, and mechanical aspects based on phonon dispersion, *ab initio* molecular dynamics (AIMD), and elastic tensor analysis, respectively. The calculated mechanical response of the nanosheet reveals the material's soft and ductile nature. The electronic and electronic transport calculations indicate that the penta- $BNSi$ monolayer satisfy the requirements for photocatalytic water splitting application within practical pH levels. The analysis of optical properties, including many-body effects, points out strong exciton

binding and high light absorption in the visible and near-UV parts of the spectrum.

Moreover, following the recent synthesis of two-dimensional (2D), layered crystals of MoSi_2N_4 and WSi_2N_4 , we design $M\text{Si}_2Z_4$ (M : Pd and Pt, Z : N and P) monolayers and investigate their structural, vibrational, mechanical, electronic, and optical properties. After proving the dynamical, thermal, and mechanical stability of the proposed systems, we characterized them via means of Raman measurement and Infrared analysis. The computed Raman and infrared spectra of the nanosheets reveal that the frequency and the intensity of the most prominent peaks are specified by the type of pnictogen atom in the structures. The obtained values of in-plane stiffness (Y_{2D}) and the Poisson's ratio (ν) indicate that $M\text{Si}_2\text{N}_4$ monolayers are stiffer than $M\text{Si}_2\text{P}_4$ nanosheets and the ν values are found to be within the same range and close to the ductile/brittle transition limit. The electronic structure investigation shows that while $M\text{Si}_2\text{N}_4$ monolayers are quasi-direct wide band gap semiconductors, the $M\text{Si}_2\text{P}_4$ monolayers are semiconductors with an indirect narrow band gap. The optical studies of the suggested systems reveal that while no bound excitons are obtained in $M\text{Si}_2\text{P}_4$ systems, $M\text{Si}_2\text{N}_4$ monolayers possess multiple bound excitons with strong exciton binding.

In the last study, we suggest an octuple atomic layer InSiN_2 ($\text{In}_2\text{Si}_2\text{N}_4$) nanosheet and investigate the effect of equi-biaxial strain on the vibrational and electronic properties of the system. InSiN_2 nanosheet shows dynamical stability up to 7% tensile and 5% compression strain with large phonon mode shifts. The dynamical instability of the structure originates from the in-plane and out-of plane acoustical mode softening. The frequencies of Raman active (RA) phonon modes soften (harden) under tensile (compressive) strains. Moreover, the modification of the electronic structure of the examined monolayer under biaxial compressive or tensile strain shows a direct to indirect bandgap transition within the strain range. Ultimately, as a new kind of 2D material crystals with unique properties, we showed in our study that the predicted ternary 2D materials are intriguing systems with potential applications in a wide range of high technological devices. We believe that our findings in this dissertation will be helpful

for readers to get an insight into the ternary 2D crystals and their fundamental physical properties.



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