Tuning the structural, electronic and dynamical properties of Janus M$_4$X$_3$Y$_3$ (M = Pd, Ni and Co; X,Y = S, Se and Te) monolayers: a DFT study†

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Based on density functional theory, the structural, electronic and vibrational properties of two-dimensional transition metal chalcogenides M$_2$X$_3$ and their Janus type M$_4$X$_3$Y$_3$, where M = Pd, Co and Ni and X = Se, S and Te, are investigated. Motivated by the successful synthesis of a 2D Pd$_2$Se$_3$ monolayer and the proof of the dynamical stability of Ni$_2$Se$_3$ and Co$_2$Se$_3$ monolayers, in terms of the phonon band dispersions, we have systemically studied the fundamental physical properties of Janus transition metal chalcogenides, such as their structural, phonon and thermodynamic stability and their electronic and mechanical properties. Our results show that Janus structures of M$_4$X$_3$Y$_3$ are energetically favorable and dynamically stable. The ab initio molecular dynamic simulations (AIMD) results clearly prove that they kept their thermal stability at room temperature. We have demonstrated their structural, electronic and vibrational properties and Raman spectra. The electronic band dispersions show that monolayer Co$_2$Se$_3$ shows half-metal properties with a moderate band gap (1.01 eV), Pd$_2$Se$_3$ has a 1.42 eV direct band gap, while Ni$_2$Se$_3$ has a 1.38 eV indirect band gap. Pd$_4$Se$_3$S$_3$, Pd$_4$Se$_3$Te$_3$ and Pd$_4$S$_3$Te$_3$ are indirect band gap semiconductors with band gaps of 1.22 eV, 1.05 eV and 0.61 eV, respectively. Ni$_4$Se$_3$S$_3$, Ni$_4$Se$_3$Te$_3$ and Ni$_4$S$_3$Te$_3$ are indirect band gap semiconductors with band gaps of 1.61 eV, 0.77 eV and 0.49 eV, respectively. While pristine Co$_2$Se$_3$ is shown to have half-metallicity (HM), the HM behaviour of the Janus Co$_4$Se$_3$Te$_3$ and Co$_4$S$_3$Te$_3$ monolayers disappear and Co$_4$Se$_3$S$_3$ remains a HM with a moderate band gap of 0.85 eV. In addition, the Raman spectra of these Janus materials are shown to exhibit totally distinctive features as compared to those of the pristine materials. This work reveals the important material properties of Janus type M$_4$X$_3$Y$_3$ monolayers, where M = Pd, Co and Ni and X = Se, S and Te, which could have wide applications in new functional devices.

1 Introduction

Since the successful synthesis of graphene, two-dimensional (2D) materials have received increasing interest in their unique properties.$^1$ Due to the band gap of graphene being zero limiting its electronic applications, there has been emerging interest in other 2D materials beyond graphene,$^2$ such as hexagonal boron nitride (h-BN),$^5$–$^7$ MXenes$^8$–$^{14}$ and transition metal di-chalcogenides (TMDCs).$^{15}$–$^{18}$ The general formula for TMDCs is MX$_2$; where M is the transition metal and X is the double chalcogenide (S, Se or Te), and they are mostly in the honeycomb lattice of the 2H phase, such as MoS$_2$, MoSe$_2$ and WS$_2$.$^{19}$–$^{20}$

Monolayer PdSe$_2$, which is a special 2D TMDC material, possesses an uncommon pentagonal structural motif and anisotropic properties$^{21}$ and has been successfully synthesized via mechanical exfoliation.$^{22}$ While bulk PdSe$_2$ has a narrow band gap of 0.03 eV, monolayer PdSe$_2$ has an indirect band gap of about 1.43 eV due to the occurrence of a remarkable quantum confinement effect. The discovery of pentagonal PdSe$_2$ makes the emerging physics related to the low symmetry structure possible and it has significant potential in piezoelectric,$^{23}$–$^{24}$ optoelectronic$^{25}$–$^{27}$ and thermoelectric$^{28}$–$^{32}$ applications. An alternative phase of 2D TMDCs is formed as a descendent of the bulk phase which is indicated in the chemical composition: M$_2$X$_3$ (M = Pd, Ni and Co; X = S, Se and Te). Pd$_2$Se$_3$, which is the one of the members of the M$_2$X$_3$ family, was synthesized by cleaving it from PdSe$_2$ by Li et al. They demonstrated that Se vacancies in the pristine PdSe$_2$ reduce the distance between the layers, melding the two layers into one, thus, it creates a new form of the Pd$_2$Se$_3$ monolayer. Pd$_2$Se$_3$ is unique in several aspects: first, the thermodynamically and kinetically stable Pd$_2$Se$_3$ is a semiconducting material with a moderate band gap of 0.45 eV and its carrier mobility (178.02 cm$^2$ V$^{-1}$ s$^{-1}$) is...
migrating to the edge instead of forming line vacancies like other TMCs, suggesting the high mobility of the V-Se9 under an electron beam. The distinct monolayer Pd2Se3 defects can enrich the structural knowledge of 2D materials and offer more possibilities for exploiting the versatile properties of 2D materials through defect engineering. Moreover, Lv et al. have extended the study to M2Se3 monolayers, where M = Pd, Co or Ni, to understand their structural stabilities and electronic, magnetic and mechanical properties. They have demonstrated that M2Se3 monolayers have an intrinsic large out-of-plane negative Poisson’s ratio (NPR) and superior mechanical flexibility, with their resistance of critical strain (50–60%) being two times greater than those of well-known 2D materials. Co2Se3 was found to be half-metallic and ferromagnetic with a high Curie temperature (>700 K)\(^{39}\). Furthermore, Xiong et al. have studied the mechanical, electronic and optical properties of orthorhombic M2X3 (M = Ni and Pd; X = S, Se and Te) (especially Ni2Se3 and Pd2S3) and their potential applications in photocatalytic water splitting within the visible and ultraviolet light regions.\(^{40}\)

An alternative way to make new 2D materials is modified 2D Janus materials, which introduces out-of-plane structural symmetry. The formation of 2D Janus materials that possess different atoms on two faces has been achieved for the tailoring of 2D materials designed at the atomic level. Although Janus 2D materials do not exist in nature, Janus monolayers of TMDs, with the MoS2 structure modified as S–Mo–Se sandwiched layers, has also been successfully synthesized\(^{31,42}\) for the first time. The characterization results showed that Janus 2D materials may have unique properties, such as strong Rashba spin splitting, a second-harmonic generation (SHG) response, large piezoelectric effect and good catalytic performance. These new materials have potential engineering applications in such fields as sensors, actuators and novel electromechanical devices.\(^{43–45}\) According to our knowledge, Janus structures of M2X3 (M = Ni, Pd and Co; X = S, Se and Te) monolayers have not been reported up to this date. Our study could motivate experimental efforts in achieving Janus structures of M2X3 monolayers for new applications in electronic, optoelectronic and thermoelectric devices.

Inspired by M2X3’s unique properties, we have constructed possible Janus structures of M2X3, which are classified into three forms: palladium derivatives (Pd4Se3S3, Pd4Se3Te3 and Pd4S3Te3), cobalt derivatives (Co4Se3S3, Co4Se3Te3 and Co4S3Te3) and nickel derivatives (Ni4Se3S3, Ni4Se3Te3, Ni4S3Te3) to investigate their structural, electronic, vibrational and high temperature dynamical stability properties using first principles methods. The paper is organized as follows: details of the computational methodology are given in Section 2. The ground-state structures of the pristine and Janus structures of M2X3 (M = Ni, Pd and Co; X = S, Se and Te) monolayers are obtained and their dynamical stabilities are tested by phonon spectrum analysis, Raman spectra and \textit{ab initio} molecular dynamic calculations. In addition, the electronic properties of the pristine and Janus structures of M2X3 are also given in Section 3. Finally, the results are concluded in Section 4.

2 Computational methodology

For the first principles calculations, the plane-wave basis projector augmented wave (PAW) method was employed in the framework of density functional theory (DFT).\(^{46}\) The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE)\(^{47}\) form was used for the exchange–correlation potential, as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^{48,49}\) The van der Waals (vdW) correction to the GGA functional was included using the Becke–Johnson (BJ) damping of the DFT-D3 method.\(^{50}\) To consider the more precise band structures, electronic calculations of Pd4Se3S3, Ni4Se3S3 and Janus M2X3 (M = Pd and Ni; X = S, Se and Te) were also performed using the spin–orbit coupling (SOC) effects and hybrid functional (HSE06) approach.\(^{51}\) In addition, to consider the strong correlation effects between the d-orbitals of Co atoms, electronic structure calculations of Co4Se3S3 and Co-based Janus M2X3 (M = Co; X = S, Se and Te) monolayers were performed using Dudarev’s GGA+U approach.\(^{52}\) In our calculations, the Hubbard on-site Coulomb parameter (U) was taken into consideration and the U value of the Co atom was set to be 3 eV. Analysis of the charge transfer in the structures was determined by the Bader technique.\(^{53}\) Electronic and geometric relaxations of the pristine single-layer M2Se3 (M = Pd, Ni and Co) and Janus structures of the M2X3 (M = Ni, Pd and Co; X = S, Se and Te) monolayers were performed on 5- and 10-atom unit cells, respectively. The kinetic energy cut-off for plane-wave expansion was set to be at least 290 eV and the energy was minimized until its variation in the following steps became 10\(^{-5}\) eV. The Gaussian smearing method was employed for the total energy calculations and the width of the smearing was chosen to be 0.05 eV. The total Hellmann–Feynman forces in the unit were reduced to 10\(^{-3}\) eV Å\(^{-1}\) for the structural optimization. A minimum of 6 \times 6 \times 1 \Gamma\text{-centered} \text{k-point} samplings were used for the two primitive unit cells. To avoid interaction between the neighboring layers, a vacuum space of at least 25 Å was implemented in the calculations. To check the dynamic stability, we used the density functional perturbation theory (DFPT) using the small displacement methodology.\(^{54,55}\) The force constant matrix was constructed by the slight displacements of a maximum 4 \times 4 \times 1 supercell whose Brillouin zone (BZ) was sampled with a maximum of 6 \times 6 \times 1 \text{k-points} by implementing the PHONOPY code,\(^{56}\) depending on the unit cell size. We also increased the electronic degrees of freedom to 10\(^{-8}\) eV to ensure a reasonable convergence. The phonon frequencies and the corresponding
off-resonant Raman activities were calculated at the point of the BZ using the same methodology. Additionally, ab initio molecular dynamics simulations (AIMD) were performed to assess the thermal stability of the Janus structures of M₂X₃ (M = Ni, Pd and Co; X = S, Se and Te) monolayers. The initial configurations of these monolayers were annealed at room temperature (300 K). AIMD simulations in the NVT ensemble lasted for 10 ps with a time step of 1.0 fs and the temperature was controlled using the Nose–Hoover thermostat.

3 Results and discussion

3.1 Pristine M₂Se₃ (M = Pd, Ni and Co) monolayers

First, we have examined the geometric optimization of monolayer Pd₂Se₃, Co₂Se₃ and Ni₂Se₃, which show significant structural similarity. All of the geometric structures are built up with 10 atoms in a unit cell; 4 of the atoms are M type atoms (Pd, Co and Ni), which are sandwiched between 6 Se atoms which are placed half-and-half above and below the M type atoms (see Fig. 1). We have continued our calculations with Pd₂Se₃ and Ni₂Se₃, which have nonmagnetic (NM) ground states, while Co₂Se₃, which has the electronic configuration of 3d⁷⁴s² and Co⁡⁺ has unpaired electrons, which gives rise to the magnetic state of the Co-based Janus structure.

In our theoretical framework, the relaxed structural parameters, i.e., the lattice parameters (a and b), of the two-dimensional Pd₂Se₃, Co₂Se₃ and Ni₂Se₃ structures are found to be 5.89 Å and 6.00 Å, 5.46 Å and 5.74 Å, and 5.37 Å and 5.82 Å, respectively. As shown in Table 1, the bond lengths (d) between the M atoms and the Se atoms vary between 2.45–2.53 Å, 2.32–2.38 Å and 2.31–2.37 Å (for M = Pd, Co and Ni, respectively). The vertical height (h), defined as the out of plane distance between the top and bottom X sublayers, is 3.86 Å for Pd₂Se₃, 3.74 Å for Co₂Se₃, and 3.75 Å for Ni₂Se₃. According to the Bader charge analysis, the Pd atom donates 0.15e, the Co atom donates 0.37e and the Ni atom donates 0.30e to the Se atoms. The cohesive energies (per atom) of the pristine X₂Se₃ (X = Ni, Pd, Co) structures were calculated using the following relation:

\[ E_{\text{Coh}} = \frac{E(X_2Se_3) - 4 \times E(X) - 6 \times E(Se)}{10} \]  

where \( E(X_2Se_3) \) is the total energy of the X₂Se₃ (X = Ni, Pd and Co) monolayers and \( E(X) \) and \( E(Se) \) are the single isolated atom energies of Ni, Pd and Co and Se, respectively. The calculated cohesive energies \( E_{\text{Coh}} \) for Pd₂Se₃, Ni₂Se₃ and Co₂Se₃ are 3.73, 4.06 and 4.12 eV per atom, respectively. Our results indicate that they are energetically stable and these materials can be synthesized.

The vibrational properties, shown in Fig. 1(d–f), show that the 2D Pd₂Se₃, Co₂Se₃ and Ni₂Se₃ monolayers are dynamically stable, as previously demonstrated by Lv et al.⁹ All of the structures have 30 phonon modes. The phonon modes with the highest frequencies at the Γ point are 252.7 cm⁻¹, 303.1 cm⁻¹ and 315.1 cm⁻¹ for Pd₂Se₃, Co₂Se₃ and Ni₂Se₃, respectively. The significant difference of the phononic calculation compared with earlier work⁹ is the increase in the frequency of the S point of Co₂Se₃ with most of the phonon modes still having positive frequencies.

The band structures of the 2D Pd₂Se₃ and Ni₂Se₃ monolayers with the HSE + SOC calculation and Co₂Se₃ with the GGA+U calculation (the majority spin is colored in blue and the minority spin is in orange) were calculated and are presented in Fig. 2. Interestingly, it can be clearly seen that the FM Co₂Se₃ shows the half-metal property with a moderate band gap (1.01 eV) for the spin-up state (blue lines) while the band can cross the Fermi level for the spin-down state (orange lines). The NM Pd₂Se₃ and Ni₂Se₃ monolayers both show indirect band gaps. The Pd₂Se₃ monolayer has an 1.42 eV direct band

**Table 1** Calculated parameters for the pristine X₂Se₃ unit cell: lattice constants: a and b, M–Se bond lengths: d, vertical height: h, average charge transfer from the M type atom: \( \rho \), cohesive energy per atom: \( E_{\text{Coh}} \), and electronic band gap: \( E_g \)  

<table>
<thead>
<tr>
<th>X₂Se₃</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>d (Å)</th>
<th>h (Å)</th>
<th>( \rho ) (e)</th>
<th>( E_{\text{Coh}} ) (eV)</th>
<th>( E_g ) (eV)</th>
</tr>
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<tr>
<td>Pd₂Se₃</td>
<td>5.80</td>
<td>6.00</td>
<td>2.45–2.53</td>
<td>3.86</td>
<td>–0.15</td>
<td>3.73</td>
<td>1.42</td>
</tr>
<tr>
<td>Ni₂Se₃</td>
<td>5.37</td>
<td>5.82</td>
<td>2.31–2.37</td>
<td>3.75</td>
<td>–0.30</td>
<td>4.06</td>
<td>1.38</td>
</tr>
<tr>
<td>Co₂Se₃</td>
<td>5.46</td>
<td>5.74</td>
<td>2.32–2.38</td>
<td>3.74</td>
<td>–0.37</td>
<td>4.12</td>
<td>—</td>
</tr>
</tbody>
</table>
with the valence band maximum (VBM) and the conduction band minimum (CBM) lying at the $\Gamma$ point. The Ni$_2$Se$_3$ monolayer has an indirect band gap of 1.38 eV (VBM: $X$–$S$ – CBM: $\Gamma$).

3.3 Structural and electronic properties

In the geometric optimization calculations, the structural phases of M$_4$X$_3$Y$_3$ negligibly change with respect to their pristine structures. In the Co derivatives, the lattice constant varies by a maximum of 0.42 Å and also the Ni-Se bond length varies between 2.30–2.37 Å, the Ni–S bond length varies between 2.18–2.25 Å and the Ni–Te bond length varies between 2.49–2.59 Å in the two dimensional Janus materials. In the Co derivatives, the lattice constant varies by a maximum of 0.22 Å and also the Co–Se bond length varies between 2.30–2.40 Å, the Co–S bond length varies between 2.18–2.27 Å and the Ni–Te bond length varies between 2.49–2.59 Å in the two dimensional Janus materials. In the Ni derivatives, the lattice constant varies by a maximum of 0.35 Å and also the Ni–Se bond length varies between 2.30–2.43 Å and the Pd–Te bond length varies between 2.61–2.67 Å in the two dimensional Janus materials.

As expected, changing the chalcogen type of one face leads to differences in the thickness of the studied materials. It is seen that there is a total of 0.65 Å variation in thickness from the Pd$_2$Se$_3$ type, with the thicknesses of the Pd derivatives ranging between 3.21–4.07 Å. Also, there is a total of 0.17 Å variation in thickness from the Ni$_2$Se$_3$ type, with the thicknesses of the Ni derivatives ranging between 3.59–3.92 Å. Furthermore, it is seen that there is a total of 0.21 Å variation in thickness from the Co$_2$Se$_3$ type, with the thicknesses of the Co derivatives ranging between 3.53–3.94 Å.

According to the Bader charge analysis, the transition metal type atoms donate most of the e in the M$_4$X$_3$Y$_3$ Janus structures; 0.20e is donated when M is Pd, 0.36e is donated when M is Ni and 0.45e is donated when M is Co.

The cohesive energies (per atom) of the Janus M$_4$X$_3$Y$_3$ (M = Pd, Ni and Co; X, Y = S, Se and Te) monolayers were calculated using the following relation:

$$E_{\text{Coh}} = \frac{|E(M, X, Y) - 4 \times E(M) - 3 \times E(X) - 3 \times E(Y)|}{10}$$

where $E(M, X, Y)$ is the total energies of the M$_4$X$_3$Y$_3$ (M = Pd, Ni and Co; X, Y = S, Se and Te) monolayers, $E(M)$ is the single isolated atom energies of Ni, Pd and Co and $E(X)$ and $E(Y)$ are the single isolated atom energies of S, Se and Te. The calculated cohesive energies $E_{\text{Coh}}$ for the M$_4$X$_3$Y$_3$ (M = Pd, Ni and Co; X, Y = S, Se and Te) monolayers are given in Table 2. Our results indicate that they are energetically stable and these materials can be synthesized.

### Table 2

<table>
<thead>
<tr>
<th>M</th>
<th>Pd</th>
<th>Ni</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Y</td>
<td>Se</td>
<td>Se</td>
<td>Se</td>
</tr>
<tr>
<td>E$_{\text{Coh}}$</td>
<td>38.5</td>
<td>36.5</td>
<td>43.0</td>
</tr>
<tr>
<td>E$_g$</td>
<td>1.22</td>
<td>1.05</td>
<td>0.49</td>
</tr>
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</table>

lengths are not drastically different than those in the cases of Pd$_4$Se$_3$S$_3$ and Pd$_4$Se$_3$Te$_3$. In the meantime, the Pd–S bond length varies between 2.33–2.43 Å and the Pd–Te bond length varies between 2.61–2.67 Å in the two dimensional Janus materials. In the Ni derivatives, the lattice constant varies by a maximum of 0.35 Å and also the Ni–Se bond length varies between 2.30–2.43 Å, the Ni–S bond length varies between 2.18–2.23 Å and the Ni–Te bond length varies between 2.49–2.59 Å in the two dimensional Janus materials. In the Co derivatives, the lattice constant varies by a maximum of 0.22 Å and also the Co–Se bond length varies between 2.30–2.40 Å, the Co–S bond length varies between 2.18–2.27 Å and the Ni–Te bond length varies between 2.49–2.59 Å in the two dimensional Janus materials in Table 2.
The band structures of the Pd- and Ni-based Janus $M_4X_3Y_3$ monolayers were calculated using HSE and SOC and the band structures of the Co-based Janus $M_4X_3Y_3$ monolayers with GGA+U were calculated, which are presented in Fig. 4. Pd$_4$Se$_3$S$_3$, Pd$_4$Se$_3$Te$_3$, and Pd$_4$S$_3$Te$_3$ are indirect band gap semiconductors with energy band gaps of 1.22 (VBM: $\Gamma$ – CBM: S), 1.05 (VBM: X – CBM: Y) and 0.61 (VBM: X – CBM: Y) eV, respectively. Ni$_4$Se$_3$S$_3$, Ni$_4$Se$_3$Te$_3$, and Ni$_4$Se$_3$S$_3$ are indirect band gap semiconductors with energy band gaps of 1.61 (VBM: X – CBM: Y) and 0.77 (VBM: S – CBM: Y) and 0.49 (VBM: S – CBM: Y) eV, respectively (see Table 1). As discussed above, this is due to Co$^{2+}$ (3d$^7$) having unpaired electrons, which give rise to the magnetic state of the half-metallicity (HM) with a moderate band gap (1.01 eV) with Co$_4$Se$_3$S$_3$ and Co$_4$Se$_3$Te$_3$ monolayers disappears and Co$_4$Se$_3$S$_3$ remains a HM with a moderate band gap (0.85 eV) (see Fig. 4).

### 3.4 Vibrational properties with Raman spectra and thermal properties

It is seen in Fig. 5 that the Pd variations and Ni variations have mostly positive phonon modes. Co$_4$Se$_3$S$_3$ and Co$_4$S$_3$Te$_3$ are quite stable at positive frequencies. It appears that Pd$_4$Se$_3$Te$_3$ has phonon softening at the phonon branch with the highest frequency, which is calculated to be 241.3 cm$^{-1}$. On the other hand, the other Pd variations, Pd$_4$Se$_3$S$_3$ and Pd$_4$S$_3$Te$_3$, have phonon hardening at the phonon branch with the highest frequency. There is a 4.7 cm$^{-1}$ difference between the highest frequency of Pd$_4$Se$_3$S$_3$ (429.5 cm$^{-1}$) and that of Pd$_4$Se$_3$Te$_3$ (424.8 cm$^{-1}$) and about a 176.8 cm$^{-1}$ difference from that of Pd$_4$Se$_3$S$_3$ (827.7 cm$^{-1}$) at the $\Gamma$ point. In the phonon spectrum of Pd$_4$Se$_3$S$_3$, there appears to be 1 triply degenerate and 4 doubly degenerate modes, while the other Pd variations show only singly and doubly degenerate modes, where Pd$_4$Se$_3$Te$_3$ acquires 1 doubly degenerate mode and Pd$_4$Se$_3$S$_3$ has 2 doubly degenerate modes.

The out-of-plane phonon mode of Pd$_4$Se$_3$S$_3$ at 143.6 cm$^{-1}$ arises from the vibration of the Se and S atoms. There are two Raman active out-of-plane phonon modes at 228.4 and 283.6 cm$^{-1}$ of Pd$_4$Se$_3$S$_3$, which can be seen in Fig. 5. It is also seen that the Raman active phonon mode at 257.9 cm$^{-1}$ appears from the in-plane vibration of the Se atoms. The phonon mode with the highest frequency of the Pd$_4$Se$_3$S$_3$ dominates the remaining Raman active modes by the in-plane movement of the S atoms. Pd$_4$Se$_3$Te$_3$ has a Raman active phonon mode in the low-frequency regime at 99.5 cm$^{-1}$ that appears from the out-of-plane motion of the Pd and Te atoms. The two Raman active modes at 153.7 and 110.1 cm$^{-1}$ happen from the out-of-plane motion. The phonon mode at 177.3 cm$^{-1}$ resembles the significant Raman active mode which occurs from the in-plane motion of the Te atoms and the out-of-plane motion of the Se atoms. An out-of-plane phonon mode occurs at 208.3 cm$^{-1}$ and the phonon mode with the highest frequency results from the in-plane motion of the Se atoms. The Janus structure Pd$_4$Se$_3$Te$_3$ has phonon softening and the other types have phonon hardening at the phonon mode with the highest frequency and the Ni derivatives are similar; Ni$_4$Se$_3$Te$_3$ has phonon softening at the phonon branch with the highest frequency, which is calculated to be 294.6 cm$^{-1}$. On the other hand, the other Ni variations, Ni$_4$Se$_3$S$_3$ and Ni$_4$Se$_3$Te$_3$, have phonon hardening at the phonon branch with the highest frequency. There is a 37.9 cm$^{-1}$ difference between the highest frequency of Ni$_4$Se$_3$S$_3$ (411.6 cm$^{-1}$) and that of Ni$_4$Se$_3$Te$_3$ (376.7 cm$^{-1}$) and about a 96.5 cm$^{-1}$ difference from that of Ni$_4$Se$_3$S$_3$ (315.1 cm$^{-1}$) at the $\Gamma$ point. In the Ni variations, it is seen that Ni$_4$Se$_3$Te$_3$ has a triply degenerate mode. The doubly degenerate mode number of the Ni Janus structures are 3, 4 and 6 for Ni$_4$Se$_3$S$_3$, Ni$_4$Se$_3$Te$_3$ and Ni$_4$Se$_3$S$_3$, respectively.

The Ni Janus structures seem to be more Raman active than the Pd variations. Firstly, the Raman active phonon modes of Ni$_4$Se$_3$S$_3$ can be seen in Fig. 5. The phonon mode at 146.7 cm$^{-1}$ occurs from the in-plane motion of the Ni atoms and the out-of-plane motion of the Se atoms. A quite smaller Raman active phonon mode can be seen at 146.7 cm$^{-1}$; on the other hand, the dominant Raman active phonon mode of Ni$_4$Se$_3$S$_3$ vibrates at the doubly degenerate mode at 244.9 cm$^{-1}$. A singly degenerate mode at 332.8 cm$^{-1}$ occurs from the in-plane motion of the Ni and the out-of-plane motion of the Se and S atoms that have quite prominent Raman activity. The phonon mode with
The highest frequency occurs from the vibration of S and Ni atoms.

The Raman activity of the two-dimensional Janus material Ni₄Se₃S₃ is studied. A Raman active phonon mode arises at the low-frequency regime (82.0 cm⁻¹), occurring from the out-of-plane vibrations of the Se and Te atoms and the in-plane motion of the Ni atoms. A doubly degenerate mode at 157.4 cm⁻¹ has prominent Raman activity. The most dominant
Fig. 7  The fluctuations of the total energies of the Janus $M_X Y_3$, where $M = \text{Pd, Co and Ni}$ and $X = \text{Se, S and Te}$, during the AIMD simulations at 300 K. The insets are snapshots of the structures at the end of the simulations at the end of each 2 ps.
Raman active out-of-plane phonon mode occurs at 169.8 cm$^{-1}$. On the other hand, a single degenerate mode with minor Raman activity with the out-of-plane motion of the Se and Te atoms and the in-plane motion of the Ni atoms is seen to vibrate at 173.2 cm$^{-1}$. It is also seen that an average Raman active phonon mode with out-of-plane motion oscillates at 254.8 cm$^{-1}$.

In terms of the Raman activity, Ni$_4$S$_2$Te$_4$ differs from the other materials whose Raman activities were studied. The most dominant Raman mode occurs in the low-frequency regime at 87.0 cm$^{-1}$. A single degenerate Raman active phonon mode with the out-of-plane motion of the S and Ni atoms and the in-plane motion of the Te atoms is found at 141.1 cm$^{-1}$. A breathing-like Raman active mode at 184.1 cm$^{-1}$ results from the out-of-plane motion of the atoms. The two phonon modes with nearly similar atomic motions at 220.8 and 305.6 cm$^{-1}$ develop from the out-of-plane oscillations of the S and Te atoms and the in-plane vibrations of Ni atoms, respectively. The phonon mode at 352.6 cm$^{-1}$ results from most of the vibration of the out-of-plane motions of the S atoms.

For the Co variations, the Janus structures Co$_4$Se$_3$S$_3$ and Co$_4$S$_3$Te$_3$ appear to have higher frequencies than that of Co$_2$Se$_3$ (378.0 and 359.3 cm$^{-1}$, respectively) at the $\Gamma$ point. Another important thing to note is that while the peak at the S point of Co$_2$Se$_3$ was at 491.4 cm$^{-1}$, Co$_4$Se$_3$S$_3$ has a significantly higher frequency at 669.5 cm$^{-1}$. On the other hand, Co$_4$Se$_3$S$_3$ shows 2 triply degenerate modes and 4 doubly degenerate modes, while Co$_4$S$_3$Te$_3$ has 3 doubly degenerate modes.

In addition, the thermal stabilities are examined by performing ab initio molecular dynamics (AIMD) simulations using the NVT ensemble with a fixed particle number, volume and temperature. For the AIMD simulations, a 40-atom supercell is used for each single layer with a $k$-mesh of $4 \times 4 \times 1$. The thermal stability investigations start with the optimized structure of the Janus M$_4$X$_3$Y$_3$ single layers, where M = Pd, Co and Ni and X = Se, S and Te, at 0 K. We further extend the thermal stability calculations up to room temperature (300 K). During the simulations, the temperature is kept at the given temperatures and the fluctuations of the total energy and the changes of these Janus atomic structures during the simulations are shown in Fig. 7. The time step is set to 1 fs (1000 steps) with a total simulation time of 10 ps. The structure snapshots are taken at the end of the each simulation every 2 ps. The fluctuations of the total energy are shown on top of each other for each 2 ps. As can be seen in Fig. 7, none of the single layers undergo structural reconstruction at 300 K, indicating the thermal stability. The energies of these systems systematically correspond with their optimized geometries, confirming their thermal stability of Janus M$_4$X$_3$Y$_3$ single layers, where M = Pd, Co and Ni and X = Se, S and Te. Our results showed that Pd$_4$Se$_3$S$_3$, Pd$_4$Se$_3$Te$_3$, and Pd$_4$S$_3$Te$_3$ are indirect band gap semiconductors with energy band gaps of 1.22 (VBM: $\Gamma$ – CBM: S), 1.05 (VBM: X – CBM: Y) and 0.61 (VBM: X – CBM: Y) eV, respectively. Ni$_4$Se$_3$S$_3$, Ni$_4$Se$_3$Te$_3$ and Ni$_4$S$_3$Te$_3$ are indirect band gap semiconductors with energy band gap of 1.61 (VBM: X – CBM: $\Gamma$), 0.77 (VBM: S – CBM: Y) and 0.49 (VBM: S – CBM: Y) eV, respectively. Co$_2^+$ (3d$^7$) has unpaired electrons, which give rise to the magnetic state of the Co$_2$Se$_3$ monolayer. While pristine Co$_2$Se$_3$ was calculated to show half-metallicity (HM) with a moderate band gap (1.01 eV) and large intrinsic ferromagnetism, the HM behaviour of the Janus Co$_4$Se$_3$Te$_3$ and Co$_4$S$_3$Te$_3$ monolayers disappears and Co$_4$Se$_3$S$_3$ remained a HM with a moderate band gap (0.85 eV). In addition, the ab initio MD calculations confirmed the stability of the Janus structures at room temperature. Our work will be useful in the understanding and design for possible potential applications based on Janus 2D materials.

4 Conclusion

In summary, we have investigated the structural, electronic and mechanical properties of Janus single layers of M$_4$X$_3$Y$_3$, where M = Pd, Co and Ni and X = Se, S and Te. Phonon spectrum analysis and high temperature ab initio MD calculations reveal the dynamical stability of these monolayers, apart from Co$_4$Se$_3$Te$_3$. Due to the contribution of the d orbitals, the dynamical stability of Co$_4$Se$_3$Te$_3$ should be investigated with some corrections in the future. The vibrational properties were computed with the aim of understanding and characterizing the origin of the Raman active peaks. By making Janus structures of these transition metal chalcogenides to investigate the mechanical properties of Janus single layers of M$_4$X$_3$Y$_3$, the electronic band dispersions were shown to vary with using heavier/lighter chalcogen atoms. To get more accurate electronic band structures of the pristine and Janus M$_4$X$_3$Y$_3$ monolayers, where M = Pd, Co and Ni and X = Se, S and Te, the HSE + SOC approximation is taken into account for the Pd-based pristine and Janus Pd$_4$X$_3$Y$_3$ monolayers, where X = Se, S and Te, and the Ni-based pristine and Janus Ni$_4$X$_3$Y$_3$ monolayers, where X = Se, S and Te, while GGA+$U$ is taken into account for the Co-based pristine and Janus Co$_4$X$_3$Y$_3$ monolayers, where X = Se, S and Te. Our results showed that Pd$_4$Se$_3$S$_3$, Pd$_4$Se$_3$Te$_3$, and Pd$_4$S$_3$Te$_3$ are indirect band gap semiconductors with energy band gaps of 1.22 (VBM: $\Gamma$ – CBM: S), 1.05 (VBM: X – CBM: Y) and 0.61 (VBM: X – CBM: Y) eV, respectively. Ni$_4$Se$_3$S$_3$, Ni$_4$Se$_3$Te$_3$ and Ni$_4$S$_3$Te$_3$ are indirect band gap semiconductors with energy band gap of 1.61 (VBM: X – CBM: $\Gamma$), 0.77 (VBM: S – CBM: Y) and 0.49 (VBM: S – CBM: Y) eV, respectively. Co$_2^+$ (3d$^7$) has unpaired electrons, which give rise to the magnetic state of the Co$_2$Se$_3$ monolayer. While pristine Co$_2$Se$_3$ was calculated to show half-metallicity (HM) with a moderate band gap (1.01 eV) and large intrinsic ferromagnetism, the HM behaviour of the Janus Co$_4$Se$_3$Te$_3$ and Co$_4$S$_3$Te$_3$ monolayers disappears and Co$_4$Se$_3$S$_3$ remained a HM with a moderate band gap (0.85 eV). In addition, the ab initio MD calculations confirmed the stability of the Janus structures at room temperature. Our work will be useful in the understanding and design for possible potential applications based on Janus 2D materials.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
