Ferroelectric engineering of two-dimensional group-IV monochalcogenides: The effects of alloying and strain

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In this work, we studied the stability and ferroelectricity of two-dimensional (2D) group-IV monochalcogenides MX (M = Ge, Sn, or Pb; X = S, Se, or Te). Two competing crystal structures of these 2D compounds have been considered, including the rippled crystal structure with a space group of $Pmn2_1$, which can be obtained from exfoliation, and the $P\bar{3}m1$ hexagonal crystal structure containing the X-M-M-X building blocks. We find that the total energies of the rippled phases of PbX, SnS and SnSe are lower than those of the corresponding hexagonal phases; particularly, the rippled phases of SnS and SnSe exhibit spontaneous polarizations and ferroelectricity. On the other hand, the hexagonal phases of GeX and SnTe are energetically more stable than the corresponding rippled phases; because the hexagonal phases are centrosymmetric, these 2D compounds are non-ferroelectric. To engineer the ferroelectricity of 2D group-IV monochalcogenides, we have investigated the effects of alloying and equibiaxial strain. Based on density functional theory calculations, we find that the rippled phases of GeX and SnTe can be stabilized via Pb alloying to achieve ferroelectricity. In addition, it is also found that equibiaxial tensile strain gives rise to ferroelectricity in the rippled phases of 2D PbX compounds.

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1. Introduction

Ferroelectric materials exhibiting spontaneous polarization are important functional materials used for manufacturing sensors [1,2] and nonvolatile random-access memories [3,4]. With the emerging requirements of miniaturization and lightweight for devices and systems, two-dimensional (2D) ferroelectric materials with atomic thickness have attracted much research interest. On the surface of ferroelectric materials, however, the spontaneous polarization causes surface charge aggregation, forming a depolarization field which is detrimental for practical applications. For ferroelectric bulk materials, the depolarization field acts only on the surface and has a relatively minor effect. Nonetheless, for ferroelectric thin films, the influence of the depolarization field becomes so strong that it can even lead to structural phase transitions and the removal of ferroelectricity. Fong et al. used synchrotron radiation X-ray to measure the atomic positions in $PbTiO_3$ and found that the ferroelectricity disappears when the thickness is smaller than 12 Å [5]. Junquera et al. predicted from first-principles calculations that the $SrTiO_3/BaTiO_3/SrTiO_3$ sandwich structure also has a critical thickness of about 24 Å, below which the system becomes non-ferroelectric [6]. On the other hand, it has been proposed that 2D van der Waals (vdW) materials may provide a new mechanism to overcome the critical thickness limit [7].

Two-dimensional materials usually have different properties from the corresponding bulk phases due to the quantum confinement effect. Since the discovery of graphene, there has been an increasing interest in the search for new 2D materials. In the past decade, a number of 2D materials have been successfully synthesized, including 2D boron nitride [8,9], transition metal dichalcogenides [10], and black phosphorus [11,12]. In particular, the 2D group-IV monochalcogenides MX (M = Ge or Sn; X = S or Se) with a rippled crystal structure have been predicted theoretically to have robust in-plane spontaneous polarizations [13–18], which give rise to ferroelectricity [16], photovoltaic effects [17], and photostriction [18]. Experimentally, monolayer SnSe has been successfully synthesized [19]. In a recent study, Chang et al. have synthesized a closely related monolayer SnTe, which also shows an in-plane spontaneous polarization [7].

Despite the extremely attractive ferroelectricity of 2D group-IV

monochalcogenides, Sa et al. have reported that they have a hexagonal crystal structure containing X-M-M-X (M = Ge, Sn, Pb; X = Se, Te) building blocks [20]. Because this hexagonal crystal structure is centrosymmetric, it is non-ferroelectric. The rippled structure and the hexagonal structure are both demonstrated to be dynamically stable from phonon calculations. It was found in our previous work that the total energies of the rippled phases of GeTe and SnTe are higher than those of the corresponding hexagonal phases [21]. Therefore, the rippled phases may transform into the hexagonal phases if the thickness is large enough. Based on the space-group symmetry, the rippled structure does not contain centrosymmetric operations and it may exhibit spontaneous polarization, whereas the hexagonal structure contains centrosymmetric operations and spontaneous polarization is not allowed. Therefore, it is critical to carry out a systematic study of the relative stabilities of the rippled and hexagonal crystal structures to better understand the ferroelectricity of 2D group-IV monochalcogenides.

Besides structural phase transition, strain engineering also plays an important role in ferroelectricity. For 2D materials, strain can be readily induced via lattice mismatch between substrates and 2D layers. Therefore, the effects of strain are of great significance for manipulating 2D ferroelectric materials. Fei et al. showed that the polarizations of monolayer monochalcogenides change linearly with strain [22]. Moreover, ferroelectric phase transitions may also be induced via strains [23]; for example, it was found in our recent study that non-ferroelectric PbTe monolayer transforms into a new ferroelectric phase under equibiaxial tensions [21]. Nonetheless, a systematic understanding of the strain effects on the ferroelectricity of 2D group-IV monochalcogenides is still missing.

In this work, we have studied the relative stabilities of the two competing crystal structures, i.e., the rippled and hexagonal structures, and the ferroelectric phase transitions of 2D group-IV monochalcogenides from first-principles calculations. We found that the 2D rippled phases of SnS and SnSe are energetically more favorable and exhibit spontaneous polarizations. The 2D rippled phases of the three lead chalcogenides are also more stable than the corresponding hexagonal phases, but they do not exhibit
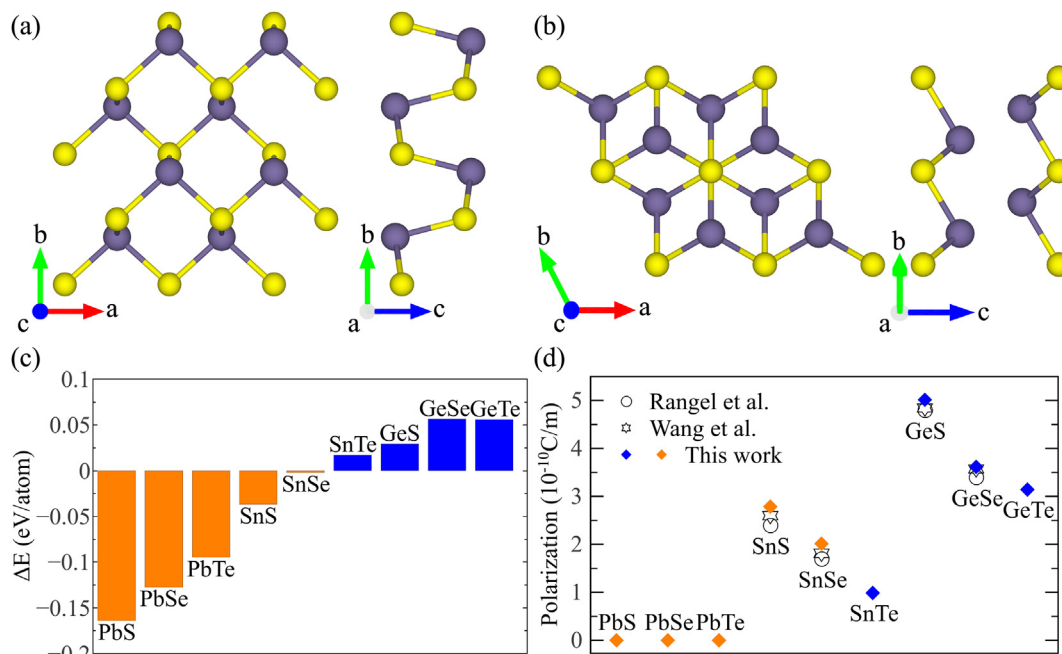
spontaneous polarization. On the other hand, the 2D rippled phases of GeX and SnTe are less stable than the corresponding hexagonal phases that are non-ferroelectric. It is found that the more stable hexagonal phases of GeX and SnTe originate from the stronger Ge-Ge and Sn-Sn interactions, and that Pb-alloying is very effective in stabilizing the rippled phases that show ferroelectricity. Moreover, we have also found that equibiaxial tension can induce spontaneous polarization in the rippled phases of PbX. Our theoretical findings provide a more complete understanding of the ferroelectric properties of 2D group-IV monochalcogenides.

2. Computational details

Theoretical calculations were performed using density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) [24]. The exchange correlation potential was described by the generalized gradient approximation with the functional of Perdew, Burke, and Ernzerhof. The plane wave cutoff energy was set to 500 eV and the energy convergence criterion was 10^{-8} eV. A vacuum layer of approximately 20 Å was applied to avoid interaction between periodic images. A k-point density of about $2\pi \times 0.02$ Å^{-1} was adopted to mesh the Brillouin zones with the Γ-centered Monkhorst-Pack method. The Berry phase approach [25] was applied to calculate the spontaneous polarization. A supercell of $7 \times 7 \times 1$ containing 196 atoms and a k-point mesh of $1 \times 1 \times 1$ were used to calculate the phonon dispersions using the finite displacement method as implemented in Phonopy [26].

3. Results and discussion

Two competing crystal structures have been proposed in the literatures for 2D group-IV monochalcogenides, i.e., the rippled and hexagonal crystal structures (see Fig. 1(a) and b). It is seen that the hexagonal crystal structure is obviously thicker than the rippled structure. Both of these two crystal structures of 2D group-IV monochalcogenides have been shown to be dynamically stable [20,21], however, their relative energetic stabilities have not been

Fig. 1. The rippled crystal structure (a) and the hexagonal crystal structure (b) of 2D group-IV monochalcogenides; (c) the total energy difference between the rippled phase and the hexagonal phase ($\Delta E = E_{\text{rippled}} - E_{\text{hexagonal}}$); (d) spontaneous polarizations of the rippled phases of different 2D group-IV monochalcogenides [14,17].
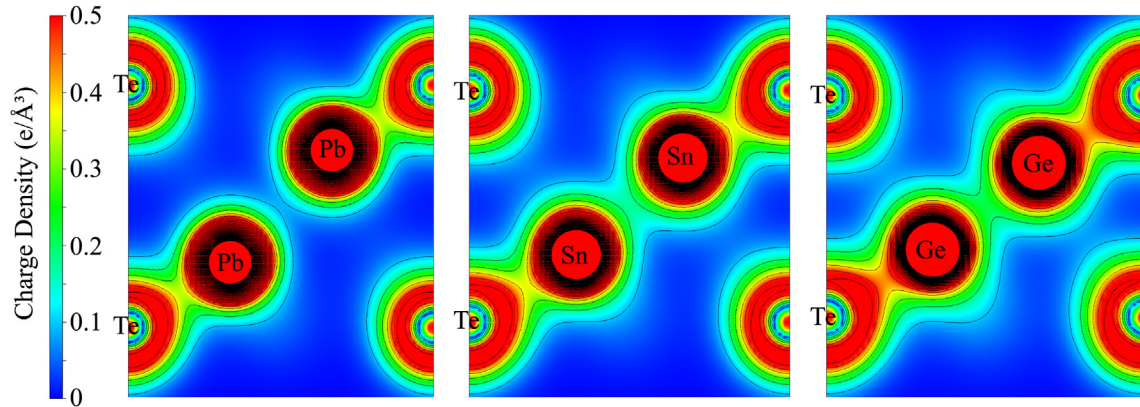
Fig. 2. Charge density distribution in the 2D hexagonal phases of PbTe, SnTe and GeTe.

discussed. Because of the distinctively different ferroelectric properties of the two competing crystal structures, it is paramount to better understand their stabilities. Therefore, we have firstly calculated the total energy differences ($\Delta E = E_{\text{rippled}} - E_{\text{hexagonal}}$) between the two competing crystal structures for nine 2D group-IV monochalcogenides MX (M = Ge, Sn, or Pb; X = S, Se, or Te). As shown in Fig. 1(c), positive ΔE (in blue) denotes that the hexagonal crystal structure is more stable, while negative ΔE (in orange) indicates that the rippled crystal structure is more stable. It is interesting to note that a heavier cation is beneficial for the stability of the rippled crystal structure, while a heavier anion is generally beneficial for the stability of the hexagonal crystal structure. Although the energy difference is affected by both cation and anion, the energetically preferable crystal structure depends more strongly on the cation.

Fig. 1(d) shows the polarizations of 2D group-IV monochalcogenides in their rippled phases. It is seen that although the 2D rippled phases of PbX are more stable than the corresponding hexagonal phases, they do not have spontaneous polarizations. On the other hand, despite the 2D rippled phases of other compounds exhibit spontaneous polarizations, only 2D rippled SnS and SnSe are energetically favorable. Therefore, we can divide these 2D group-IV monochalcogenides into three groups: (1) SnS and SnSe of which the rippled phases are stable and ferroelectric, (2) PbX of which the rippled phases are stable but non-ferroelectric, and (3) SnTe and GeX of which the rippled phases are ferroelectric but energetically unstable. It is also interesting to note that heavier cations or anions decrease the spontaneous polarization; therefore, the highest spontaneous polarization is observed in 2D rippled GeS.

From the total energy calculations, it is known that the energy difference between the rippled and hexagonal crystal structures depends strongly on the cation. The hexagonal crystal structure is energetically less favorable when heavy cations are involved. To better understand this behavior, the charge density distributions in the 2D hexagonal phases of PbTe, SnTe and GeTe are calculated and shown in Fig. 2. The hexagonal phases consist of four atomic layers with the sequence of Te-M-M-Te (M = Ge, Sn, or Pb). A strong chemical bond between M − Te can be observed in all three compounds. Nonetheless, the chemical bond between M-M becomes significantly weaker when the cation becomes heavier; e.g., the strongest and weakest interactions are found in-between two Ge atoms and two Pb atoms, respectively. The weaker interaction between the heavier cations in the hexagonal structure, therefore, is believed to be responsible for the decreased stability.

From the above analysis, it is known that in order to achieve ferroelectricity, it is important to stabilize the 2D rippled phases of

SnTe and GeX (X = S, Se, or Te). Because the competing hexagonal phases become energetically less favorable when heavier cations are involved, we have investigated the effects of Pb alloying on the phase stability. One Ge (Sn) atom in a unit cell or a $2 \times 2 \times 1$ supercell was substituted by Pb to simulate an alloying concentration of 50% or 12.5%. The evolutions of the total energies of the rippled and hexagonal phases with different alloying concentrations are shown in Fig. 3. We find that Pb alloying is very effective in stabilizing the ferroelectric rippled phase; e.g., a Pb alloying concentration of only ~10% can stabilize the rippled phase of GeS. Nonetheless, higher alloying concentrations are needed to stabilize the rippled phases of GeSe and GeTe because of the larger energy barriers. The spontaneous polarizations of Pb-doped GeS, GeSe, GeTe, and SnTe with a 50% doping concentration are 2.84×10^{-10}, 2.51×10^{-10}, 2.28×10^{-10}, and 0.82×10^{-10} C/m, respectively, lower than that of the corresponding pristine MX. However, because a lower Pb doping concentration is needed to stabilize the
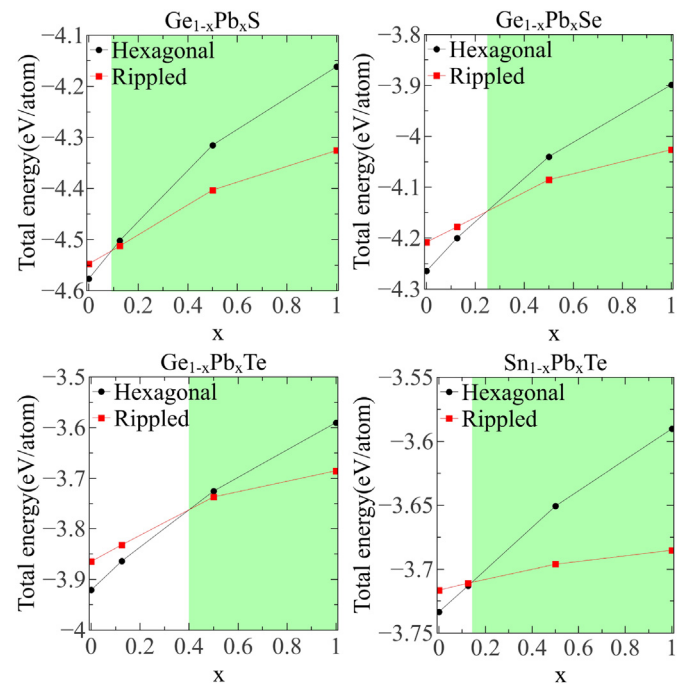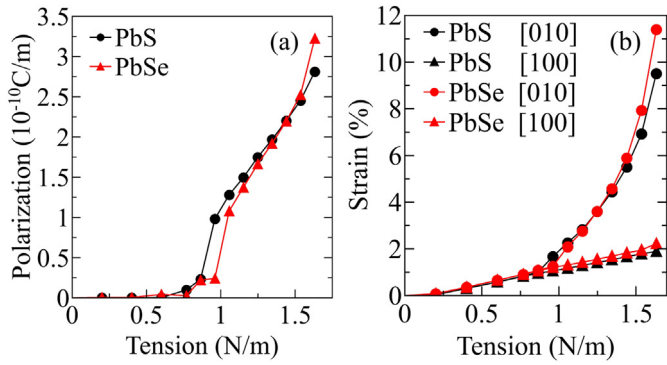

Fig. 3. The total energies of the rippled phases and the hexagonal phases of GeX (X = S, Se, or Te) and SnTe at different Pb alloying concentrations. The green shaded area represents the region where the rippled phase becomes energetically stable.
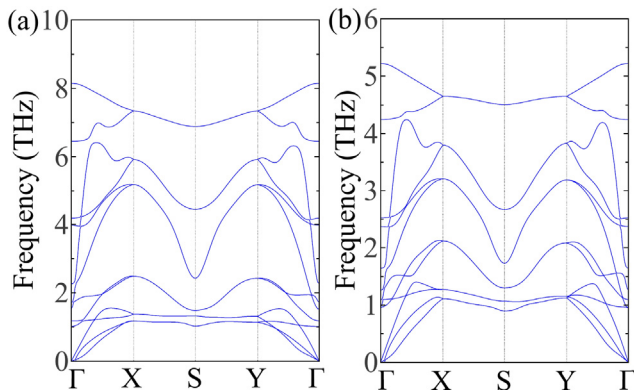
Fig. 4. (a) Polarizations along the [010] direction of the 2D rippled phases of PbS and PbSe as functions of in-plane equibiaxial tensions. (b) Normal strains along the [010] and [100] directions as functions of in-plane equibiaxial tensions.

Table A.1
The structure information of the rippled and hexagonal phases of 2D group-IV monochalcogenides obtained from DFT calculations.

	Rippled			Hexagonal		
	a (Å)	b (Å)	Space group	a (Å)	b (Å)	Space group
PbS	4.25	4.25	P4/nmm	4.03	4.03	P$\bar{3}$m1
PbSe	4.41	4.41	P4/nmm	4.17	4.17	P$\bar{3}$m1
PbTe	4.64	4.64	P4/nmm	4.42	4.42	P$\bar{3}$m1
SnS	4.08	4.31	Pmn2$_1$	3.95	3.95	P$\bar{3}$m1
SnSe	4.29	4.40	Pmn2$_1$	4.09	4.09	P$\bar{3}$m1
SnTe	4.56	4.57	Pmn2$_1$	4.33	4.33	P$\bar{3}$m1
GeS	3.64	4.52	Pmn2$_1$	3.65	3.65	P$\bar{3}$m1
GeSe	3.97	4.28	Pmn2$_1$	3.80	3.80	P$\bar{3}$m1
GeTe	4.24	4.39	Pmn2$_1$	4.05	4.05	P$\bar{3}$m1

rippled structures, it is expected that the actual decrease of spontaneous polarization is smaller. Therefore, it is demonstrated that 2D ferroelectric rippled phases of SnTe and GeX may be stabilized via Pb alloying.

The 2D rippled phases of PbX (X = S, Se, or Te) are stable but they do not exhibit spontaneous polarization. We recently found that a suitable equibiaxial strain can induce a ferroelectric transition in 2D PbTe [21]. In this work, we have further investigated the effects of equibiaxial strain on the polarizations of the 2D rippled phases of PbS and PbSe. By applying an equibiaxial tension, we relaxed the 2D rippled phases to obtain the corresponding strain and polarization along the [010] direction. It is seen from Fig. 4 that when tension is smaller than ~0.8 N/m, the polarization is close to zero and the lattice parameters in the [010] and [100] directions remain equivalent for both 2D PbS and PbSe. Interestingly, when the applied tension becomes larger than ~0.8 N/m, the lattice parameters in the [010] and [100] directions are no longer equivalent and the polarization along the [010] direction gradually increases. Our results demonstrate that the 2D rippled phases of both PbS and PbSe go through ferroelectric phase transitions under an equibiaxial tension of approximately 0.8 N/m.

To examine the dynamical stabilities of the 2D rippled phases of PbS and PbSe under in-plane equibiaxial tension, their phonon dispersions are calculated using the finite displacement method. It is seen from Fig. 5 that no imaginary phonons exist in PbS and PbSe under a tension of ~1.1 N/m, at which the corresponding polarization is equal to ~1.25×10^{-10} C/m. Because this polarization value is comparable to that of the 2D rippled phase of SnTe (~0.99×10^{-10} C/

m), in which robust ferroelectricity was recently observed in experiments, it is expected that stable ferroelectricity can be induced in 2D PbS and PbSe via strain.

4. Summary

In summary, we have systematically studied the energetics and spontaneous polarizations of 2D group-IV monochalcogenides based on DFT calculations. We find that the 2D monochalcogenides can be divided into three groups; (1) the rippled phases of SnS and SnSe are energetically stable and exhibit spontaneous polarizations; (2) the rippled phases of GeX (X = S, Se, or Te) and SnTe are robust ferroelectrics but they are energetically unstable compared to the corresponding hexagonal phases; (3) the rippled phases of PbX (X = S, Se, or Te) are energetically favorable but they do not exhibit spontaneous polarizations. It is found that Pb alloying can effectively stabilize the rippled phases of the 2D group-IV monochalcogenides as Pb weakens the interaction between cations in the hexagonal phases. Furthermore, in-plane equibiaxial strain can lead to a ferroelectric phase transition in the rippled phases of PbX. The findings presented in this work provide important guidelines for realizing robust ferroelectricity in 2D group-IV monochalcogenides.

Appendix

Fig. 5. Phonon dispersions of the 2D rippled phases of (a) PbS and (b) PbSe under an in-plane equibiaxial tension of ~1.1 N/m.

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