Prediction of intrinsic ferroelectricity and large piezoelectricity in monolayer arsenic chalcogenides

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Two-dimensional materials that exhibit spontaneous electric polarization are of notable interest for functional materials. However, despite many two-dimensional polar materials are predicted in theory, only a few of them have been successfully fabricated and confirmed to demonstrate desired piezoelectricity or ferroelectricity. We provide strong evidence that the Pmn21 phase of arsenic chalcogenides As2X3 (X=S, Se, and Te), which include the recently synthesized monolayer orpiment, are intrinsic ferroelectrics and demonstrate strong in-plane piezoelectricity. Particularly, we found the calculated energy barriers for collectively reversing the electric polarization or moving a 180° domain wall are reasonable compared to previously reported ferroelectrics. We propose a high symmetry structure (with Pmmn space group) transforms into the ferroelectric Pmn21 phase by a soft B2u phonon mode. By studying other soft modes of the high symmetry Pmmn structure, we identify several undiscovered metastable polymorphs, including a polar phase (with a P21 space group) with sizable piezoelectricity.

Materials lacking inversion symmetry may display useful properties such as piezoelectricity and ferroelectricity, which have wide applications in modern industries. In particular, ferroelectric materials are not only prototypical systems for studying spontaneous symmetry breaking and structural phase transitions, but also key components for non-volatile memory devices, piezoelectric sensors, photocatalysis, and many other technologically important applications [1–3]. Driven by the need for further miniaturization of electronic devices, researchers have devoted significant efforts to reduce the thickness of thin-films ferroelectrics [4–6]. Despite the depolarization field [7, 8], which usually inhibits the electric polarization of thin-film ferroelectrics, a few groups have demonstrated ferroelectricity sustains in bulk ferroelectrics with thickness down to ~ 1 nm[9, 10]. Compared to conventional bulk ferroelectrics, the advantage of Van der Waals materials is free of dangling bonds on the surface. The recent discovery of ferroelectricity in monolayer or few-layer Van der Waals materials offer new opportunities for shrinking the size of ferroelectric devices to the atomically thin regime. [11–15] First-principles calculations also show that a large number of two-dimensional (2D) materials are piezoelectric. Remarkably, some of them[16, 17] even demonstrate giant piezoelectric effects, which can be more than two-orders-of-magnitude stronger than those of bulk piezoelectric materials.

Currently, our understanding of the fundamental physical properties of 2D piezoelectric and ferroelectric systems is in an early stage, and the lack of a robust and economical fabrication process for high-quality 2D ferroelectric samples hinders mass production and applications [18]. Among 2D ferroelectric materials predicted with first-principles theories [16, 19–22], only a few, such as monolayer SnTe [13] and In2Se3 [14], have so far been synthesized and confirmed to be ferroelectric. First-principles prediction of piezoelectricity or switchable electric polarization in readily fabricated 2D materials is important for enriching the toolbox of 2D non-centrosymmetric materials with technological interests.

Through first-principles calculations, we show ample evidence that three monolayer arsenic chalcogenides (As2X3, X = S, Se, Te) with the Pmn21 space group will exhibit spontaneous and reversible in-plane polarization. Among these three materials, the Pmn21 As2S3, i.e., monolayer orpiment, has recently been synthesized through mechanical exfoliation [23]. Moreover, we predict the existence of several novel metastable polymorphs of As2S3. Both ferroelectric monolayer orpiment and these new polymorphs can be related to the soft zone-center modes of a hypothetical high-symmetry phase. Remarkably, our calculations show some of these polymorphs have large piezoelectric coefficients comparable to those of group IV-VI compounds [16].

The rest of this paper is organized as follows. We first study the crystal structures, electric polarization, total energies, and stability of different arsenic chalcogenides polymorphs. We will show how these polymorphs are related to the soft modes of a high symmetry Pmmn structure. Next, by studying the process of collectively switching electric dipoles and moving domain walls, we discuss the reversibility of reversing the electric polarization in...
the Pmn2₁ phases. We will demonstrate the strong piezoelectric effects in some of these polymorphs. The properties of arsenic chalcogenides are compared with other 2D ferroelectric and piezoelectric materials, including those studied experimentally or solely predicted in theory.

FIG. 1. The crystal structure of (a) monolayer orpiment and (b) monolayer anorpiment. The z-axis is perpendicular to the layer plane and points outwardly. The red arrow shows the direction of polarization.

Under ambient conditions, bulk As₂S₃ can be either amorphous or crystalline. Bulk orpiment and anorpiment, which were found in natural minerals [24], are two common crystalline As₂S₃ phases with noncentrosymmetric layered structures bounded by Van der Waals interactions. To date, two-dimensional anorpiment has not been synthesized, while monolayer and few-layer orpiment has been successfully exfoliated and demonstrates better chemical stability than phosphorene under low light conditions [23]. Our calculated total energy of monolayer orpiment is lower than that of monolayer anorpiment by 73 meV/formula unit (f.u.), suggesting better stability of monolayer orpiment compared to monolayer anorpiment. A finite bandgap is required for sustaining the ferroelectricity of 2D materials with in-plane polarization. Monolayer orpiment and anorpiment have indirect bandgaps around 2.2 eV calculated with the Perdew-Burke-Ernzerhof (PBE) functional [25]. The band structures are presented in the Supplementary Information Fig. S1.

As shown in Fig. 1(a), monolayer orpiment is highly anisotropic and consists of rings connected by six corner-sharing AsS₃ units, which have a pyramidal shape. The space group of monolayer orpiment is Pmn2₁ (space group index 31), which includes a mirror-reflection to the x-axis, but no symmetry with the y-axis, as illustrated in Fig. 1(a). Crystals with such symmetry property can exhibit a spontaneous electric polarization along the x-axis. Monolayer anorpiment has a more irregular structure and electric polarization pointing in the y-direction, as shown in Fig. 1(b).

Bulk As₂Se₃ can be found in mineral laphamite with a similar structure as orpiment [26], while bulk As₂Te₃ with the orpiment-like structure is yet to be found. Monolayer As₂Se₃ and As₂Te₃ with the orpiment-like structure and Pmn2₁ symmetry were theoretically shown to be stable [27]. Also we check the stability of monolayer As₂Se₃ and As₂Te₃ with the anorpiment-like structure (Pc space group). They both show dynamical instability with imaginary phonon modes.

Using first-principles methods based on modern polarization theory [28, 29], we calculate that intrinsic monolayer orpiment does have a spontaneous electric polarization of 71 pC/m, which is a necessary condition for its ferroelectricity. In bulk orpiment, the electric polarization in neighboring layers aligns in an antiferroelectric order. Therefore, bulk orpiment shows no macroscopic polarization and the net polarization of a few-layer orpiment shows an odd-even effect. Only samples with odd numbers of layers show net electric polarization. We also calculate the electric polarization of monolayer As₂Se₃ and As₂Te₃ are 54 pC/m and 45 pC/m, respectively, which decreases as the chalcogen component changes from sulfur to tellurium.

As a classical example of a displacive transition, the ferroelectric phase transition of perovskite oxide like PbTiO₃ is explained by a zone-center vibrational mode which vanishes at the phase transition. Similarly, we propose the ferroelectricity of monolayer orpiment is also driven by a soft mode of a high-symmetry structure with space group Pmnm (index 59). The unit cell of the Pmnm structure is shown schematically in Fig. 2(a). Different from monolayer orpiment (the Pmn2₁ phase) which only has mirror symmetry to xz-plane, the Pmnm structure of As₂S₃ has additional mirror symmetry with yz-plane. This high-symmetry Pmnm structure is dynamically unstable with five soft optical phonon modes at the Γ point. To quantify contributions of a zone-center soft phonon mode to the structural transition from the high-symmetry Pmnm structure to Pmn2₁ phase, we calculate the projection of an atomic displacement vector ∆R = R_{Pmnm} − R_{Pmn2₁} on soft phonon modes:

\[ \eta[p] = \frac{\Delta R}{|\Delta R|} \cdot u_p \]

where \( u_p \) is the normalized polarization vector of a zone-center phonon \( p \). We find \( \eta[B_{2u}] = 86\% \), and other four soft zone-center modes contribute less than 1 percent to ∆R. This is expected since the B_{2u} mode is the only one that breaks the inversion symmetry and also has the deepest double-well potential curve among zone-center soft modes. Therefore the B_{2u} mode is the dominant
phonon mode driving the structural transition from the unstable Pmmn structure to the Pmn21 phase of As$_2$S$_3$. As shown in Fig. 2(b), the main effect of B$_{2u}$ optical mode is to shift the As atoms along the x-axis (i.e., perpendicular to the y-axis) and break the reflection symmetry to $yz$-plane. The relative shifts between different S atoms are smaller comparing to the displacement of As atoms in the B$_{2u}$ mode.

We also examine the roles of other four soft zone-center modes, namely B$_{3g}$, B$_{1g}$, B$_{3u}$, and A$_u$ modes, by collectively displacing atomic coordinates of the high symmetry Pmmn structure by $\Delta \mathbf{R}_p = Q \cdot \mathbf{u}_p$, where $\mathbf{u}_p$ is the normalized polarization vector of phonon mode $p$. As shown in Fig. 2(a), one can easily identify structures that correspond to the local minima (shown as small spheres) on the double-well curve of total energy versus general coordinate $Q$. Further relaxing local minima structures may lead to new metastable phases of As$_2$S$_3$, which may also carry spontaneous polarization. Since the structural relaxation moves the local minima that correspond to the B$_{3u}$ mode back to monolayer orpiment, we will not discuss it further.

Interestingly, B$_{3g}$ and B$_{1g}$ modes transform the high-symmetry Pmmn structure into metastable P2/c and P2$_1$/m phases, respectively. As shown in Fig. 2(c), both P2/c and P2$_1$/m phase show unusual one-dimensional chain structures consists of interconnected AsS$_3$ pyramidal units. These two phases show zero macroscopic polarization since the polarization of neighboring AsS$_3$ pyramidal units point in opposite directions and cancel with each other. The phonon spectra of P2/c and P2$_1$/m phases calculated with density functional perturbation theory (DFPT) [34] shows no negative phonon modes, which indicates the dynamical stability. To assess the kinetical stability of these two phases under finite temperature, we carried out ab initio molecular dynamics (MD) simulations for these two phases under $T = 30$, 100, 200, and 300 K. The P2/c phase is stable with small thermal distortions under 30 K, but transitions to an orpiment-like structure when $T$=100 K. The P2$_1$/m phase is stable up to 200 K and transforms into an orpiment-like structure under 300 K. Details on DFPT and MD calculations are presented in Supplementary Information.

A more complicated case is the soft A$_u$ mode. Relaxing the local minima structure corresponding to the A$_u$ mode leads to a dynamically unstable P2$_1$2$_1$2 structure without a net electric polarization. Such an unstable structure has doubly-degenerate soft phonon modes at the X point which can stabilize the structure by doubling the unit cell along x-axis. The final stable structure we find has the P2$_1$ space group symmetry and a rectangle unit cell with 20 atoms, as shown in Fig. 2(d). This P2$_1$ phase is dynamically stable without imaginary phonon modes and kinetically stable under MD simulations with
FIG. 3. (a). (top) Selected intermediate states on the transition path of inverting the polarization direction of monolayer orpiment. Red arrows show the main movement of As ions between consecutive intermediate structures. The dashed curves are used to represent the atomic displacements that cross the unit-cell boundary. (bottom) The evolution of the total energies of intermediate structures along the transition path. (b). A comparison between the energy barriers $E_{\text{barrier}}$ of arsenic chalcogenide and other ferroelectrics. All data are calculated with density functional theory and the nudged-elastic-band method. We also note bi- and tri-layer WTe$_2$ also shows ferroelectricity with a smaller $E_{\text{barrier}}$ of less than 1 meV/atom\cite{11, 30}. The mechanism of ferroelectricity in doped HfO$_2$ is still an open problem\cite{31, 32}. A recent experiment suggests the Gd doped HfO$_2$ thin film has the Pca2$_1$ phase\cite{33}.

$T = 300$ K. The P2$_1$ phase is a polar structure with spontaneous polarization of 38 pC/m pointing in the $y$-direction. We note the formation of the ferroelectric P2$_1$ metastable phase is induced by an “antiferrodistortive” transition which is related to finite-momentum phonon modes. This is in contrast with the “ferrodistortive” transition due to the zone-center phonon found in monolayer orpiment and many perovskite ferroelectrics.

The total energy of the P2$_1$ phase As$_2$S$_3$ is 59 meV/f.u. lower than that of monolayer anorpiment, and only 14 meV/f.u. higher than that of monolayer orpiment. Even though the P2/c and P2$_1$/m phases are shown to be metastable, they have total energies which are about 600 meV/f.u. higher than that of monolayer orpiment, because they are composed with one-dimensional chain-like structures bounded by weak Van der Waals interaction.

We perform a similar analysis on the soft modes of the high-symmetry Pmnnm structure of As$_2$Se$_3$ and As$_2$Te$_3$. Similar to As$_2$S$_3$, they both have a $B_{2u}$ mode driving the displacive transition to the Pmnnm phase. Like As$_2$S$_3$, As$_2$Se$_3$ also has a non-centrosymmetric metastable phase with the P2$_1$ space group. In Table I, we list all the stable arsenic chalcogenides studied in this work. We mention only the zone-center soft modes are studied in this work. It is also interesting to study the finite-momentum soft modes, which also appear in the phonon spectrum of the Pmnnm structure and may lead to other interesting polymorphs.

| Formula   | Space group | $P$ (pC/m) | (The direction of P) |
|-----------|-------------|------------|----------------------|
| As$_2$S$_3$ | Pmn2$_1$    | 71 (x)     | (Monolayer orpiment) |
| As$_2$Se$_3$ | Pc          | 47 (y)     | (Monolayer anorpiment) |
| As$_2$Te$_3$ | Pmn2$_1$    | 54 (x)     |                     |
|            | P$_2_1$     | 18 (y)     |                     |

The reversibility of electric polarization is a necessary condition for ferroelectrics and also important for the application in data storage. Using the nudged elastic band method\cite{35}, we find a minimal-energy-barrier transition path for reversing the electric polarization of an infinite large monolayer orpiment. We show important intermediate structures and the corresponding energies on the transition path of As$_2$S$_3$ in Fig. 3 (a). On the minimal energy transition path, three important intermediate structures labeled as $A$, $B$, and $A'$ are found. Structure $A$ and $A'$ are related by a 180° rotation around
the z-axis. The structure B is structurally akin to the unstable P21212 structure. The initial and final structures on the transition path correspond to monolayer orpiment with electric polarization pointing in opposite directions. The process of reversing electric polarization goes in the sequence \{initial \rightarrow A \rightarrow B \rightarrow A' \rightarrow final\}, which consists of four major steps. Each step mainly involves shifting a single As atom along the x-axis. For example, in the first step \{initial \rightarrow A\}, the major structural change is the displacement of As1 (i.e., the arsenic atom at the bottom of the unit cell shown in Fig. 3 (a)) along the negative x-direction. Similarly, in the second step \{A \rightarrow B\}, we observe the movement of As2 along the negative x-direction to pass the boundary of the unit cell. Similar energy profiles for reversing the electric polarization of As2Se3 and As2Te3 (with Pnn21 space group) are calculated and shown in the Fig. S2 and Fig. S3 of Supplementary Information. In Fig. 3 (b), we compare energy barriers $E_{\text{barrier}}$ of As2X3 (X = S, Se, Te) with those of other ferroelectrics, which are either studied experimentally\[14, 15, 20, 32, 33, 36–39\] or solely predicted in theory\[21, 22, 38, 40–42\]. The range of calculated $E_{\text{barrier}}$ covers two orders of magnitudes from 0.6 meV to 116 meV. The $E_{\text{barrier}}$ of As2X3 are notably smaller than those of two room-temperature ferroelectrics, namely $T_d$-WTe2 and monolayer d1T-MoTe2, and a few predicted ferroelectrics such as GeS and SC2CO2. Such comparison suggests it is easier to switch the polarization direction of As2X3 than some of the previously proposed ferroelectrics.

In practical situations, domain-wall shifting and domain growing mediate the process of reversing electric polarization of ferroelectrics. Formation energies of domain walls and energy barriers for moving domain walls indicate how difficult it is to form and grow a domain, respectively. We studied the atomistic structure of the 180° domain walls parallel to the x-axis in As2X3 (X = S, Se, or Te). For example, the structure of the 180° domain wall in As2Se3 is shown schematically in the top panel of Fig. 4. Our calculations indicate the energy costs of forming and moving the 180° domain wall along x-axis are reasonable compared to other ferroelectrics. In detail, the calculated domain-wall formation energies $E_{\text{dw}}^{\text{form}}$ are 178, 209, and 247 meV/f.u. (i.e., 43, 50, and 58 meV/Å) for monolayer As2S3, As2Se3, and As2Te3, respectively. Previous calculations show the $E_{\text{dw}}^{\text{form}}$ of group IV-VI two-dimensional materials ranges from 8 meV/Å to 116 meV/Å \[38\]. This range covers those of 2D As2X4 ferroelectrics. The $E_{\text{dw}}^{\text{form}}$ of In3Se3 is 220 meV/f.u. \[20\], comparable to those of As2X3. Assuming the thickness of monolayer As2X3 is 6.0 Å, we convert the $E_{\text{dw}}^{\text{form}}$ of As2S3, As2Se3, and As2Te3 to be 115, 133, and 155 mJ/m², which is compared to those of common bulk ferroelectrics, such as PbTiO3 (132 mJ/m² for 180° domain wall and 35.2 mJ/m² for 90° domain wall) \[43\], BaTiO3 (7.5 mJ/m²) \[43\], and BiFeO3 (205 to 1811 mJ/m²) \[44\]. Using nudged-elastic-band method, we calculate the energy barriers $E_{\text{dw}}^{\text{barrier}}$ for moving the 180° domain walls are 466 meV/f.u., 255 meV/f.u., and 70 meV/f.u. (i.e., 113 meV/Å, 54 meV/˚A, and 16 meV/Å) for monolayer As2S3, As2Se3, and As2Te3, respectively, as shown in the bottom panel of Fig. 4. This suggests the 180° domain wall of As2X3 becomes easier to shift as the chalcogen element X changes from sulfur to tellurium. Compared to bulk ferroelectrics, the $E_{\text{dw}}^{\text{barrier}}$ of monolayer As2Te3 and As2Se3 are of the same order-of-magnitude as those of bulk conrundum derivatives ranging from 14 meV/f.u. to 197 meV/f.u. \[43\]. Compared to other two-dimensional ferroelectrics, $E_{\text{dw}}^{\text{barrier}}$ of monolayer As2S3 is more than an order-of-magnitude higher than those of group IV-VI two-dimensional ferroelectrics (less than 1.6 meV/Å) \[38\], but similar to that of monolayer In3Se3, which ranges from 280 meV/f.u. to 400 meV/f.u. \[20\]. These comparisons support that the energy costs for forming and moving the 180° domain wall of As2X3 are in a reasonable range.

Similar to monolayer group IV-VI compounds and black phosphorene, monolayer arsenic chalcogenides studied in this work are super flexible. We calculate Young’s modulus of monolayer orpiment to be 8.5 N/m along the x-axis and 33.7 N/m along the y-axis, which are more than one-order-of-magnitude smaller than those of graphene (345 N/m) \[46, 47\] and also significantly smaller than that of black phosphorene (21 ÷ 56 N/m) \[48, 49\]. To our knowledge, monolayer orpiment is among the softest 2D material ever fabricated. Such remarkable structural flexibility motivates us to investigate the piezoelectricity of arsenic chalcogenides. We calculate the elasticity tensor and the third rank piezoelectric coefficients,
TABLE II. Elasticity tensor elements (N/m ) and piezoelectric coefficients (10^{-10} C/m for \( e_{ij} \) and pm/V for \( d_{ij} \)).

| Space group (Point group) | Material | \( C_{11} \) | \( C_{22} \) | \( C_{12} \) | \( e_{11} \) | \( e_{12} \) | \( d_{11} \) | \( d_{12} \) |
|--------------------------|----------|-------------|-------------|-------------|--------------|--------------|--------------|--------------|
| Pmn2\(_1\) (C\(_{2v}\))  | As\(_2\)S\(_3\) | 11.07       | 43.38       | 10.40       | 4.36         | -1.75        | 55.7         | -17.4        |
|                         | As\(_2\)Se\(_3\) | 13.86       | 41.76       | 10.03       | 6.71         | -1.49        | 61.7         | -18.4        |
|                         | As\(_2\)Te\(_3\) | 18.09       | 34.65       | 9.72        | 9.09         | -1.48        | 61.9         | -21.6        |
| P2\(_1\) (C\(_2\))      | As\(_2\)S\(_3\) | 18.63       | 16.29       | 3.42        | -0.85        | 0.22         | -5.0         | 2.4          |
|                         | As\(_2\)Se\(_3\) | 21.51       | 23.76       | 2.65        | -0.91        | -0.33        | -4.1         | -0.9         |
| Pc (C\(_3\))            | As\(_2\)S\(_3\) | 21.63       | 9.25        | 8.00        | -1.99        | 1.93         | -24.9        | 42.4         |

defined as follow:

\[
C_{ijkl} = \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}
\]

\[
e_{ijk} = \frac{\partial P_i}{\partial \epsilon_{jk}}
\]

\[
d_{ijk} = \frac{\partial P_i}{\partial \sigma_{jk}}
\]

We adopt the Voigt notation which defines the simplified indexing \( \{1\} = \{xx\}, \{2\} = \{yy\}, \{3\} = \{zz\}, \{4\} = \{yz\}, \{5\} = \{xy\}, \{6\} = \{xy\} \). For example, the third-rank piezoelectric constants and the elasticity tensor elements are written with the following convention \( e_{12} = e_{xyy}, e_{11} = e_{xxx}, C_{11} = C_{xxx}, C_{22} = C_{yyy}, \text{and} C_{12} = C_{xxyy} \). We study the elasticity tensor elements and piezoelectric coefficients for six non-centrosymmetric arsenic chalcogenide. We only consider the variation of \( P_x \) for Pmn2\(_1\) phase and \( P_y \) for P2\(_1\) and Pc phase subject to strain. The number of independent piezoelectric coefficients can be reduced by symmetry properties. For example, materials with Pmn2\(_1\) space group (C\(_{2v}\), point group) have at most five non-zero piezoelectric coefficients \( d_{11}, d_{12}, d_{13}, d_{35}, \) and \( d_{26} \). The strain and stress of 2D materials along the out-of-plane direction (the \( z \) direction) are zero, which lead to \( d_{13} = d_{35} = 0 \) [50]. The piezoelectric strain coefficients \( d_{ij} \) can be calculated in either the direct or the indirect method. Our results calculated with indirect and direct methods agree well with each other. With the direct method, we apply small uniaxial strain to the system and relax both the lattice constant orthogonal to the uniaxial strain and atomic coordinates. Then the piezoelectric strain coefficients \( d_{ij} \) are computed from the ratio of the change of electric polarization to the stress induced by the applied strain. In the indirect method, we use the chain rule

\[
e_{ijk} = \sum_{nm} \frac{\partial P_i}{\partial \sigma_{nm}} \frac{\partial \sigma_{nm}}{\partial \epsilon_{jk}} = \sum_{nm} d_{imn} C_{nm,ij}
\]

Given \( C_{ij} \) and \( e_{ij} \), one can solve for \( d_{ij} \) of the Pmn2\(_1\) phases from the following linear equations [16]

\[
e_{11} = d_{11}C_{11} + d_{12}C_{21}
\]

\[
e_{12} = d_{13}C_{12} + d_{12}C_{22}
\]

Similar equations can be also derived for P2\(_1\) and Pc phases.

As shown in Table II, the piezoelectric strain coefficients \( d_{ij} \) of Pmn2\(_1\) and Pc phases are one-order-of-magnitude larger than those of common two-dimensional polar materials such as 2H-MoSe\(_2\) (\( d_{11} = 3.73 \text{ pm/V} \)) [51], 2H-WSe\(_2\) (\( d_{11} = 2.79 \text{ pm/V} \)) [51], hexagonal group III-V materials (0.02 < \( d_{11} < 5.50 \text{ pm/V} \)) [52], and multilayer janus transition metal chalcogenide MoSTe (5.7 < \( d_{33} < 13.5 \text{ pm/V} \)) [17]. On the other hand, the piezoelectric stress constants \( e_{ij} \) of arsenic chalcogenides is originated from their super flexibility, i.e., small elasticity tensor components. Compared to group IV-VI monolayers with giant piezoelectricity, the \( d_{ij} \) coefficients of Pmn2\(_1\) and Pc phases is on the same order as that of 2H-MoSe\(_2\), 2H-WSe\(_2\), and so on [17, 51, 52]. This indicates the large \( d_{ij} \) coefficients of arsenic chalcogenides is originated from their super flexibility, i.e., small elasticity tensor components.

In summary, we employ ab initio methods to predict the intrinsic ferroelectricity and strong piezoelectricity in arsenic chalcogenides, which include the recently synthesized monolayer orpiment. By analyzing the soft optical modes of the high-symmetry Pmnm structure of arsenic chalcogenides, we find these soft modes can lead to several undiscovered metastable polymorphs. The Pmn2\(_1\) ferroelectric phases can be related to the soft B\(_{2g}\) phonon mode of a high-symmetry Pmmn structure. We investigate the feasibility of switching the electrical polarization in the Pmn2\(_1\) phase and compare ferroelectrics. The energy barrier of coherently flip all electrical dipoles and that of moving a 180\(^\circ\)-domain wall in two-dimensional Pmn2\(_1\) As\(_2\)X\(_3\) are in a proper range compared with other ferroelectrics. Moreover, superior structural flexibility results in large piezoelectric response in a few polymorphs. Such a unique combination of unusual structures, pliability, strong piezoelectricity, and predicted ferroelectricity make 2D arsenic chalcogenides candidates for small-sized, flexible electronic devices.

Computation Details: Our first-principles calculations are based on pseudopotential density functional theory implemented in Quantum Espresso [53, 54] and PBEsol [55, 56]. All results, except for electronic band structures, are calculated with the PBEsol exchange-correlation functional, which performs better on structural parameters of bulk orpiment and anorpiment than the Perdew-Burke-Ernzerhof (PBE) [25] functional ac-
According to our benchmark presented in the section S1 of the Supplementary Information. DFPT phonon spectra, MD simulation results, and structure parameters of new metastable $\text{As}_2\text{S}_3$ polymorphs are also presented in Supplementary Information, which cites these references [34, 58–62].

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SUPPLEMENTARY MATERIALS

 COMPUTATIONAL DETAILS

We find the PBEsol [57] functional performs better than the PBE [25] functional in describing the structural parameters of bulk orpiment and anorpiment, as shown in Table S1 and Table S2. Therefore we use the PBEsol functional for structural relaxations, phonon spectra, calculating electric polarization, and nudged elastic band for finding transition path, as implemented in Quantum Espresso [53, 54]. We compute the electronic band structures to check the finite band gap of ferroelectric phases using real-space based code PARSEC [55, 56]. The parameters and pseudopotentials used in our calculations are listed in Table S3.

TABLE S1. Comparisons between experimental structural parameters of bulk orpiment and those calculated with different exchange-correlation functionals.

| Method | a (Å) | b (Å) | c (Å) | α | β | γ | Ω cell (Å³) |
|--------|-------|-------|-------|---|---|---|-------------|
| Expt.  | 4.256 | 12.191| 9.577 | 90.00° | 90.00° | 90.68° | 467.685 |
| PBE    | 4.624 | 11.368| 11.054| 90.00° | 89.98° | 90.30° | 581.060 |
| PBEsol | 4.032 | 11.529| 9.481 | 90.00° | 89.99° | 90.49° | 440.664 |

TABLE S2. Comparisons between experimental structural parameters of bulk anorpiment and those calculated with different exchange-correlation functionals.

| Method | a (Å) | b (Å) | c (Å) | α | β | γ | Ω cell (Å³) |
|--------|-------|-------|-------|---|---|---|-------------|
| Expt.  | 5.758 | 8.717 | 10.268| 78.152° | 75.817° | 89.861° | 488.377 |
| PBE    | 5.932 | 9.081 | 11.226| 80.783° | 79.464° | 89.923° | 586.587 |
| PBEsol | 5.834 | 8.483 | 9.983 | 79.870° | 80.214° | 89.632° | 479.152 |

TABLE S3. Parameters for DFT calculations

|                  |                  |
|------------------|------------------|
| k-point grids for orpiment | 11 × 4          |
| k-point grids for anorpiment | 12 × 8          |
| Vacuum space along c-direction | 16.4 Å          |

| Structural relaxations |
|------------------------|
| Pseudopotential        | Ultrasoft [59] (PSlibrary [58]) |
| Wave-function cut-off  | 45 Ryd            |
| Force threshold        | 5 × 10⁻⁵ Ryd/Bohr |
| Pressure threshold     | 0.005 kbar        |

| Band structure calculations |
|-----------------------------|
| Real-space grid spacing    | 0.4 Bohr           |
| Pseudopotential            | Norm-conserving [60]|

ELECTRONIC BAND STRUCTURES
FIG. S1. DFT-PBE band structures of orpiment and anorpiment

TRANSITION PATH FOR SWITCHING ELECTRIC POLARIZATION

FIG. S2. (Top) Selected intermediate states on the transition path of inverting the polarization direction of Pmn2\textsubscript{1} monolayer As\textsubscript{2}Se\textsubscript{3}. (Bottom) The evolution of the total structural energies along the transition path.
FIG. S3. (top) Selected intermediate states on the transition path of inverting the polarization direction of Pmn2\(_1\) monolayer As\(_2\)Te\(_3\). (bottom) The evolution of the total structural energies along the transition path.

**PHONON SPECTRA AND CRYSTAL STRUCTURES**

Using density functional perturbation theory[34], we calculated phonon spectra of As\(_2\)S\(_3\), As\(_2\)Se\(_3\), and As\(_2\)Te\(_3\), as shown in Fig S4, Fig S5, and Fig S6, respectively. We can see the unstable P2\(_1\)2\(_1\)2 structure exhibits a pair of degenerate imaginary phonon modes at \(X = [0.5, 0.0, 0.0]\), as shown in Figure S4(a). The degenerate modes at \(X\) double the unit cell and stabilize the P2\(_1\) phase. The stable P2\(_1\) phase does not show soft modes, as shown in Figure S4(b).
FIG. S4. Phonon spectra of As$_2$S$_3$ polymorphs

As$_2$Se$_3$

FIG. S5. Phonon spectra of As$_2$Se$_3$ polymorphs

The lattice vectors and atomic coordinates of different structures are presented in Listing S1.
FIG. S6. Phonon spectra of pmn2\textsubscript{1} As\textsubscript{2}Te\textsubscript{3}

Pmmn structure of As\textsubscript{2}S\textsubscript{3} 
Lattice parameters (Å): 
a 4.129954938, 0.000000000 
b 0.000000000, 11.402219811  
Coordinates (Å):  
As \(-1.03248871, -3.67579877, 0.69229195\)  
As \(1.03248871, 2.02531139, -0.69229164\)  
As \(1.03248871, 4.41872470, 0.69229195\)  
S \(1.03248871, 2.87210862, 1.36331353\)  
S \(-1.03248871, -2.82900131, -1.36331406\)  
S \(-1.03248871, 3.57192699, -1.36331406\)  
S \(1.03248871, -2.12918269, 1.36331353\)  
S \(-1.03248871, 0.37146298, 0.01192853\)  
S \(1.03248871, -5.32964694, -0.01192894\)

Pmn2\textsubscript{1} As\textsubscript{2}S\textsubscript{3} (monolayer orpiment) 
lattice parameter (Å):  
a 4.129954938, 0.000000000  
b 0.000000000, 11.402219811  
Coordinates (Å):  
As \(-0.78838333, -3.73406013, 0.65021405\)  
As \(1.27660367, -1.22413313, -0.65020095\)  
As \(1.27675267, 1.96710887, -0.65022995\)  
As \(-0.78838333, 4.47694087, 0.65020905\)  
S \(0.70236367, 2.86359687, 1.34184805\)  
S \(-1.36278833, -2.83754813, -1.34184895\)  
S \(-1.36257233, 3.58043787, -1.34187895\)  
S \(0.70214467, -2.12065013, 1.34185105\)  
S \(-1.51335233, 0.37149187, 0.34851005\)  
S \(0.55163667, -5.32960013, -0.34846295\)

P2\textsubscript{1} As\textsubscript{2}S\textsubscript{3} 
lattice parameter (Å): 
a 9.140844301, 0.000000000  
b 0.000000000, 9.633042893  
Coordinates (Å):  
As \(1.032879891, -0.447660690, 2.007661110\)  
As \(2.889794050, 2.522275499, 1.762040671\)  
As \(5.553478817, 4.368380638, 2.781077416\)  
As \(3.697323949, 7.339269714, 3.024970212\)  
As \(5.574539852, 0.520412353, 2.976945725\)  
As \(8.220077802, 2.470169237, 2.352806321\)  
As \(10.154209918, 5.337023545, 1.811079211\)  
As \(7.507960998, 7.286061158, 2.437278794\)  
S \(5.233876693, 6.104398232, 4.231566760\)  
S \(1.351134408, 1.288583336, 0.556965600\)  
S \(3.142394988, 6.039483486, 1.274622971\)
S 3.444944123, 1.221942370, 3.512018844
S 1.601750696, 3.660499754, 3.271997208
S 4.987798288, -1.156759994, 1.515936422
S 9.521600238, 6.597808934, 3.546849250
S 6.208138780, 1.781379754, 1.241612456
S 6.972694092, 5.391060683, 2.166592803
S 8.251929321, 0.575025987, 3.032345915
S 7.080080540, 3.310164111, 4.155262645
S 8.646197396, -1.505702607, 0.634696666

P2/c As$_2$S$_3$
lattice parameter (Å):
a 3.775174327, -0.098237029
b -0.298757377, 11.627475696
Coordinates (Å):
As 1.382863367, -0.002019562, 2.821668423
As 3.983200758, 2.778337720, 1.966295672
As 3.121068068, 5.762598078, 1.966831336
As 1.946235555, 8.641191708, 2.822208383
S 3.389440975, 7.047731188, 3.800371481
S 1.651231928, 1.283112914, 0.988127000
S 1.677741182, 7.358449905, 0.988805406
S 3.715706613, 1.492990547, 3.799692290
S 1.666751363, 4.319075810, 3.184534875
S 3.701716705, -1.543779172, 1.603921024

P2,1/m As$_2$S$_3$
lattice parameter (Å):
a 3.892782025, 0.000000000
b 0.000000000, 12.015813930
Coordinates (Å):
As 1.456775251, 0.098695679, 2.890745128
As 4.152746082, 2.916060442, 1.897761135
As 4.152747877, 6.104132174, 1.897767729
As 1.456796829, 8.921504963, 2.890741220
S 3.886580601, 7.332425340, 3.783325510
S 1.725376942, 1.327907816, 1.006576567
S 1.725386391, 7.692385006, 1.006571637
S 3.886586652, 1.687878419, 3.783329513
S 1.689661516, 4.810225739, 2.880388852
S 3.941341962, -1.495908851, 1.905296310

Pmn2; As$_2$Se$_3$
lattice parameter (Å):
a 4.041384840, 0.000000000
b 0.000000000, 12.058039544
Coordinates (Å):
As 2.416958874, 0.108990888, 3.078197772
As 0.396598248, 2.861114184, 1.873332349
As 0.398625453, 6.112061941, 1.873550697
As 2.416978937, 8.864113290, 3.077950933
Se 1.945041332, 1.149469585, 0.989996912
Se 3.965839575, 7.152794899, 3.961652185
Se 3.965708042, 1.820562462, 3.961467912
Se 1.945122943, 7.823217376, 0.989902175
Se 1.863276642, 4.846601547, 3.025819225
Se 3.884035485, 10.489714816, 1.925674954

P2, As$_3$Se$_3$
lattice parameter (Å):
a 9.346608167, 0.000000000
b 0.000000000, 9.191859000
Coordinates (Å):
As -1.124860922, 6.837450869, 0.590291424
As 1.650284499, 8.760156608, 17.994158356
As 3.461520325, 1.878374097, 17.409702932
As 0.668639249, 3.801074701, 0.005839449
As 3.576602722, 5.640188301, -0.459603129
As 5.372287873, 8.811716615, 17.381561699
As 8.106651861, 0.681106666, 18.459596443
MOLECULAR DYNAMICS SIMULATIONS

We carried out ab initio molecular dynamics (MD) simulations for all the new metastable phases at different temperatures. The Berendsen thermostat[61] is used to control temperature. The time step for MD is 5 fs. Lattice parameters are fixed during MD simulations. For P2/c and P2_1/m phases, we use 2×2 supercells with 40 atoms for MD simulations. For P2_1 phase, we use 2×1 supercell, which also include 40 atoms. The evolution of total energy with time T is plotted for three metastable phases, as shown in Figure S7. The P2/c structure remains stable with thermal distortions under 30 K, but transitions to orpiment under 100 K. The P2_1/m is stable under 200 K, but transitions to orpiment under 300 K.
FIG. S7. Evolution of energies in MD simulations and snapshots of structures in the end of simulations.

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