Electronic Supplementary Information

Prediction of scale-free ferroelectricity in elemental ferroelectric compound of M_2X_5 with distinctive structural prototype

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1. Details of first-principles calculations on ferroelectricity

Our first-principles calculations were performed by employing Vienna Ab initio Simulation Package (VASP)¹ within the framework of density functional theory^{2, 3}. The generalized gradient approximation in the functional type of Perdew-Burke-Ernzerhof⁴ was employed for projected augmented wave pseudopotential⁵ and the energy cutoff was set to 500 eV. The M₂X₅ (M=A1, Ga, In, Tl, X=S, Se, Te) monolayers were simulated in xy-plane and a vacuum space of ~20 Å was introduced along zdirection to eliminate interactions between neighboring images. Based on conventional cell of M_2X_5 monolayers, the atomic positions and lattice constants were fully optimized with the energy convergence criteria of 10^{-6} eV, where the BZ was sampled by a $8 \times 2 \times 1$ k-point mesh. For strain engineering, only atomic positions were relaxed for In₂Te₅ monolayers under a given tensile strain, and ground state were determined by optimizing initial structures with the inner Te atoms in planer-coordinated chain purposely fixing to or moving away from central sites. The obtained crystal structures were employed to calculate/analyze the total energy, electronic property, and bonding feature of M_2X_5 monolayers, and their band structures were calculated by considering spin-orbit coupling effect.

The spontaneous ferroelectricity (FE) polarization (P_s) and switching energy barrier (E_b) were evaluated by respectively using the Berry phase method ^{6, 7} and Climbing Image Nudged-Elastic-Band (CI-NEB) method ^{8, 9}, based on the primitive cell of M_2X_5 monolayers with 9×5×1 **k**-point sampling in its BZ. The Berry phase method enables calculating the electric dipole moments for the states of opposite FE polarizations, which enables us evaluating the P_s by the formula of $P_s = \Delta p/2S$. Here the $\Delta p = p_1 - p_2$ is the difference between the dipole moments of opposite FE polarizations, and S is the area of primitive cell. In addition to E_b , CL-NEB method was also employed to reveal the scale-free ferroelectricity by expending conventional cell of M_2X_5 monolayers into 1×2×1 supercell that contains four FE chains, whose BZ is sampled by 8×1×1 k-mesh.

2. Details of first-principles calculations on stability

The possibility of fracturing In₂Te₅ under strains was checked by calculating the formation energy of removing one atom from $3 \times 2 \times 1$ supercell of In₂Te₅ under a given strain based on the formula of $E_{\text{form}} = E_{\text{defect}} + \mu_0 - E_{\text{perfect}}$. Here the E_{perfect} and E_{defect} is respectively the total energy of In₂Te₅ without removing atom and with the vacancy defect of V_{In}, V_{Te1}, V_{Te2}, or V_{Te3}. The V_{In} (V_{Te1}) corresponds to removing one In (Te) atom in the wrinkled spacer chain formed by vertex-sharing In-Te tetragons, while V_{Te2} and V_{Te3} is respectively formed by removing the surrounded and inner Te atoms in the planar-coordinated Te chain. μ_0 represents the chemical potential of the removed atom. For the vacancy defect of V_{Te1} , V_{Te2} , or V_{Te3} , μ_0 is the chemical potential μ_{Te} of the removed Te atom. Under Te-rich condition, μ_{Te} is evaluated from the hexagonal bulk phase of Te element, while, under In-rich condition, the μ_{Te} is determined by $\mu_{Te} = (E_{In2Te5} - 2\mu_{In})/5$. Here E_{In2Te5} is the total energy per primitive cell of the synthesized In₂Te₅ at equilibrium state and μ_{In} is evaluated from the face-center-cubic bulk phase of In element. For the vacancy defect of V_{In} , μ_0 is the chemical potential μ_{In} of the removed In atom. Under In-rich condition, μ_{In} is also evaluated from the face-center-cubic bulk phase of In element. Under Te-rich condition, the μ_{In} is determined by $\mu_{In} = (E_{In2Te5} - 5\mu_{Te})/2$. Here E_{In2Te5} is also the total energy per primitive cell of the synthesized In₂Te₅ at equilibrium state and the μ_{Te} is also evaluated from the hexagonal bulk phase of Te element.

Based on density functional perturbation theory ¹⁰, phonon spectra were calculated to estimate dynamic stability by expending primitive cell of M_2X_5 monolayers into $6\times3\times1$ supercell and the corresponding BZ is sampled by a $2\times2\times1$ **k**-point mesh, which were implemented by interfacing PHONOPY package ¹¹ to VASP ¹. The thermodynamic stability of M_2X_5 monolayers at room temperature was checked by performing *ab initio* molecular dynamics (AIMD) simulations ¹² by expending conventional cell of M_2X_5 monolayers into $4\times2\times1$ supercell based on the VASP ¹. The AIMD simulations lasted 5000 fs with the time step of 2 fs under the NVT ensemble, where the temperature of 300 K was controlled by the Nose-Hoover thermostat. Furthermore, the mechanical stabilities of M_2X_5 (M=Al, Ga, In, Tl, X=S, Se, Te) monolayers at ground states are checked by calculating elastic constants C_{ij} (Table S1). The Born criterion ^{13, 14} of $C_{11} \times C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$ is not only satisfied by the experimentally synthesized In₂Te₅ and Al₂Te₅, but also satisfied by Ga₂Te₅, Tl₂Te₅, Al₂S₅, Ga₂S₅, In₂S₅, Tl₂S₅, In₂Se₅, and Tl₂Se₅, demonstrating the mechanical stability of the listed M_2X_5 monolayers in Table S1.

Materials	C ₁₁ (N/m)	C ₂₂ (N/m)	C ₆₆ (N/m)	C ₁₂ (N/m)
Al ₂ Te ₅	38.54	9.98	9.52	4.44
In ₂ Te ₅	31.60	8.14	6.74	3.85
Ga ₂ Te ₅	37.67	9.11	9.09	5.11
Tl ₂ Te ₅	29.46	8.52	6.28	5.74
Al ₂ S ₅	40.33	14.12	7.98	1.90
Ga ₂ S ₅	36.25	10.61	7.05	2.09
In ₂ S ₅	25.05	6.78	3.01	0.84
Tl ₂ S ₅	19.54	4.18	2.05	0.40
In ₂ Se ₅	23.76	6.69	5.03	1.51
Tl ₂ Se ₅	19.45	4.12	3.64	1.60

Table S1. The elastic constants C_{ij} of M_2X_5 monolayers.

Reference

- 1. G. Kresse and J. Furthmüller, Comput. Mater. Sci., 1996, 6, 15-50.
- 2. P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864-B871.
- 3. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133-A1138.
- 4. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
- 5. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
- 6. N. A. Spaldin, J. Solid State Chem., 2012, 195, 2-10.
- 7. J. Bonini, D. Vanderbilt and K. M. Rabe, *Phys. Rev. B*, 2020, **102**, 045141.
- 8. G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901-9904.
- 9. G. Henkelman and H. Jónsson, *The Journal of Chemical Physics*, 2000, **113**, 9978-9985.
- 10. S. Baroni, S. de Gironcoli, A. Dal Corso and P. Giannozzi, *Rev. Mod. Phys.*, 2001, **73**, 515-562.
- A. Togo, L. Chaput, T. Tadano and I. Tanaka, J. Phys.: Condensed Matter, 2023, 35, 353001.
- 12. S. Nosé, J. Chem. Phys., 1984, 81, 511-519.
- 13. M. Born, K. Huang and M. Lax, Am. J. Phys., 1955, 23, 474-474.
- 14. F. Mouhat and F.-X. Coudert, *Phys. Rev. B*, 2014, **90**.

3. Supplementary figures



Figure S1. The Brillouin zone and high-symmetry points for the (a) conventional cell and (b) primitive cell of M_2X_5 monolayer.



Figure S2. (a-c) Band structure of equilibrated In_2Te_5 monolayer, where the magnitude of dots is respectively drawn proportionally to the contributions of (a) out-of-plane *p*orbitals of surrounded Te atoms in planar-coordinated chain, (b) *p*-orbitals of Te and (c) *p*-orbitals of In atoms in wrinkled spacer chain. (d) Projected density-of-states (PDOS) for the out-of-plane *p*-orbitals of surrounded Te atoms in planar-coordinated chain (red lines), *p*-orbitals of Te (green lines) and *p*-orbitals of In (blue lines) atoms in wrinkled spacer chain. Here the projected plane of *p*-orbitals is the ones where the planarcoordinated chain locating.



Figure S3 (a, b) Formation energy E_{form} of various vacancy defects (V_{In}, V_{Te1}, V_{Te2}, and V_{Te3}) in strained In₂Te₅ monolayer evaluated under (a) Te-rich and (b) In-rich conditions. (c) The phonon spectra of FE In₂Te₅ monolayer with ξ =20% (blue lines) and ξ =22% (red lines). (d) The variations of total energy during the AIMDs for 13% strained In₂Te₅ monolayer at 300 K, where the inset is the crystal structure of In₂Te₅ after simulating 5000 fs.



Figure S4. Atomic vibration modes for the imaginary acoustic phonons at (a) x, (b) h_1 , (c) c, and (d) h point in the phonon spectra of $\xi = 9\%$ strained In₂Te₅ monolayer without ferroelectric displacement (red colored lines of figure 3c in main text).



Figure S5. Phonon spectra of equilibrated (a) In_2Te_5 , (b) Al_2Te_5 , (c) Ga_2Te_5 , and (d) Tl_2Te_5 monolayer.



Figure S6. Phonon spectra of equilibrated (a) Al_2S_5 , (b) Ga_2S_5 , (c) In_2S_5 , (d) Tl_2S_5 , (e) In_2Se_5 , (f) Tl_2Se_5 monolayer with intrinsic ferroelectricity.



Figure S7. The variations of total energy during AIMDs for (a) In₂Te₅, (b) Al₂Te₅, (c) Ga₂Te₅, (d) Tl₂Te₅ at 300 K. Insets are the crystal structures after simulating 5000 fs.



Figure S8. The variations of total energy during AIMDs for (a) Al₂S₅, (b) Ga₂S₅, (c) In₂S₅, (d) Tl₂S₅, (e) In₂Se₅, and (f) Tl₂Se₅ at 300 K. Insets are the crystal structures after simulating 5000 fs.



Figure S9. The variations of total energy during AIMD simulations at 300 K for 13% strained In_2Te_5 monolayer with (a) V_{In} , (b) V_{Te1} , (c) V_{Te2} , and (d) V_{Te3} defects mentioned in section 2. Insets are the crystal structures after simulating 5000 fs, where the gray arrows indicate the robust FE chains against the existence of local defects.



Figure S10. The schematic plot for the integration of in-plane ferroelectric tunnel junction (FTJ) based on M_2X_5 with scale-free ferroelectricity. The dark green layer in the left panel denotes the M_2X_5 shown in the right panel, where the gray arrows indicate the directions of FE chains. The in-plane polarization induced band bending of valence and conduction bands around the boundary are plotted by light blue shapes. Depending on the polarization direction that can be manipulated by the writing (W) electrode, one of the edges could be conducting or insulating, which will change the effective potential barrier between the reading (R) electrode and the substrate, therefore realizing bistable states with different tunneling currents. For ideal case, the width of in-plane FTJ and the distance between neighboring FTJ could be decreased to unit-cell-scale along the

direction perpendicular to the ferroelectric chain in M_2X_5 due to the associated scalefree feature, while that along the direction parallel to the ferroelectric chain can be controlled by depositing electrode patterns because the ferroelectricity is robust against local disorders that may be induced electrodes. For practical case, if one cannot pattern every electrode for each ferroelectric chain, sparse electrode pattern with each electrode connecting several ferroelectric chains is also feasible for the integration of in-plane FTJ, which is still beneficial to elevate the density of memory.