

Robust Two-Dimensional Ferroelectricity in Single-Layer γ -SbP and γ -SbAs

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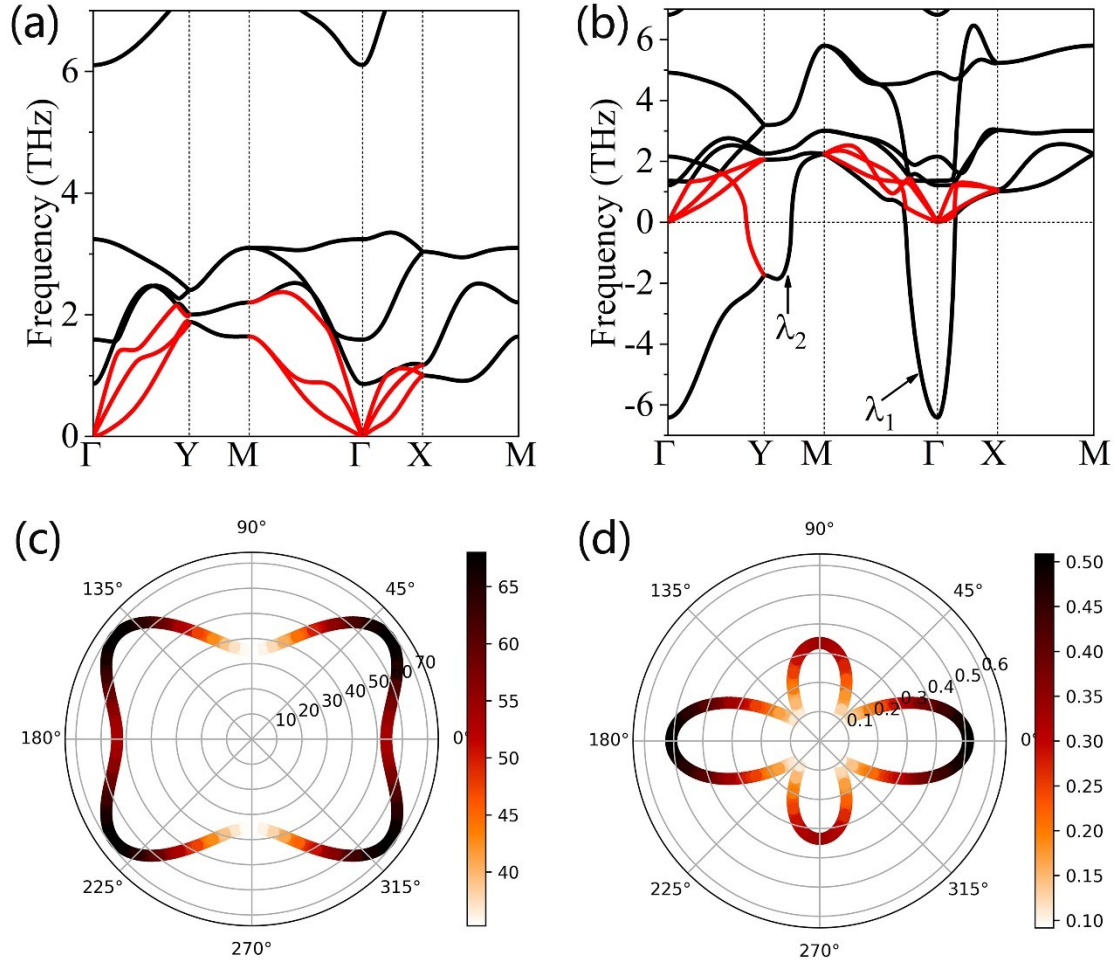


Fig. S1 (a) and (b) Phonon spectra of the structures A and B of monolayer γ -SbP, respectively. The angular dependence of Young's modulus (c) and Poisson's ratio (d) of the γ -SbP monolayer. The zero degree corresponds to the x axis.

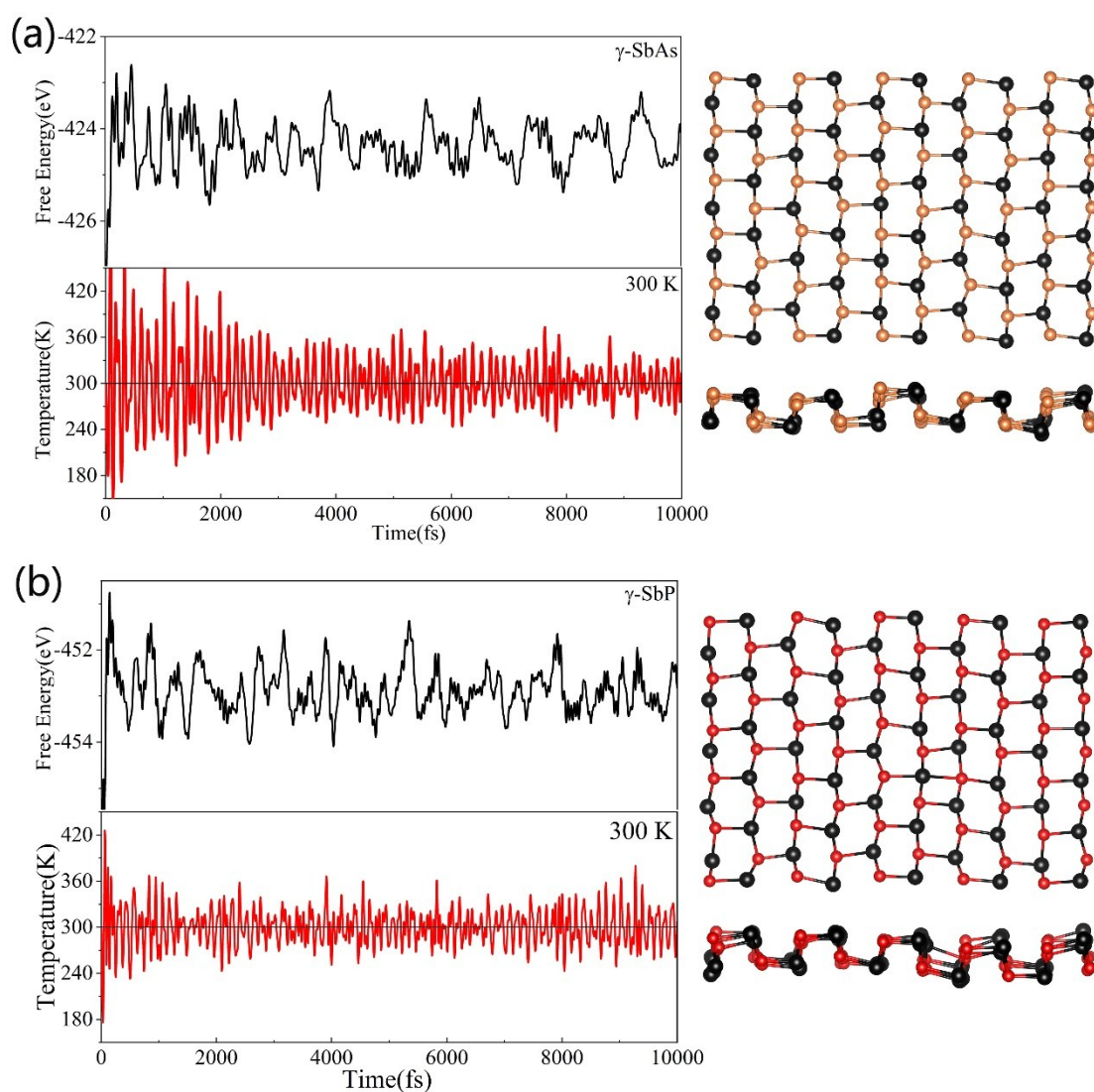


Fig. S2 (a)-(b) The picture on the left indicates fluctuation of temperature and total energy ($5 \times 5 \times 1$ supercell) at 300 K in AIMD simulation during the time scale of 10 ps. The picture on the right shows Top and side views of atomic structure snapshots from AIMD simulations.

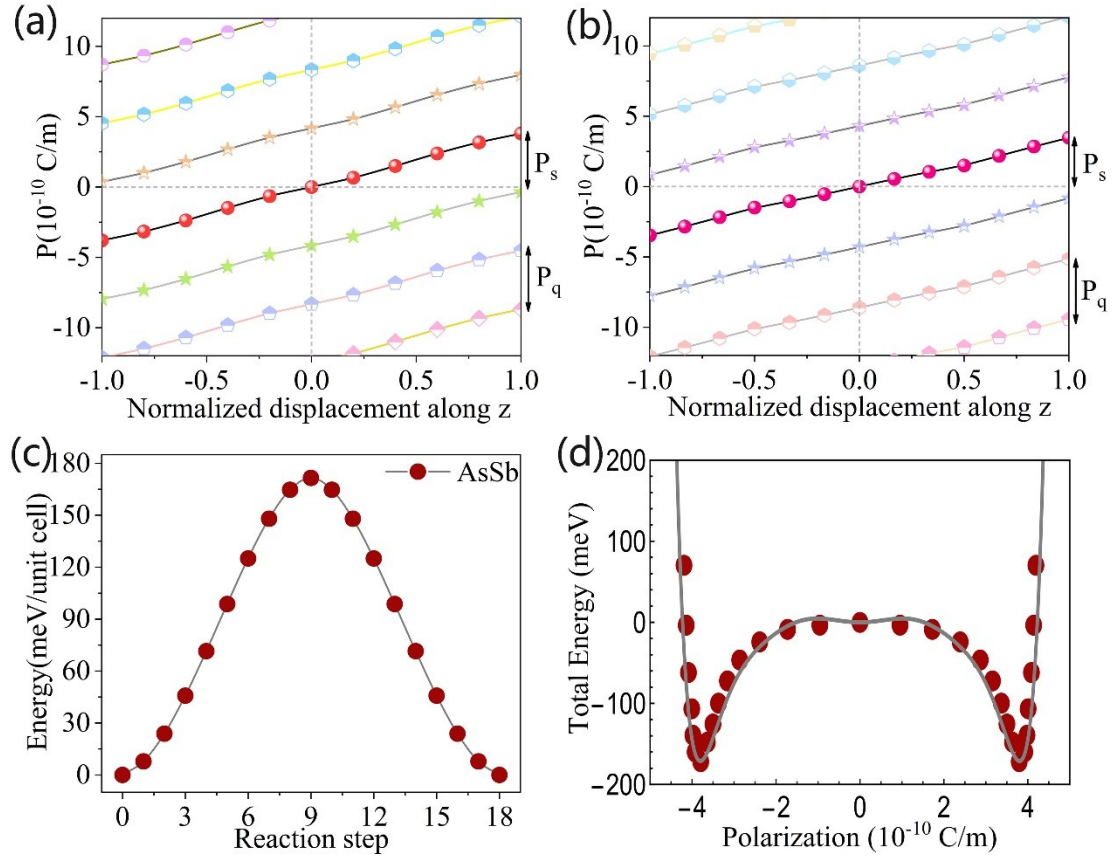


Fig. S3 Calculated total polarization of γ -SbP(a) and γ -SbAs(b) as a function of normalized displacement where the centrosymmetric paraelectric phase (0% displacement) is at the center, and two ferroelectric ground states are at two ends. P_s represents the spontaneous polarization and P_q represents the polarization quanta. (c) Double-well potential vs. polarization of monolayer γ -SbAs. (d) the energy profiles as a function of switching step number in the NEB computations.

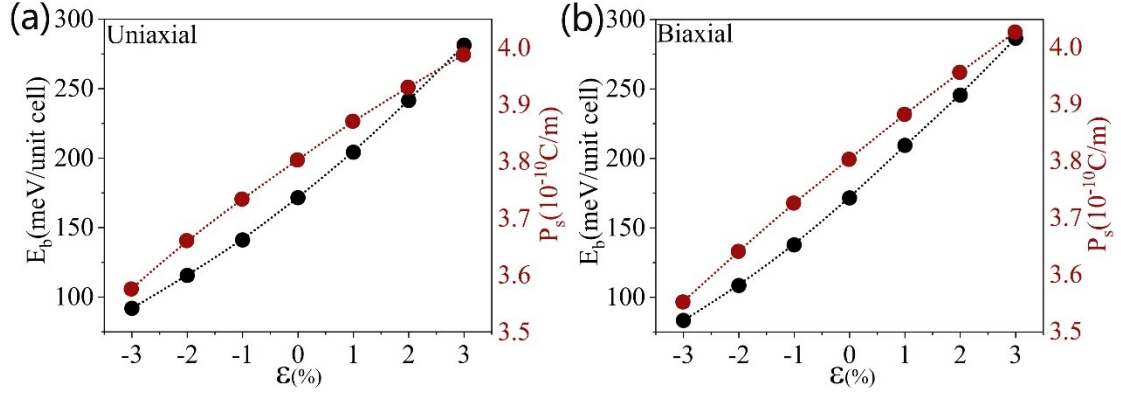


Fig. S4 The polarizations and energy barrier as a function of the applied (a) Uniaxial and (b) Biaxial strain for γ -SbAs, respectively.

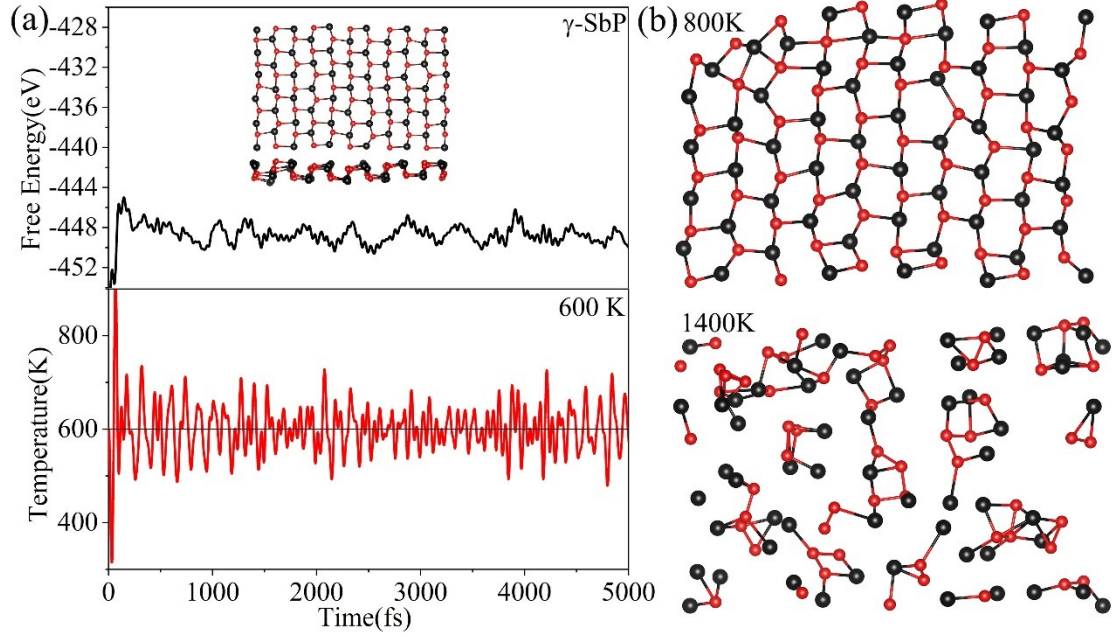


Fig. S5 (a) Variation of free energies and temperature of γ -SbP during ab initio molecular dynamics simulations (AIMD) at the temperature of 600 K. The insets show the corresponding snapshots at the end of the MD simulation from side and top views. (b) the snapshot taken from the end of AIMD simulation at the temperature of 800 K and 1400K, respectively.

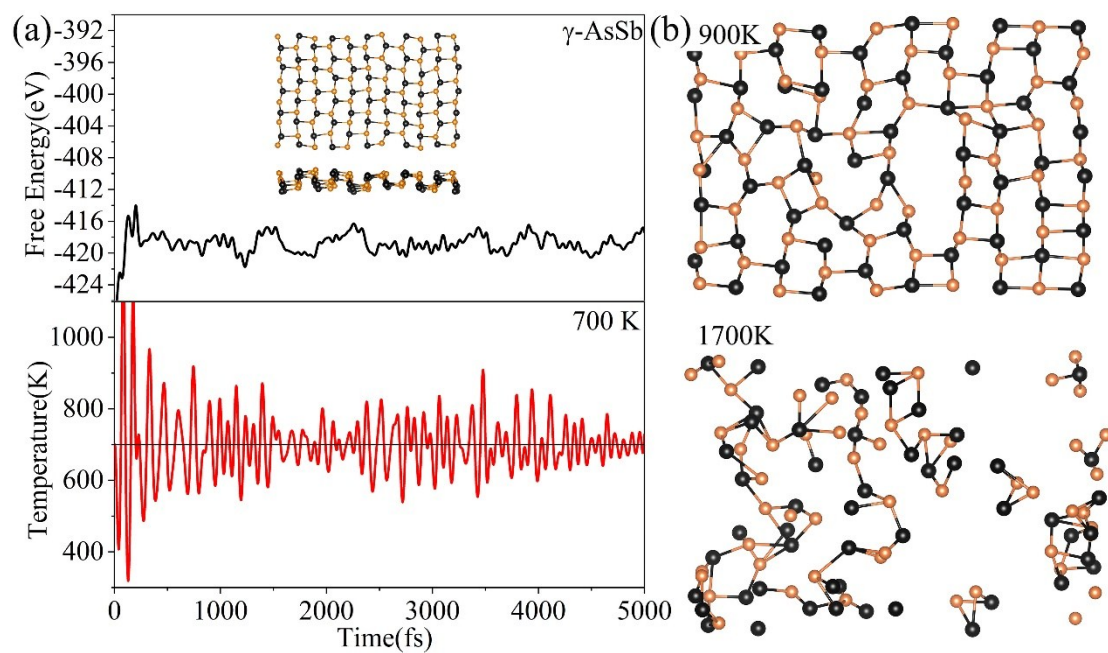


Fig. S6 (a) Variation of free energies and temperature of γ -SbAs during ab initio molecular dynamics simulations (AIMD) at the temperature of 700 K. The insets show the corresponding snapshots at the end of the MD simulation from side and top views. (b) the snapshot taken from the end of AIMD simulation at the temperature of 900 K and 1700K, respectively.

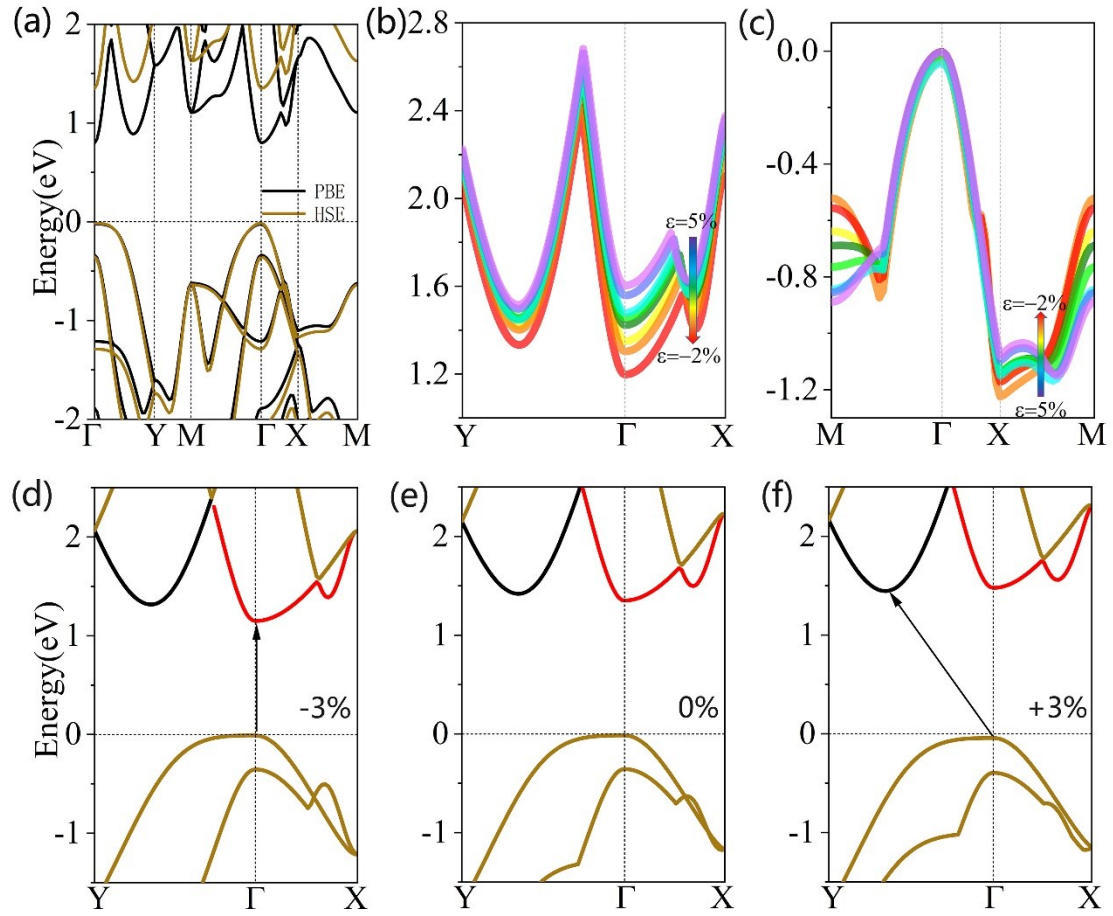


Fig. S7 Band structures of monolayer γ -SbAs. Changes in the (b) conduction-band bottom and (c) the valence-band top with increasing uniaxial strain. (d) Band structures for monolayer γ -SbAs with $\pm 3\%$ strain and with unstrained.

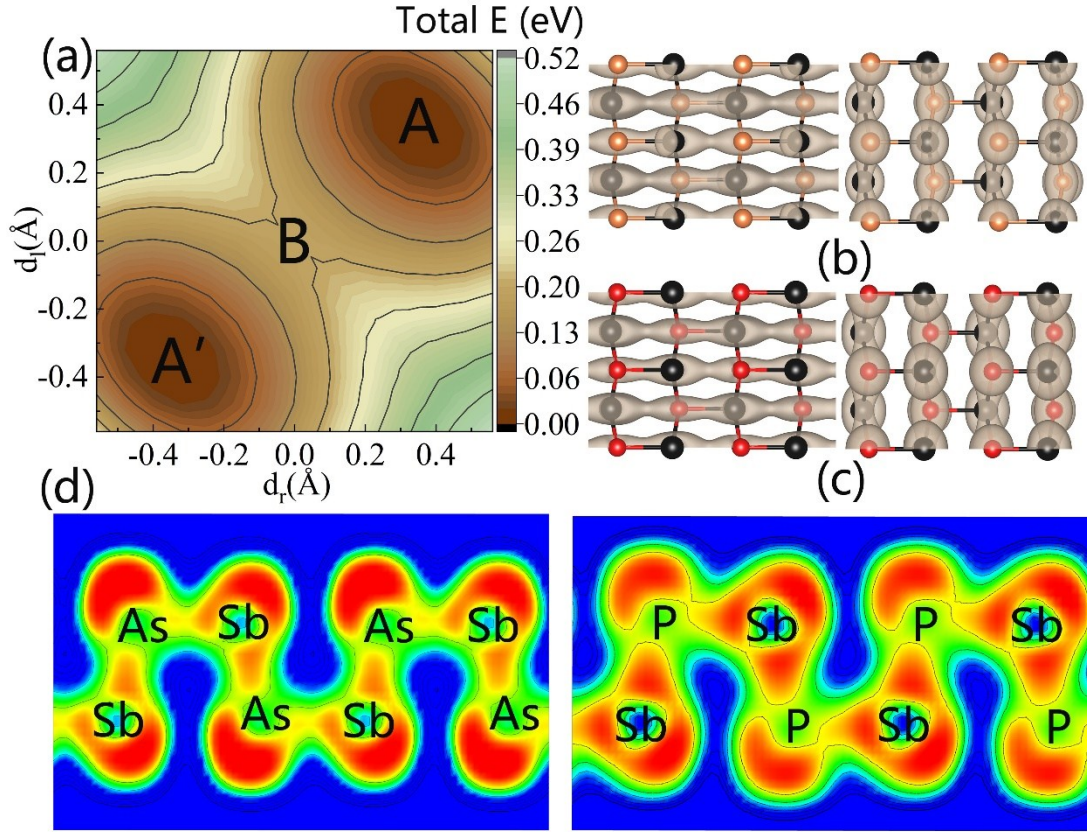


Fig. S8 (a) The free-energy contour plot of monolayer γ -SbAs according to the displacements (d_l , d_r). The corresponding partial charge density at CBM (top panel) and VBM (below panel) are presented in (b) γ -SbAs and (c) γ -SbP, respectively. All the Fermi levels are pinned in 0 eV and the isosurface of the partial charge density is at $0.002 \text{ e } \text{\AA}^{-3}$. (d) Electron localization function (ELF) of monolayer γ -SbX; ELF = 1 (red) and 0 (blue) indicate accumulated and vanishing electron density, respectively.

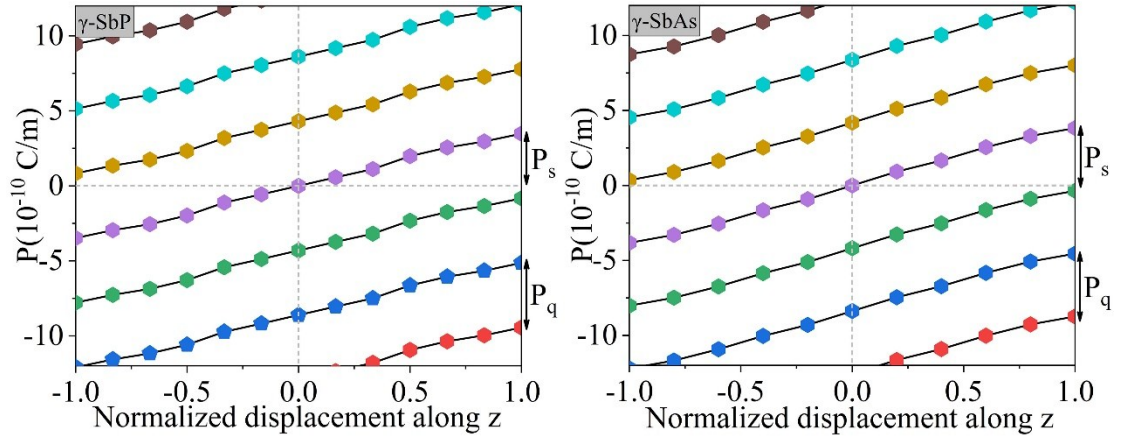


Fig. S9 Calculated total polarization of γ -SbP(a) and γ -SbAs(b) with VDW correction as a function of normalized displacement where the centrosymmetric paraelectric phase (0% displacement) is at the center, and two ferroelectric ground states are at two ends. P_s represents the spontaneous polarization and P_q represents the polarization quanta.

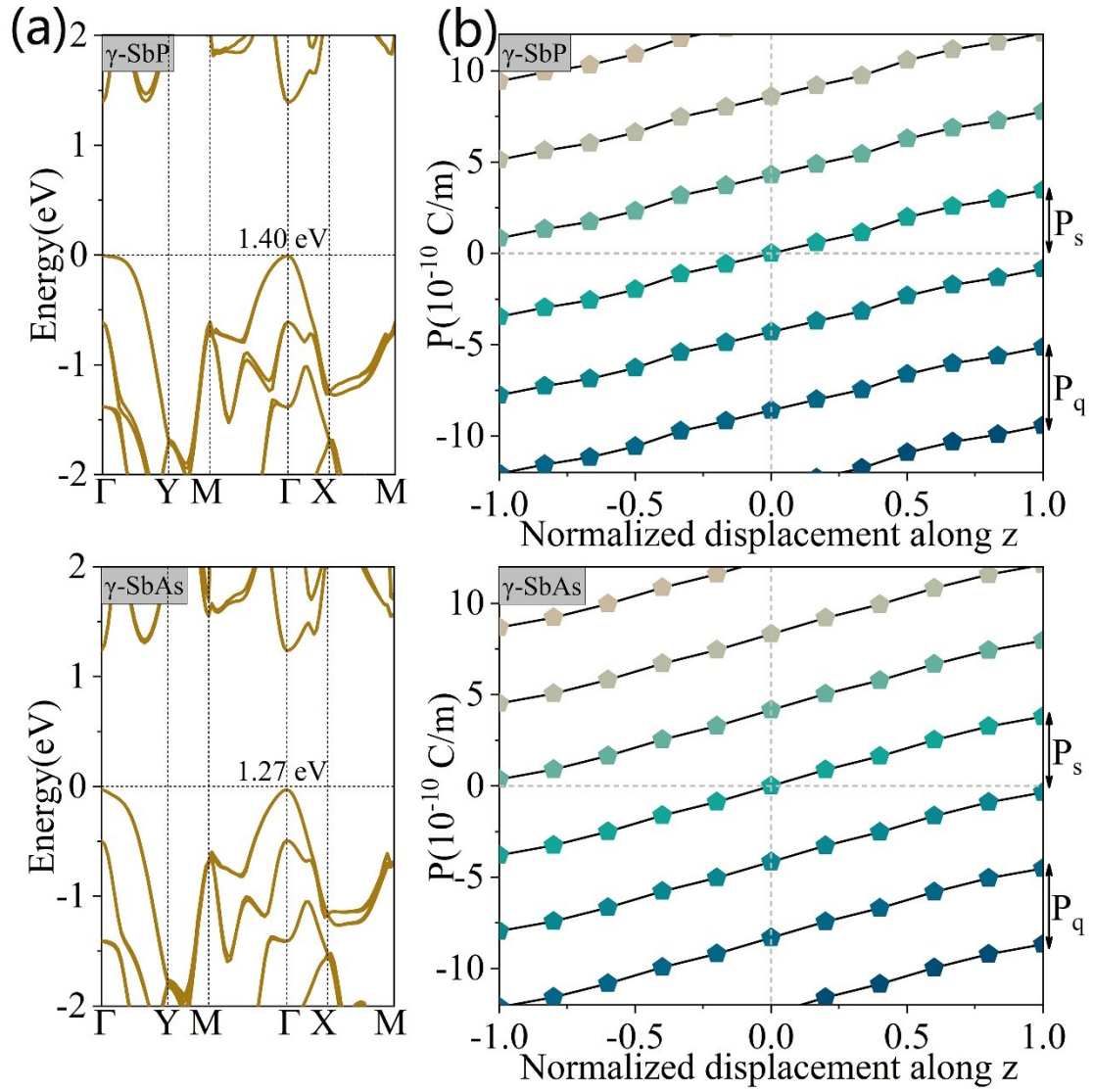


Fig. S10 (a) Band structure of γ -SbX with SOC calculated using HSE06 functional. (b) Calculated total polarization of γ -SbP(a) and γ -SbAs(b) with SOC as a function of normalized displacement where the centrosymmetric paraelectric phase (0% displacement) is at the center, and two ferroelectric ground states are at two ends. P_s represents the spontaneous polarization and P_q represents the polarization quanta.

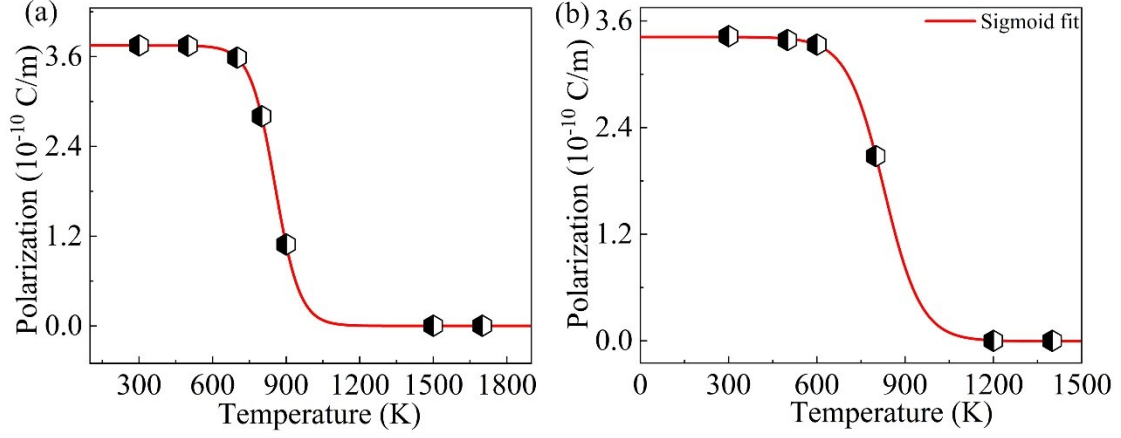


Fig. S11 Temperature dependence of polarization of γ -SbAs (a) and γ -SbP (b) obtained from ab initio MD simulations. The red lines are Sigmoid fits of MD results. The estimated Curie temperatures is 854.77 K (828.22K) for the γ -SbAs (γ -SbP) monolayer.

Details for Monte Carlo simulations:

We used the Landau theory with the polarization P as the order parameter. The

system free energy is expressed in the Landau-Ginzburg-type expansion:

$$E = \sum_i \left[\frac{A}{2}(P_i^2) + \frac{B}{4}(P_i^4) + \frac{C}{6}(P_i^6) + \frac{E}{8}(P_i^8) + \frac{F}{10}(P_i^{10}) \right] + \frac{D}{2} \sum_{\langle i,j \rangle} (P_i - P_j)^2$$

, where P_i is the polarization of each unit cell, $\langle i,j \rangle$ denotes the nearest neighbor. We use the mean-field approximation to investigate the dipole-dipole interaction. The first three terms are associated with the energy contribution from the local modes up to the sixth order for γ -SbP and tenth order for γ -SbAs. The last term captures the coupling between the nearest local modes, which include the 2D geometrical character and are crucial for the ordering and the phase transition. After we obtained the value of parameters by fitting, this model is used in the Monte Carlo simulations to investigate the temperature effects and the phase transition. The fitted values of the parameters are shown in Table S1.

Table S1 The fitted parameters A, B, C, E, and F are used to describe the double-well potential. D is the constant representing the mean-field approximation interaction between the nearest neighbors.

Material	A	B	C	E	F	D
γ -SbAs	19.984	-25.188	6.282	-0.6976	0.026	9.284
γ -SbP	-18.556	-5.324	0.5748	—	—	8.466

Details for SOC and van der Waals (vdW) correction:

We also checked the effect of the van der Waals (vdW) correction with the DFT-D2 method. The optimized lattice parameters for SL γ -SbAs (γ -SbP) are calculated to be $a = 6.21 \text{ \AA}$ ($5.93 \text{ \AA}$) and $b = 3.82 \text{ \AA}$ ($3.71 \text{ \AA}$), respectively, which are only slightly different from the results without considering van der Waals correction. Meanwhile, we also examined the electronic polarization under the van der Waals (vdW) correction, as seen in Table S2 and Fig. S8. It can be seen that the electronic polarization was marginally affected, bringing a change only about parts per thousand. The above analysis indicates that we can focus on result without the vdW correction. We also performed test calculations with including SOC. As seen in Fig. S9(a), the including of SOC has marginally decreased the band gaps, which are 1.27 eV and 1.40 eV for SL γ -SbAs and γ -SbP, respectively. However, as shown in Fig. S9(b), the test of the relevant ferroelectric physics yielded qualitatively the same results without considering SOC.

Table S2 The optimized lattice constants, spontaneous polarization P_s (pC/m) at zero temperature for SL γ -SbX with VDW correction.

Material	a	b	P_s
γ -SbAs	6.21	3.82	383
γ -SbP	5.93	3.71	348