

Large in-plane negative piezoelectricity and giant nonlinear optical susceptibility in elementary ferroelectric monolayers

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Negative piezoelectrics contract in the direction of an applied electric field, which is opposite to the behavior of normal piezoelectrics and rare in dielectric materials. The advent of low-dimensional ferroelectrics, with unconventional mechanisms of polarity, opens a fertile branch in the search for candidates with prominent negative piezoelectricity. Here, the distorted α -Bi monolayer, a newly identified elementary ferroelectric with a puckered black-phosphorus-like structure [Gou *et al.*, *Nature (London)* **617**, 67 (2023)], is computationally studied, which manifests a large negative in-plane piezoelectricity (with $d_{33} \sim -26$ pC/N). Its negative piezoelectricity originates from its unique buckling ferroelectric mechanism, namely intercolumn sliding. Consequently, a moderate tensile strain can significantly reduce its ferroelectric switching energy barrier, while compressive strain can significantly enhance its prominent nonlinear optical response. The physical mechanism of in-plane negative piezoelectricity also applies to other elementary ferroelectric monolayers.

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I. INTRODUCTION

Piezoelectrics, which allow interconversion between an electric signal and a mechanical force, are highly interesting in physical mechanisms [1–4] and essential for microelectromechanical applications such as sonars, actuators, and pressure sensors [5,6]. Generally, piezoelectricity is characterized by the piezoelectric coefficients e_{ij} and d_{ij} , which denote the changes in polarization in response to the lattice deformation (strain η) and applied force (stress σ), respectively.

Normal piezoelectrics have positive longitudinal piezoelectric coefficients ($e_{33} > 0$ or $d_{33} > 0$ assuming the polar axis is along z); namely, the magnitude of polarization is more likely to increase (decrease) when a tensile (compressive) strain or stress is applied along the polar direction [7,8], as depicted in Fig. 1(a). Negative piezoelectrics with $e_{33} < 0$ or $d_{33} < 0$ are exotic and valuable in electromechanical system devices. For instance, by designing a heterostructure combining ultrathin normal piezoelectric and negative piezoelectric layers, a strong bending function can be achieved, as shown in Fig. 1(b). However, previously only the ferroelectric polymer poly(vinylidene fluoride) (PVDF) and its copolymers were among the few examples in this category [9].

Recently, a few more negative piezoelectrics were theoretically predicted or experimentally found [10–17]. For example, Liu and Cohen predicted several hexagonal ABC ferroelectrics with negative piezoelectricity, which derive from the domination of the negative clamped-ion term over the positive but small internal-strain contribution [10]. You *et al.* observed the out-of-plane negative piezoelectric response in ferroelectric CuInP_2S_6 and ascribed it to the reduced dimensionality of

a van der Waals (vdW) layered structure [12]. Ding *et al.* predicted an additional contribution to negative piezoelectricity in the ZrI_2 vdW bulk; namely, the interlayer sliding ferroelectricity is the dominant source [15]. These efforts have greatly pushed forward the physical understanding of negative piezoelectricity and enlarged the scope of candidate materials. In particular, the emergence of two-dimensional (2D) ferroelectrics provides a promising platform to explore negative piezoelectricity, due to the unique origins of their polarity.

One of the latest advancements in 2D ferroelectrics is the discovery of elementary ferroelectrics, which are conceptually different from traditional ferroelectric compounds involving at least two ions (anion plus cation). In 2018, Xiao *et al.* predicted the α -phase As, Sb, and Bi monolayers with puckered black-phosphorus-like structures to be 2D ferroelectrics [18], and very recently, the α -Bi monolayer was experimentally confirmed [19]. Such an exciting branch of research provides great opportunities to explore exotic dielectric properties.

In this paper, the piezoelectricity of elementary ferroelectric monolayers has been studied using density functional theory (DFT) calculations. Taking the α -Bi monolayer as the representative material, our calculations reveal a large negative piezoelectric coefficient, which originates from its unique ferroelectric mechanism. The puckered structure can mimic the intercolumn sliding, leading to a similar but much stronger effect compared with that in interlayer sliding ferroelectrics. Furthermore, its nonlinear optical response is found to be rather prominent, which can be further enhanced by compressive strain.

II. COMPUTATIONAL METHODS

DFT calculations are performed using the Vienna *ab initio* simulation package (VASP) [20]. The projector

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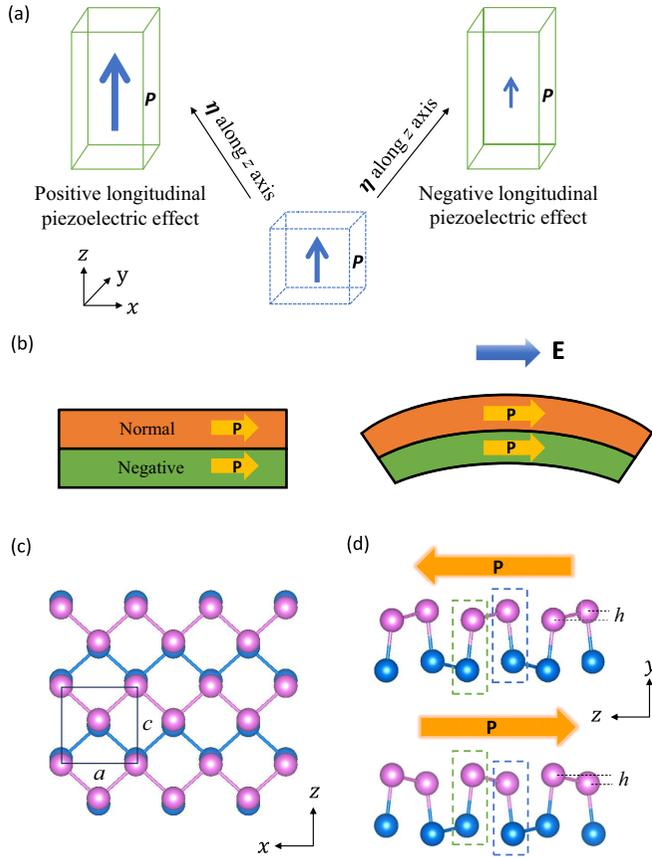


FIG. 1. (a) Schematic of positive and negative longitudinal piezoelectric effects. The assumed applied strain is along the z axis. (b) Schematic of the mechanical bending in a normal/negative piezoelectric heterostructure. (c) and (d) Structure of the ferroelectric α -Bi monolayer. The upper and lower Bi atoms are distinguished by colors. (c) Top view. The primitive cell is indicated by the black rectangle. (d) Side views of the two degenerate polar states. The buckling h corresponds to the intercolumn (dashed boxes) sliding. Such a sliding can induce an in-plane polarization, similar to the sliding ferroelectric mechanism in vdW layered structures. For piezoelectric tensor analysis, the in-plane polar axis is defined as the z axis.

augmented wave (PAW) pseudopotentials are Bi_d ($5d^{10}6s^26p^3$), As ($4s^24p^3$), Sb ($5s^25p^3$), Ge_d ($3d^{10}4s^24p^2$), Se ($4s^24p^4$), Zr_{sv} ($4s^24p^65d^25s^2$), and I ($5s^25p^5$), as recommended by VASP. The plane-wave cutoff energy is fixed at 400 eV. The default exchange-correlation functional is treated using the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) [21], unless specifically stated. Other functionals have also been tested, including the Perdew-Burke-Ernzerhof functional revised for solids (PBEsol) parametrization of the GGA [22] and the Perdew-Zunger parametrization of the local density approximation (LDA) [23,24].

The coordinates of the α -Bi monolayer are shown in Fig. 1(c), with the y axis as the out-of-plane direction. To simulate a monolayer, a 25-Å vacuum layer is added to avoid the interaction between two neighboring slices. For Brillouin zone sampling, a Γ -centered $11 \times 1 \times 11$ Monkhorst-Pack k -point mesh is adopted for Sb, Bi, and GeSe monolayers, and

an $11 \times 6 \times 3$ k -point mesh is adopted for the ZrI₂ bulk. Both the lattice constants and atomic positions are fully optimized iteratively until the Hellmann-Feynman force on each atom and the total energy are converged to 0.01 eV/Å and 10^{-6} eV, respectively.

The ferroelectric polarization is calculated using the Berry phase method [25], and the possible ferroelectric switching path is evaluated by the linear interpolation between the optimized ferroelectric (FE) state and the optimized paraelectric (PE) state. To calculate the piezoelectric stress coefficients e_{ij} , density functional perturbation theory (DFPT) is employed [26], with more dense $15 \times 1 \times 15$ and $13 \times 7 \times 4$ k -point meshes used for sampling for the monolayers and bulk, respectively. The elastic stiffness tensor matrix elements are calculated using VASPKIT [27].

Second-harmonic generation (SHG) susceptibilities are calculated using the ABINIT package [26,28–30]. A dense k -point mesh of $50 \times 1 \times 50$ is used for sampling, and 40 electronic bands are used to calculate the SHG susceptibility tensor.

To simulate the uniaxial in-plane strain, the lattice constant along the strain direction is fixed, while all atomic positions and other directional lattice constant(s) are fully relaxed. Then the changes in polarization in response to an applied strain η and stress σ can be gauged by the piezoelectric stress tensor e_{ikl} and piezoelectric strain tensor d_{ikl} , respectively. The formulas can be expressed as follows:

$$e_{ikl} = \left(\frac{\partial P_i}{\partial \eta_{kl}} \right)_E = - \left(\frac{\partial \sigma_{kl}}{\partial E_i} \right)_\eta, \quad (1)$$

$$d_{ikl} = \left(\frac{\partial P_i}{\partial \sigma_{kl}} \right)_E = \left(\frac{\partial \eta_j}{\partial E_{kl}} \right)_\sigma, \quad (2)$$

where $i, k, l \in \{1, 2, 3\}$, with 1, 2, and 3 corresponding to x , y , and z . P and E denote the polarization and electric field, respectively. Using the Voigt notation, e_{ikl} and d_{ikl} can be reduced to e_{ij} and d_{ij} , respectively, where $j \in \{1, 2, 3, \dots, 6\}$ and $1 \mapsto 11$ (xx), $2 \mapsto 22$ (yy), $3 \mapsto 33$ (zz), $4 \mapsto 23$ or 32 (yz or zy), $5 \mapsto 13$ or 31 (xz or zx), and $6 \mapsto 12$ or 21 (xy or yx).

III. RESULTS AND DISCUSSION

A. Negative piezoelectricity

The distorted α -Bi monolayer with a black-phosphorus-like structure has an orthorhombic lattice (space group $Pmn2_1$, No. 31), as shown in Figs. 1(c) and 1(d). A unit cell consists of four Bi atoms, forming the upper and lower sheets. Our DFT-optimized lattice constants agree well with the experimental values, as shown in Table I, which indicates the reliability of our calculation.

The symmetry of the $Pmn2_1$ space group (point group $mm2$) allows five independent elements of the piezoelectric tensor matrix: e_{31} , e_{32} , e_{33} , e_{24} , and e_{15} [31,36]. For 2D materials, usually only the in-plane stresses and strains are allowed, while the out-of-plane direction (i.e., the y axis here) is stress and strain free [31,37], i.e., $\sigma_2 = \sigma_4 = \sigma_6 = 0$. Thus the piezoelectric tensor matrix can be reduced as follows:

$$e = \begin{pmatrix} 0 & 0 & e_{15} \\ 0 & 0 & 0 \\ e_{31} & e_{33} & 0 \end{pmatrix}. \quad (3)$$

TABLE I. DFT-calculated basic physical properties of the α -Sb and α -Bi monolayers, in comparison with the ZrI₂ bulk and the GeSe monolayer. The polarizations are in units of pC/m and $\mu\text{C}/\text{cm}^2$ for the monolayers and the bulk, respectively. The piezoelectric stress coefficients e_{ij} are in units of 10^{-10} C/m and 10^{-10} C/m² for the monolayers and bulk, respectively. Here, the space group for all four materials is $Pmn2_1$ (No. 31). For all monolayers, the out-of-plane direction is along the b axis, while for ZrI₂ bulk the c axis is the vdW stacking direction. It should be noted that in our GGA-PBE calculation, the α -As monolayer exhibits a symmetric structure with space group $Pmna$ (No. 53), different from a previous LDA result [18]. More details and tested results with different exchange-correlation functionals can be found in the SM [31].

| Structure | a (Å) | c (Å) | b (Å) | Polarization | e_{33} | e_{31} | d_{33} (pC/N) | Gap (eV) |
|-------------------------------|---------|---------|---------|--------------|----------|----------|-----------------|----------|
| Sb | 4.36 | 4.73 | | 21 | -2.7 | -1.1 | -19.2 | 0.23 |
| Bi | 4.57 | 4.83 | | 16 | -5.1 | -2.1 | -25.9 | 0.31 |
| Bi (Expt. [32]) | 4.54 | 4.75 | | | | | | |
| Bi (Expt. [33]) | 4.5 | 4.8 | | | | | | |
| Bi (Calc. [18]) | 4.39 | 4.57 | | | | | | |
| ZrI ₂ | 3.75 | 14.81 | 6.86 | 0.37 | -0.061 | -0.002 | -1.416 | 0.19 |
| ZrI ₂ (Calc. [15]) | 3.75 | 14.80 | 6.87 | 0.39 | -0.061 | -0.001 | -1.445 | 0.15 |
| GeSe | 3.97 | 4.28 | | 360 | 11.5 | -3.3 | 100.1 | 1.27 |
| GeSe (Calc. [34,35]) | 3.99 | 4.26 | | 367 | 13.3 | -3.0 | | |

Similarly, there are four independent elements of the elastic stiffness tensor C for a 2D rectangular lattice (C_{11} , C_{13} , C_{33} , C_{55}) [31,38]:

$$C = \begin{pmatrix} C_{11} & C_{13} & 0 \\ C_{31} & C_{33} & 0 \\ 0 & 0 & C_{55} \end{pmatrix}. \quad (4)$$

Then the piezoelectric strain coefficients d_{ij} can be calculated based on the piezoelectric stress tensor e and the elastic stiffness tensor C , as follows:

$$d_{ij} = \sum_{k=1}^3 e_{ik} C_{kj}^{-1}. \quad (5)$$

The calculated longitudinal piezoelectric stress and strain coefficients (e_{33} and d_{33}) of the α -Sb and α -Bi monolayers are also summarized in Table I, in comparison with the ZrI₂ bulk (an interlayer sliding vdW ferroelectric) and the GeSe monolayer (a conventional ion-displacive-type ferroelectric). The complete piezoelectric tensors and elastic stiffness tensors can be found in the Supplemental Material (SM) [31]. Our calculated results show that there are larger negative piezoelectric coefficients in elementary ferroelectric monolayers than in ZrI₂. Furthermore, although the structure of the GeSe monolayer is similar to that of the α -Bi monolayer, it exhibits a normal piezoelectric response, due to its different ferroelectric mechanism (to be discussed later).

The origin of in-plane negative piezoelectricity in the α -Bi monolayer can be traced back to its ferroelectric mechanism. As previous studies have revealed [18,19], the distorted structure with buckling h breaks the centrosymmetry of the α -Bi monolayer and induces charge transfer in each puckered sheet (see the orbital-projected charge density distributions of FE and PE phases in Fig. S2 of the SM [31]), giving rise to the in-plane polarization. Such buckling makes the origin of its ferroelectricity similar to the recently reported sliding ferroelectricity in layered structures [15,39–43], as shown in the left panels of Figs. 2(a) and 2(b). Taking interlayer sliding ferroelectric ZrI₂ as an example [Fig. 2(b)], the interlayer interaction in the polar stacking mode causes charge

redistribution within each ZrI₂ layer, leading to an electric dipole along the stacking direction. By analogy, the unique buckling can be considered as a kind of intercolumn sliding in the α -Bi monolayer. Keeping this similarity in mind, the negative piezoelectricity of the α -Bi monolayer is natural. Namely, with compressive strain along the polar axis, the neighbor columns become closer. Such a squeeze effect strengthens the polarization originating from intercolumn sliding, as appears in interlayer sliding ferroelectric ZrI₂ bulk [15]. Our DFT calculation confirms such an exotic evolution tendency in both the α -Bi monolayer and the ZrI₂ bulk, as shown in Fig. 2: The shorter the lattice constant along the polar axis, the stronger the ferroelectric distortion and the larger the polarization.

Despite the similarity, interactions entailing intercolumn sliding, which involves covalent bonds, should be much stronger than interactions entailing interlayer sliding, which involves the vdW interaction. As a result, the induced negative piezoelectricity in the α -Bi monolayer is 18.3 times that in the ZrI₂ bulk, as shown in Table I, which is of the same order of magnitude as the so-called giant negative piezoelectricity of CuInP₂S₆ (experimental value of approximately -95 pC/N and DFT-calculated value of approximately -18 pC/N) [12]. Note that the giant negative piezoelectricity of CuInP₂S₆ is out of plane due to the soft vdW layer, while that of our α -Bi monolayer is in plane, with totally different mechanisms.

For the GeSe monolayer with conventional ferroelectric origin, though its structure is similar to the α -Bi monolayer, the compressive (tensile) strain along the polar axis can only reduce (increase) its microscopic ferroelectric order parameter θ and thus generally exhibits a normal piezoelectricity, as shown in Fig. 2(c).

Following the analysis of Refs. [17,44], the piezoelectric stress coefficients e_{33} can be decomposed into two parts: the clamped-ion term \bar{e}_{33} and the internal-strain term e'_{33} . \bar{e}_{33} denotes the change of polarization P due to the uniform distortion of the lattice with the atomic fractional coordinates fixed, and e'_{33} denotes the piezoelectric response to the atomic relaxations that release the internal strain. The calculated coefficients of the α -Bi monolayer and the GeSe monolayer are summarized in Table II. It is clear that the α -Bi monolayer has

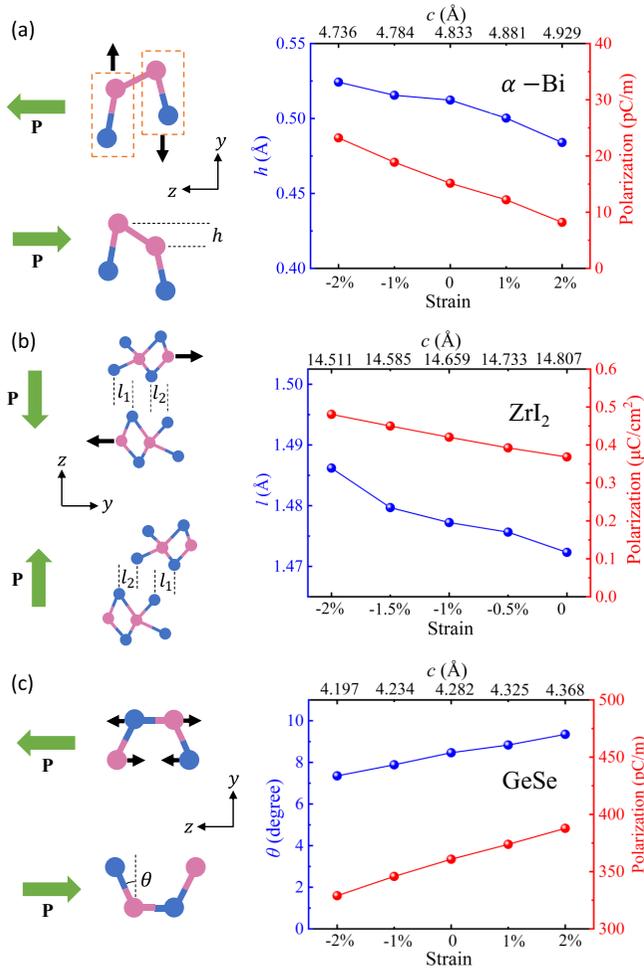


FIG. 2. Comparison of piezoelectricity with different mechanisms. Left panels: the microscopic order parameters for ferroelectric distortions, i.e., h , $l = l_1 + l_2$, and θ . Here, l is the order parameter of the sliding ferroelectric, which denotes the sliding length between the two degenerate ferroelectric states. The atomic movements during the ferroelectric switching process are indicated by black arrows. Green arrows show the vectors of polarizations. Right panels: uniaxial strain dependence of ferroelectric order parameters and corresponding polarizations. The uniaxial strains are applied along their polar directions. (a) Intercolumn sliding ferroelectric α -Bi monolayer. (b) Interlayer sliding ferroelectric ZrI_2 bulk. (c) Ion-displacive type ferroelectric GeSe monolayer. The α -Bi monolayer and ZrI_2 bulk show similar evolutions of the order parameter and polarizations, for their similar sliding mechanisms, which are opposite to the ion-displacive type ferroelectric GeSe monolayer.

TABLE II. Calculated clamped-ion (\bar{e}_{ij}) and internal-strain (e'_{ij}) piezoelectric stress coefficients of Bi and GeSe monolayers. The piezoelectric coefficients are in units of 10^{-10} C/m.

| | Clamped ion | | | Internal strain | | |
|------|----------------|----------------|----------------|-----------------|-----------|-----------|
| | \bar{e}_{31} | \bar{e}_{33} | \bar{e}_{15} | e'_{31} | e'_{33} | e'_{15} |
| Bi | 2.6 | 0.6 | 1.3 | -4.7 | -5.7 | -5.6 |
| GeSe | -7.1 | -0.3 | -7.1 | 3.9 | 11.9 | 14.0 |

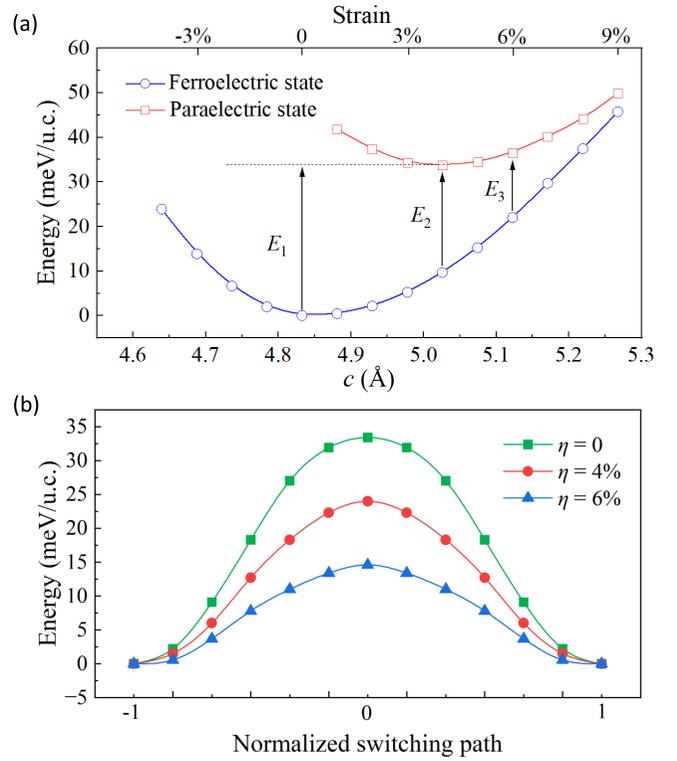


FIG. 3. (a) Comparison of energy curves for the ferroelectric state and paraelectric state as a function of the lattice constant of c . (b) The ferroelectric switching barriers at different conditions of strains. E_1 , E_2 , and E_3 in (a) are the barrier heights in (b). Here, u.c., unit cell.

a dominant negative internal-strain e'_{33} contribution (detailed Born effective charge and internal strain tensors can be found in the SM [31]) whereas the clamped-ion term \bar{e}_{33} is positive but small. This result is opposite to the negative piezoelectricity in the so-called *ABC* ferroelectrics with strong ionic bonds [10], where the clamped-ion term \bar{e}_{33} is negative and dominates the positive internal-strain e'_{33} , but similar to the vdW layered compounds BiTeX [13]. In contrast, the GeSe monolayer possesses a negative clamped-ion term \bar{e}_{33} , while the much larger positive internal-strain e'_{33} decides the total positive piezoelectricity.

An interesting consequence of negative piezoelectricity is the contracted lattice constant along the polar axis, which was also observed in negative piezoelectric WO_2X_2 ($X = \text{Br}$ and Cl) monolayers [45]. Figure 3(a) shows the energy curves of the ferroelectric state and the undistorted paraelectric state as a function of lattice constant c . As expected, the optimized lattice constant c is 4% longer in the paraelectric state, and thus a tensile strain can reduce the energy gain from ferroelectric distortion, which is beneficial to lowering the energy consumption during the ferroelectric switching. As demonstrated in Fig. 3(b), the ferroelectric switching barriers are significantly reduced upon application of uniaxial tensile strains along the c axis, e.g., 70% lower at strain $\eta = 6\%$.

The in-plane piezoelectric stress coefficients e_{33} and e_{31} as a function of compressive and tensile strains are also studied. In general, e_{33} and e_{31} increase with the uniaxial compressive

strain but decrease with the tensile strain. These results can be found in Fig. S3 of the SM [31].

B. Prominent SHG signal

Optical second-harmonic generation (SHG) is a powerful tool to characterize ferroelectric materials, in particular vital for 2D ferroelectrics as these are difficult to characterize with conventional electrical methods [46–49]. In fact, although many 2D ferroelectrics have been claimed experimentally, determining their precise polarizations from direct electrical measurement remains challenging [50]. Considering the narrow band gap of the α -Bi monolayer (~ 0.31 eV in the GGA calculation), direct electrical measurement of its ferroelectricity and piezoelectricity may be tough. Therefore optical SHG is an essential route to characterize the polarization and its change upon the application of strain.

Generally, the SHG intensity I can be estimated as

$$I \propto (P^{2\omega})^2 = (P_a^{2\omega})^2 + (P_b^{2\omega})^2 + (P_c^{2\omega})^2, \quad (6)$$

where $P^{2\omega}$ is the second-harmonic polarization generated by the electric field $E(\omega)$ component of incident light with angular frequency ω . a , b , and c are the crystal orientations, as shown in Fig. 1(c). The components of $P_i^{2\omega}$ can be expressed as [51]

$$P_i^{2\omega} = \varepsilon_0 \sum_{jk} \chi_{ijk}^{(2)}(-2\omega, \omega, \omega) E_j(\omega) E_k(\omega), \quad (7)$$

where ε_0 is the vacuum permittivity and $\chi_{ijk}^{(2)}$ is the SHG susceptibility.

For the α -Bi monolayer with $Pmn2_1$ space group (point group $mm2$), there are five independent elements in the SHG susceptibility tensor matrix: $\chi_{113}^{(2)} = \chi_{131}^{(2)}$, $\chi_{223}^{(2)} = \chi_{232}^{(2)}$, $\chi_{311}^{(2)}$, $\chi_{322}^{(2)}$, and $\chi_{333}^{(2)}$, while other tensor elements are rigidly zero as required by the symmetry. Using a simplified notation, $P_i^{2\omega}$ can be given by [51]:

$$\begin{bmatrix} P_a^{2\omega} \\ P_b^{2\omega} \\ P_c^{2\omega} \end{bmatrix} = 2\varepsilon_0 \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_a^2 \\ E_b^2 \\ E_c^2 \\ 2E_bE_c \\ 2E_aE_c \\ 2E_aE_b \end{bmatrix} \\ = 2\varepsilon_0 \begin{bmatrix} 2d_{15}E_aE_c \\ 2d_{24}E_bE_c \\ d_{31}E_a^2 + d_{32}E_b^2 + d_{33}E_c^2 \end{bmatrix}, \quad (8)$$

where d_{il} are the so-called d coefficients which are usually used to represent SHG susceptibility $\chi^{(2)}$. The subscripts are linked by the intrinsic permutation symmetry, namely $d_{il} \rightarrow d_{ijk} \rightarrow \frac{1}{2}\chi_{ijk}^{(2)}$ [51].

The calculated SHG susceptibilities χ_{ijk} of the α -Bi monolayer at $\hbar\omega = 1.17$ eV (i.e., wavelength $\lambda = 1064$ nm, which is frequently used in SHG experiments) are shown in Fig. 4(a), in comparison with other nonlinear optical materials. At $\hbar\omega = 1.17$ eV, a giant susceptibility is obtained, $\chi_{311}^{(2)} = 3.09 \times 10^5$ pm/V, which is much higher than that of the GeSe monolayer ($\sim 10^3$ pm/V [31,54]), the MoS₂ monolayer ($\sim 10^2$ pm/V at 810 nm [31,54,55]), and potassium dihydrogen

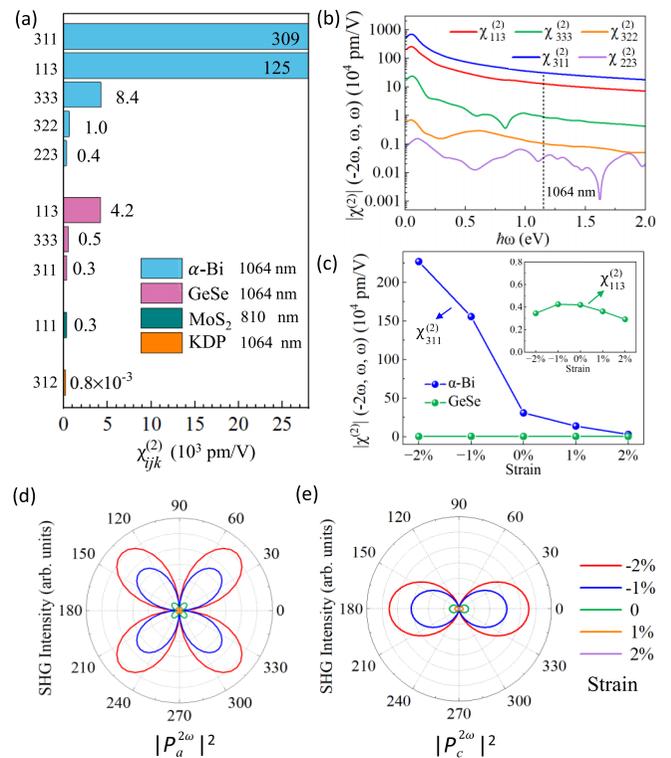


FIG. 4. Calculated SHG properties of the ferroelectric α -Bi monolayer. (a) The magnitudes of five independent SHG susceptibilities of the α -Bi monolayer, in comparison with other nonlinear optical materials. The values of MoS₂ at 810 nm and KDP are taken from Refs. [52,53]. (b) SHG susceptibilities as a function of the frequency of incident light. (c) The dominant susceptibility $\chi_{311}^{(2)}$ at 1064 nm under moderate uniaxial strains. Inset: the maximum component $\chi_{113}^{(2)}$ of GeSe monolayer at 1064 nm for comparison. (d) and (e) The polar plot of SHG components under uniaxial strains, with a perpendicular incident light. The whole SHG signal is the sum of these two components.

phosphate (KDP; ~ 0.76 pm/V [52], a well-known standard SHG reference). The SHG susceptibilities as a function of the light frequency are plotted in Fig. 4(b); they are even larger in the low-energy region. In this sense, the distorted α -Bi monolayer is a very prominent nonlinear optical material.

The large negative piezoelectricity can also be reflected in the SHG signal. Taking the largest element $\chi_{311}^{(2)}$ as an example, Fig. 4(c) shows its evolution under uniaxial strain. As expected, the compressive strain can enhance $\chi_{311}^{(2)}$. Surprisingly, such an enhancement is very large: almost one order of magnitude larger at $\eta = -2\%$. Therefore SHG can be used as a sensitive method to monitor the strain of the α -Bi monolayer. For comparison, the $\chi_{113}^{(2)}$ (the maximum susceptibility at 1.17 eV) of the GeSe monolayer is rather insensitive to strain.

With a perpendicular incident light along the b axis, its electric field can be expressed as $E = (E_a, E_b, E_c) = E(\cos \varphi, 0, \sin \varphi)$. Thus the nonzero $P_i^{2\omega}$ components can be derived as

$$\begin{aligned} P_a^{2\omega} &\propto \chi_{113}^{(2)} \sin(2\varphi), \\ P_c^{2\omega} &\propto \chi_{311}^{(2)} \cos^2 \varphi + \chi_{333}^{(2)} \sin^2 \varphi, \end{aligned} \quad (9)$$

where φ is the angle between the E vector and the a axis. Then the angle-dependent $P_a^{2\omega}$ and $P_c^{2\omega}$ can be obtained under uniaxial strains along the c axis, as shown in Figs. 4(d) and 4(e). The uniaxial strain can significantly enhance the SHG components $P_a^{2\omega}$ and $P_c^{2\omega}$ but will not alter their fourfold symmetry and twofold symmetry.

Last, we also examined the effect of epitaxial strain on the α -Bi monolayer. Single-layer graphene was chosen as the substrate, as was done in the experiment in Ref. [32]. After the full structural optimization, the inherent ferroelectricity of the α -Bi monolayer can be preserved by the substrate (see Fig. S5 in the SM [31]).

IV. CONCLUSION

In summary, the elementary ferroelectric α -Bi monolayer and its sister compounds have been systematically studied using DFT calculations; these calculations show that they exhibit large in-plane negative piezoelectricity ($d_{33} = -26$ pC/N) and giant nonlinear optical susceptibility ($\chi_{311}^{(2)} = 3.09 \times 10^5$ pm/V). Their negative piezoelectricity arises from

the intriguing “intercolumn” sliding ferroelectric mechanism, different from the negative piezoelectricity in CuInP_2S_6 and ABC ferroelectrics. The prominent SHG intensity in the α -Bi monolayer can be drastically enhanced with a moderate uniaxial compressive strain, while its ferroelectric switching energy barrier can be reduced by applying a uniaxial tensile strain. Our work will encourage more theoretical and experimental works on 2D negative piezoelectricity and elementary ferroelectrics, which not only refresh the physical knowledge of polarity but also offer a bright future for low-dimensional electromechanical devices.

Note added in proof. We just became aware of a very recent report on elemental ferroelectric monolayers [56], which obtained similar negative piezoelectric results.

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