

Emerging two-dimensional pentagonal $P\bar{4}2_1m$ XY_2 phases: Tunable electronic states, mechanical flexibility, and piezoelectricity

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Using a first-principles high-throughput screening approach, we systematically investigate the two-dimensional (2D) pentagonal $P\bar{4}2_1m$ XY_2 prototype family (where X and Y are main-group elements from Group IA to VIIA and with Z = 2 formula units per primitive cell) and identify 37 previously unknown stable phases exhibiting excellent thermodynamic, elastic, and dynamic stability. Analysis of valence electron count and bonding reveals that 2D $P\bar{4}2_1m$ XY_2 phases with 10, 12, and 14 valence electrons (VEs) per chemical formula are semiconducting, whereas those with 11 and 13 VEs exhibit metallic or ferromagnetic behavior. This behavior can be rationalized using a crystal-orbital approach. Notably, 2D $P\bar{4}2_1m$ SbB_2 (11 VEs), AsB_2 (11 VEs), and LiO_2 (12 VEs) are predicted to be ferromagnetic semiconductors with Heyd-Scuseria-Ernzerhof band gaps of 1.06, 1.19, and 2.75 eV, respectively. These 2D pentagonal $P\bar{4}2_1m$ XY_2 phases are promising for flexible electronics due to their low in-plane Young's modulus (6–100 N/m) and large critical strain (18%–40%). Moreover, exceptional out-of-plane piezoelectricity (with coefficients d_{36} ranging between 18 and 60 pm/V) is observed in 2D $P\bar{4}2_1m$ $SnBi_2$, $GeBi_2$, $TeGe_2$, and $PbBi_2$ due to their low shear modulus and large piezoelectric stress tensors. This work not only rationalizes the structure-electronic property correlation of the 2D pentagonal $P\bar{4}2_1m$ XY_2 prototype, but also provides valuable guidance for designing multifunctional 2D materials with tunable electronic, mechanical, and piezoelectric properties.

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I. INTRODUCTION

Since the successful exfoliation of graphene, extensive research has been devoted to exploring both the synthesis and applications of two-dimensional (2D) materials [1–3]. To date, a wide variety of structure prototypes have been discovered for 2D materials, including honeycomb lattices (e.g., graphene and *h*-BN) [4], Xenes [5], transition metal dichalcogenides [6], MXenes [7], MBenes [8–10], perovskites [11], Janus structures [12,13], and heterostructures [14]. Alongside the rapid development of computational materials science and the continuous improvement in computational power, researchers have predicted numerous novel 2D materials using diverse algorithms and methods, such as evolutionary

algorithms [15,16], particle swarm optimization [17], group and graph theory methods [18], as well as the widely adopted elemental substitution strategy [19–21]. These theoretical studies have not only significantly expanded the family of 2D materials but also provided essential guidance for experimental synthesis and application development, effectively bridging the gap between computational prediction and experimental realization [22,23].

Among various classes of 2D materials, 2D pentagonal lattices—consisting entirely or partially of pentagons—have attracted considerable attention due to their unique structural and physical properties [24–26]. In the 2D limit, such pentagonal lattices have been theoretically predicted in elemental, binary, and ternary systems with diverse space groups, for example, $P4bm$ SnN_2 [15], $P4/mbm$ HfC [24], $P1$ CdP_2 [27], Pc ZnP_2 [27], Pm $ZnPSe$ [27], $P2_1$ $CoSeS$ [28], $P2/c$ $PdPS$ [29], $P2_1/c$ Te [30], $P4_2$ SiC_5 [31], $P\bar{4}2_1m$ SiN_2 [32], NiN_2 [33], and RuS_4 [34]. Experimental advances have also confirmed the synthesizability of such 2D pentagonal materials, with

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successful realizations of PdSe₂ [35], PdS₂ [36], NiN₂ [37], and PdPSe [38]. In addition to structural diversity, 2D pentagonal lattices exhibit a variety of intriguing physical phenomena, such as auxetic behavior [15], ferroelectricity [33], ferromagnetism [39], efficient electrocatalytic nitrogen reduction activity [40], and second-harmonic generation [41], underscoring their potential applications in flexible electronics, spintronics, optoelectronics, and catalysis.

The vast diversity of structural prototypes and stoichiometries in 2D pentagonal lattices precludes a full investigation of all possible configurations in a single study. Among the many structural prototypes and stoichiometries possible in 2D pentagonal lattices, we focus here on the 2D pentagonal phases adopting the $P\bar{4}2_1m$ XY₂ (space group No. 113, with $Z = 2$ formula units per primitive cell) prototype. Since the proposal of 2D $P\bar{4}2_1m$ CC₂ (penta-graphene) in 2015 [42], approximately 36 compounds crystallizing into the 2D $P\bar{4}2_1m$ XY₂ prototype—including borides (e.g., SB₂, SeB₂, TeB₂ [43]), carbides (e.g., AlC₂ [31], GeC₂ [31]), nitrides (e.g., SiN₂ [15], AlN₂ [44]), and sulfides (e.g., BeS₂ [45])—have been theoretically reported. These known 2D pentagonal $P\bar{4}2_1m$ XY₂ phases have been found to exhibit very different electronic properties, displaying semiconducting, metallic, and even ferromagnetic behavior [44–47]. To date, the underlying physical and chemical mechanisms determining these properties remain, however, unclear. Moreover, the previously identified structures do not display a systematic distribution pattern and the chemical space accessible via elemental substitution remains largely unexplored.

To address these gaps, we systematically explore the chemical space of 2D pentagonal $P\bar{4}2_1m$ XY₂ (space group No. 113, $Z = 2$) prototype using an elemental substitution strategy, with X and Y selected from main-group elements (from group IA to VIIA) across the Periodic Table. This approach identifies 37 new 2D pentagonal $P\bar{4}2_1m$ XY₂ phases containing various Y₂ (Y = Be, B, Al, In, C, Si, Ge, Sn, Pb, N, P, As, Sb, Bi, O, S, Se, and Te) dimers, for which we comprehensively investigate structural, electronic, mechanical, and piezoelectric properties. Importantly, we uncover a clear correlation between valence electron count, dimer bonding configurations, and resulting electronic structures. This systematic exploration deepens the understanding of structure-property relationships in 2D pentagonal lattices and provides practical design guidelines for multifunctional 2D materials with tunable properties.

II. METHODS

First-principles calculations were carried out within the framework of density functional theory (DFT) using the all-electron projector augmented-wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP, version 6.3.2) [48,49]. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was employed [50,51]. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional was adopted to get a reliable estimation of band gaps of 2D pentagonal $P\bar{4}2_1m$ XY₂ phases [52]. The recommended PAW potentials were employed for all main-group elements. The corresponding valence electronic configurations are provided in the

Supplemental Material (SM) [53] (which also contains Refs. [54–60]). A kinetic cutoff energy of 600 eV was applied for the plane-wave expansion and the Brillouin zone was sampled using a Monkhorst-Pack k -point mesh with a spacing of $2\pi \times 0.04 \text{ \AA}^{-1}$. These parameters ensure the convergence of the enthalpy and force within 1×10^{-5} eV per cell and 0.01 eV/Å, respectively [61]. The calculation of the phonon dispersion curves was performed using the PHONOPY code [62]. Additional details regarding the calculation of phonon dispersions, *ab initio* molecular dynamics (AIMD), Manz bond orders [63], mechanical, magnetic, and piezoelectric properties are provided in the Methodology part of the SM.

III. RESULTS

A. High-throughput structure search by element substitution

To establish a computational benchmark, we first calculate the lattice parameters of eight previously reported 2D pentagonal $P\bar{4}2_1m$ XY₂ phases, namely SiN₂ [15], XC₂ (X = Al and Ga) [31], XB₂ (X = S, Se, and Te) [43], AlN₂ [44], and BeS₂ [45]. As summarized in Table S1, our results are in good agreement with earlier theoretical crystallographic data, validating our computational methodology [15,31,43–45].

As illustrated in Fig. 1(a), the 2D pentagonal $P\bar{4}2_1m$ XY₂ phase (space group No. 113, $Z = 2$) is composed of tilted X₂Y₃ pentagons. In this structure prototype, each X atom is tetrahedrally coordinated to four Y atoms, resulting in a nonplanar configuration. In contrast, each Y atom adopts a trigonal pyramidal coordination, being bonded to two X atoms and one Y atom, which leads to the formation of Y₂ dimers within this 2D network. According to group theory, regular pentagons—unlike equilateral triangles, squares, or hexagons—cannot periodically tile a plane without geometric distortions [64,65]. Consequently, most 2D pentagonal frameworks inherently exhibit out-of-plane buckling to attain thermodynamic stability. To comprehensively explore the chemical space of 2D pentagonal $P\bar{4}2_1m$ XY₂ phases, we establish a first-principles high-throughput computational workflow for structure screening, as illustrated in Fig. 1(b). In the first stage, 1156 candidate phases are generated via an element substitution strategy, considering main-group elements from IA to VIIA in the Periodic Table [i.e., X(Y): H-Cs, Be-Ba, B-Tl, C-Pb, N-Bi, O-Te, and F-I]. These generated structures are then fully optimized, maintaining the $P\bar{4}2_1m$ symmetry. Phases failing to retain the 2D X₂Y₃ pentagonal framework after optimization are excluded, leaving 582 phases for further analysis.

In the second stage, we evaluate the elastic stability of these remaining 582 phases, by determining whether these crystals remain stable under arbitrary small homogeneous deformations. The elastic tensors are calculated by applying six finite lattice distortions and the elastic constants are deduced from the stress-strain relationship [66]. The specific elastic stability criteria for 2D crystals are provided in the SM. Numerical results show that 399 of 582 phases exhibit excellent elastic stability.

In the third stage, the dynamic stability of these 399 phases was examined by computing their phonon dispersion curves. This systematic screening ultimately led to the identification

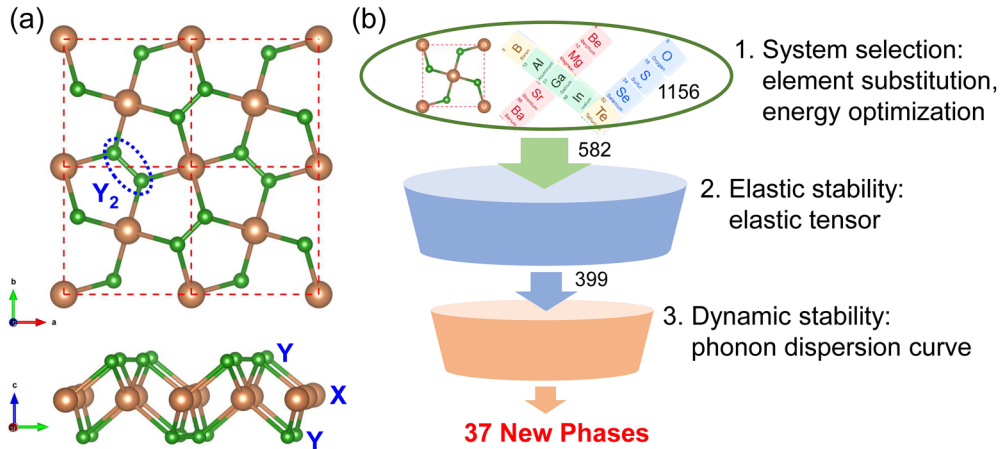


FIG. 1. Discovery of new 2D pentagonal $P\bar{4}2_1m$ XY_2 ($Z = 2$) phases: (a) crystal configuration of 2D $P\bar{4}2_1m$ XY_2 phases; (b) workflow diagram of the structure screening process of new 2D $P\bar{4}2_1m$ XY_2 phases.

of 37 new 2D pentagonal $P\bar{4}2_1m$ XY_2 phases in addition to the 36 previously reported ones—namely, SBe_2 , $SeBe_2$, $TeBe_2$, CaI_2 , $ClIn_2$, PbB_2 , GaC_2 , InC_2 , TiC_2 , AsB_2 , SbB_2 , BeN_2 , $BeAs_2$, MgN_2 , MgP_2 , $MgAs_2$, CSn_2 , CPb_2 , AlP_2 , LiO_2 , CBi_2 , $SiBi_2$, $GeBi_2$, $SnBi_2$, PbP_2 , $PbAs_2$, $PbSb_2$, $PbBi_2$, $TeGe_2$, $TeSi_2$, BeO_2 , $BeSe_2$, $BeTe_2$, MgO_2 , MgS_2 , $MgSe_2$, and $MgTe_2$ —all of which are found to be both elastically and dynamically stable. The corresponding elastic tensors are listed in Table S2 and the phonon dispersion curves are shown in Figs. S1–S6. The crystallographic parameters for all these 37 pentagonal 2D $P\bar{4}2_1m$ XY_2 phases are supplied in VASP POSCAR format at the end of the SM.

Additionally, the thermodynamic stability of these 37 newly identified 2D $P\bar{4}2_1m$ XY_2 phases was evaluated by calculating their cohesive energies according to the formula, $E_c = [2 \times E(X) + 4 \times E(Y) - E(XY_2)]/6$, where $E(X)$ and $E(Y)$ indicate the total energies of isolated X and Y atoms, respectively, and $E(XY_2)$ corresponds to that of the 2D XY_2 unit cell ($Z = 2$). The calculated cohesive energies, summarized in Table S2, range from 2.3 to 5.4 eV/atom, which are comparable to those of stanene (2.71 eV/atom) [15], germanene (3.24 eV/atom) [15], phosphorene (3.48 eV/atom) [67], silicene (3.91 eV/atom) [68], and GaN and AlN (4.2–5.2 eV/atom) [69]. These exothermic cohesive energies indicate favorable thermodynamic stability for all 37 predicted phases. Furthermore, the thermal stabilities of these phases were investigated using AIMD simulations. Given the high computational cost of AIMD simulations, nine representative compounds were selected from the 37 newly predicted $P\bar{4}2_1m$ XY_2 phases. The results show that all nine representative compounds retain their 2D frameworks without significant structural reconstruction at 300 K, indicating good thermal stability at room temperature (details refer to Figs. S7–S33 in the SM). Although AIMD simulations were not performed for all 37 phases, the consistent thermal stability observed for these representative compounds provides supporting evidence for the thermal robustness of this newly predicted $P\bar{4}2_1m$ XY_2 family.

Considering their moderate-to-high cohesive energies together with excellent mechanical, dynamic, and thermal

stability, these 37 2D $P\bar{4}2_1m$ XY_2 phases represent promising candidates for experimental realization under suitable synthesis conditions. Since these newly proposed XY_2 phases do not have known *van der Waals* (*vdW*) layered bulk counterparts, *vdW* epitaxial growth is proposed as a promising strategy for their experimental synthesis. Unlike conventional epitaxy, *vdW* epitaxy relaxes the requirement of strict lattice matching due to the weak interfacial *vdW* interaction, allowing high-quality growth on various substrates, such as mica, SiO_2/Si , and graphene/SiC [70].

In the following sections, we first examine how all proposed 2D pentagonal $P\bar{4}2_1m$ XY_2 phases (the 36 previously reported ones and the 37 newly discovered candidates) are distributed across the Periodic Table, highlighting their valence electron counts and bonding characteristics. We then analyze their electronic and magnetic properties. Finally, we investigate the mechanical and piezoelectric responses of these 2D $P\bar{4}2_1m$ XY_2 phases.

B. High-throughput structure search by element substitution valence-electron-driven bonding and electronic conductivity across 2D $P\bar{4}2_1m$ XY_2 phases

The resulting 73 phases were classified according to the total valence electrons (VEs) per XY_2 formula unit, as summarized in Table I. All phases exhibit 10, 11, 12, 13, or 14 VEs per XY_2 formula unit, corresponding to distinct electronic and magnetic behaviors governed primarily by the X_2YXY_2 structural units. The Y-Y distances and corresponding Manzt bond orders for all 73 phases are reported in Table S3, providing insight into bonding within the Y_2 units.

To rationalize the structure-electronic property relationship, we performed an orbital-based analysis of the X_2YXY_2 structural unit, modeled as $H_2Y - YH_2$ (with C_{2v} symmetry). As shown in Fig. 2(a), the interaction between two bent molecular H_2Y fragments generates four key orbitals: bonding σ , antibonding σ^* , and nonbonding in-phase n_π , and out-of-phase n_π^* orbitals [78,79]. A detailed molecular orbital interaction diagram is provided in Fig. S34 (see the

TABLE I. Correlation between valence electrons (VEs) per chemical formula and electronic conductivity of 2D $P\bar{4}2_1m$ XY_2 phases.

VEs	Phase	Conductivity
10	VI-III ₂ : SBe ₂ , SeBe ₂ , TeBe ₂ IV-III ₂ : AlI ₂ , ClIn ₂ , PbB ₂ , CB ₂ [71], CGa ₂ [31]	Semiconductor
11	III-IV ₂ : GaC ₂ , InC ₂ , TlC ₂ , AlC ₂ [31], BC ₂ [72] V-III ₂ : AsB ₂ , SbB ₂ , PB ₂ [44]	Metallic or magnetic
12	IV-IV ₂ : CSn ₂ , CPb ₂ , CC ₂ [32,42], SiC ₂ [73], GeC ₂ [47], SnC ₂ [47] VI-III ₂ : XB ₂ (X = S, Se, and Te) [43] II-V ₂ : BeN ₂ , BeAs ₂ , MgN ₂ , MgP ₂ , MgAs ₂ , BeP ₂ [74]	Semiconductor
13	III-V ₂ : AlP ₂ , BN ₂ [44], BP ₂ [44], AlN ₂ [44], GaN ₂ [44] V-IV ₂ : NC ₂ [44], PC ₂ [44] I-VI ₂ : LiO ₂	Metallic or magnetic
14	IV-V ₂ : CBi ₂ , SiBi ₂ , GeBi ₂ , SnBi ₂ , PbP ₂ , PbAs ₂ , PbSb ₂ , PbBi ₂ , CN ₂ [31], CP ₂ [46], CAs ₂ [46], CSb ₂ [46], SiN ₂ [73], SiP ₂ [75], SiAs ₂ [76], SiSb ₂ [76], GeN ₂ [15], GeP ₂ [77], GeAs ₂ [76], GeSb ₂ [76], SnP ₂ [76], SnAs ₂ [76], SnSb ₂ [76] VI-IV ₂ : TeGe ₂ , TeSi ₂ II-VI ₂ : BeO ₂ , BeSe ₂ , BeTe ₂ , MgO ₂ , MgS ₂ , MgSe ₂ , MgTe ₂ , BeS ₂ [45]	Semiconductor

SM). Figure 2(b) also depicts the Lewis structures of X_2YYX_2 species with different VEs.

10-valence-electron (10-VE) systems correspond to a fully filled bonding σ orbital which forms the highest occupied molecular orbital (HOMO), while the vacant n_π orbital is the lowest unoccupied molecular orbital (LUMO), as shown in Fig. 2(a) and Fig. S34. This electronic configuration produces a substantial HOMO–LUMO gap (1g–1gp), accounting for the semiconducting behavior of 2D 10-VE $P\bar{4}2_1m$ XY_2 phases, as observed in previously reported IV-III₂ phases (e.g., CB₂ and CGa₂) [31,71]. In 2D 10-VE $P\bar{4}2_1m$ XY_2 phases, the fully occupied σ bonding orbital yields Y–Y bond orders of ~ 1 , in agreement with calculated Manz bond order values (0.61–1.12, Table S3).

11-valence-electron (11-VE) systems feature $\sigma^2 n_\pi$ electronic states with one unpaired electron as the HOMO level, accounting for the metallicity or magnetism behavior

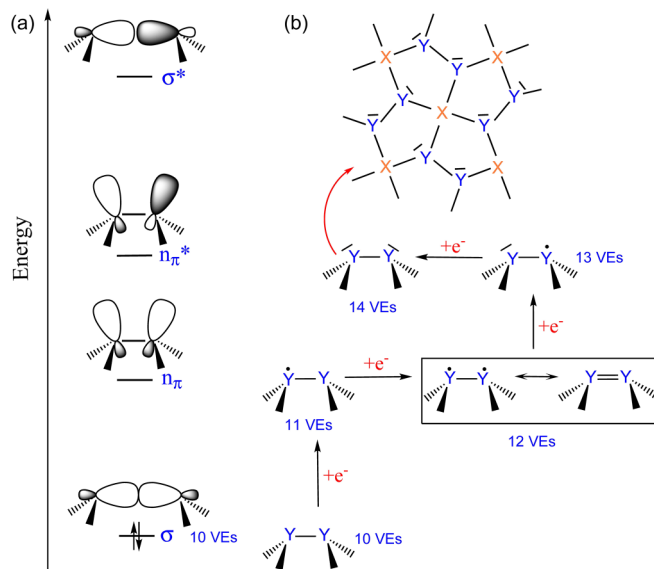


FIG. 2. Structure-electronic property relationship of 2D $P\bar{4}2_1m$ XY_2 phases: (a) schematic orbital diagram of H_2YYH_2 species (10 VEs); (b) Lewis structures of X_2YYX_2 species with 10–14 VEs.

observed in 2D extended reported XY_2 systems such as the III-IV₂ (e.g., BC₂) and V-III₂ (e.g., PB₂) phases [44,72]. The C_2^{3-} dimers exhibit short C–C bonds (1.28–1.37 Å, Manz bond orders of 1.56–2.53; see Table S3), whereas the isovalent B_2^{5-} units in 2D $P\bar{4}2_1m$ PB₂, AsB₂, and SbB₂ retain partially filled bonding, consistent with the presence of unpaired electrons.

12-valence-electron (12-VE) systems can adopt either a low-spin singlet state ($\sigma^2 n_\pi^2$) or a high-spin triplet state ($\sigma^2 n_\pi n_\pi^*$), with the energy separation between the n_π and n_π^* orbitals being strongly dependent on both composition and geometry. Increasing the electronegativity of X preferentially stabilizes the singlet state via negative hyperconjugation ($\sigma_{Y-Y} \rightarrow \sigma_{Y-X}$), consistent with the predicted stability of the 2D $P\bar{4}2_1m$ XY_2 series (Table S3). Pyramidalization at Y further tunes the electronic preference: small angles ($\approx 0^\circ$) enhance π -type interactions and favor the singlet, whereas larger angles introduce greater sp^3 character and stabilize the triplet. The Lewis structure of H_2X-XH_2 with 12 VEs is depicted in Fig. 2(b).

In the singlet state, full occupancy of the in-phase n_π orbital corresponds to a formal bond order of 2. Representative cases include the 2D $P\bar{4}2_1m$ SiC₂, GeC₂, and SnC₂ phases (C_2^{4-} ; C–C distance of 1.34–1.37 Å; Manz bond orders of 1.83–2.12; see Table S3), with analogous behavior observed in VI-III₂ and II-V₂ compounds—for example, BeN₂ and MgN₂, which feature formal N_2^{2-} units (N–N distance of ~ 1.26 Å; Manz bond orders of 1.92–2.27). In the singlet state, a clear energy gap emerges between the occupied n_π and vacant n_π^* orbitals of the molecular species X_2YYX_2 . Consistent with this molecular-orbital picture, hybrid HSE06 calculations yield band gaps of 0.8–3.26 eV across the 2D 12-VE $P\bar{4}2_1m$ XY_2 series of XC_2 (X = C, Si, Ge, and Sn, 1.36–3.26 eV) [32,47,73], XB_2 (X = S, Se, and Te, 1.9–2.0 eV) [43], and BeP₂ (0.8 eV) [74].

13-valence-electron (13-VE) systems feature a half-filled n_π^* orbital. The presence of this singly occupied orbital places the Fermi level within a partially filled band as HOMO level, resulting in metallic or magnetic behavior. Representative examples include III-V₂ (BN₂, BP₂, and AlP₂) and V-IV₂ (NC₂ and PC₂) compositions [44].

14-valence-electron (14-VE) systems contain three of the four orbitals filled, corresponding to an $\sigma^2 n_\pi^2 n_\pi^{*2}$ configuration. This electronic structure is consistent with a localized bonding picture comprising one lone pair on each Y center and a single Y–Y σ bond (see Fig. 2). In these 2D systems, the fully occupied nonbonding n_π^* orbital forms the HOMO, while the vacant σ^* orbital serves as the LUMO. The resulting HOMO-LUMO separation leads to semiconducting behavior in the 2D 14-VE systems (see Fig. 1). The IV–V₂ phase of 2D $P\bar{4}2_1m$ CN₂ exemplifies this configuration and its Lewis structure is depicted in Fig. 2(b). In 2D $P\bar{4}2_1m$ CN₂, the sp^3 -hybridized C (tetrahedral AX₄E₀) and N (trigonal-pyramidal AX₃E₁) centers satisfy the octet rule and the N–N bond distance is 1.45 Å [80], reflecting the expected single bond character (see Table S3). In an ionic representation, the N₂ unit in 2D $P\bar{4}2_1m$ CN₂ could be assigned a formal 4[−] charge (N₂^{4−}). Isoelectronic analogs, including IV₂^{6−}, V₂^{4−}, and VI₂^{2−} dimers (e.g., Si₂^{6−} in TeSi₂, Bi₂^{4−} in CBi₂, and Se₂^{2−} in BeSe₂), similarly support 14-VE frameworks, enabling IV–V₂, VI–IV₂, and II–VI₂ compositions. It is also found that not all isovalent 14-VE phases can be stabilized in this 2D $P\bar{4}2_1m$ XY₂ prototype, since the structural stability difference is dictated by atomic radius, electronegativity, and valence-orbital energies [12,15,20,31]. For the reported 2D 14-VE $P\bar{4}2_1m$ XY₂ phases of CY₂ (X = N, P, As, and Sb), SiY₂ (Y = N, P, As, and Sb), GeY₂ (Y = N, P, As, and Sb), SnY₂ (Y = P, As, and Sb), and BeS₂, the calculated HSE06 band gaps fall in the range of 1.3–6.5 eV [15,31,45,46,73,75,76,77], so these 14-VE phases are semiconducting, as expected from the electronic and bonding analysis of molecular H₂YYH₂ species.

In brief, this valence-electron-centered framework provides a unified understanding of the structural stability, bonding, and electronic conductivity properties across the 2D pentagonal $P\bar{4}2_1m$ XY₂ family. The 14-, 12-, and 10-VE phases adopting in the 2D $P\bar{4}2_1m$ XY₂ prototype are semiconducting, whereas the 13- and 11-VE phases contain unpaired electrons in the highest occupied states, potentially leading to metallic or magnetic characteristics. When the number of valence electrons per formula unit deviates from the optimal 10–14 range, for example at 9 or 15 VEs, the Y–Y bonds become significantly weakened, exhibiting a formal bond order of 0.5. As a result, stabilization of the 2D $P\bar{4}2_1m$ XY₂ prototype becomes energetically unfavorable. We also find that lowering the symmetry can stabilize the 2D pentagonal XY₂ phases; for example, 2D $P2_1/c$ Te (i.e., TeTe₂) [30], $P2_1$ Si (i.e., SiSi₂) [81], and $P4bm$ SnN₂ [15], are dynamically stable, unlike the corresponding 2D $P\bar{4}2_1m$ phases. This difference can be understood in terms of Peierls distortion. In some high-symmetry $P\bar{4}2_1m$ phases, partially filled electronic states at the Fermi level induce electronic instability, resulting in imaginary phonon modes or energetically unfavorable configurations. However, transitioning to lower-symmetry phases, such as $P2_1/c$, $P2_1$, and $P4bm$, allows bond length modulations that open a pseudogap, lower the total energy, and stabilize the lattice dynamically.

In this work, the H₂Y – YH₂ molecular model is intended as a qualitative framework to elucidate the dominant orbital interactions within the Y framework. Although the X atoms are not explicitly included in this simplified model, they primarily regulate the electron filling through charge

transfer and thus determine the occupation of the bonding and antibonding states, rather than altering the overall orbital hierarchy. Consequently, the model captures the essential electron-counting mechanism, while quantitative features of the crystal electronic structure of predicted 2D $P\bar{4}2_1m$ XY₂ phases are obtained from the first-principles calculations in the following section.

C. Dependence of electronic property on the VE count

To validate the above predictions, first-principles calculations were performed on both 37 newly predicted and 36 previously reported 2D $P\bar{4}2_1m$ XY₂ phases. At first, among the 37 newly identified 2D $P\bar{4}2_1m$ XY₂ structures, the 10-VE (SBe₂, SeBe₂, TeBe₂, PbB₂, CaI₂, and ClIn₂), 12-VE (CPb₂, CSn₂, BeN₂, MgN₂, MgP₂, BeAs₂, and MgAs₂), and 14-VE (TeGe₂, TeSi₂, CBi₂, SiBi₂, GeBi₂, SnBi₂, PbP₂, PbAs₂, PbSb₂, PbBi₂, BeO₂, BeSe₂, BeTe₂, MgO₂, MgS₂, MgSe₂, and MgTe₂) phases were confirmed as semiconductors or insulators via the HSE06 calculations, with electronic band gaps ranging from 0.8 to 6.5 eV (see Table S4). This band gap tunability by chemical composition suggests broad potential for electronic and optoelectronic applications spanning from the infrared to ultraviolet regions. Besides, Table S4 also shows the calculated band gaps of the previously reported 2D 10-, 12-, and 14-VE XY₂ phases, further validating our valence electron counting analysis in Table I. Here, taking 2D $P\bar{4}2_1m$ XY₂ SBe₂ (10 VEs), CPb₂ (12 VEs), and TeGe₂ (14 VEs) as representative examples, their HSE06 band structures and density of states (DOS) are presented in Fig. 3. As shown in Fig. 3, all three compounds exhibit typical semiconducting characteristics with indirect band gaps of 2.09, 0.82, and 1.26 eV for 2D $P\bar{4}2_1m$ SBe₂, CPb₂, and TeGe₂, respectively. Their valence band maxima originate primarily from the *p* orbitals of the Y₂ dimers, as further confirmed by the corresponding partial charge density distributions (see Fig. S35 in the SM).

In contrast, it is found that newly identified 2D $P\bar{4}2_1m$ 11-VE (SbB₂, AsB₂, GaC₂, InC₂, and TiC₂) and 13-VE (LiO₂ and AlP₂) phases exhibit metallic behavior and the DOS analysis (see Figs. S36 and S37) shows that energy states at the Fermi level originate mainly from *p* orbitals of the Y₂ dimers, consistent with partially filled bonding or antibonding orbitals. The partial charge distributions shown in Figs. S38 and S39 are consistent with the projected density of states (PDOS) analysis, further illustrating the metallic characteristics of these phases. Additionally, our calculations confirm that the previously reported 2D $P\bar{4}2_1m$ 11-VE (BC₂ [72] and PB₂ [44]) and 13-VE (NC₂ [44], PC₂ [44], BN₂ [44], BP₂ [44], AlN₂ [44], and GaN₂ [44]) phases also exhibit a metallic behavior (see Figs. S40 and S41), in agreement with early theoretical predictions.

Notably, in the PDOS panels of 2D $P\bar{4}2_1m$ SbB₂, AsB₂, and LiO₂ [see Figs. S8(a), S8(b), and S9(b)], a pronounced DOS peak at the Fermi level—primarily arising from *p* orbitals of the Y₂ dimers—indicates the electronic instability [82]. To stabilize these phases, such electronic instabilities need to be compensated, in this case through magnetic interactions. Besides, a large DOS at the Fermi level often indicates a tendency toward spontaneous ferromagnetism [15,82,83]. Therefore, we further investigate the

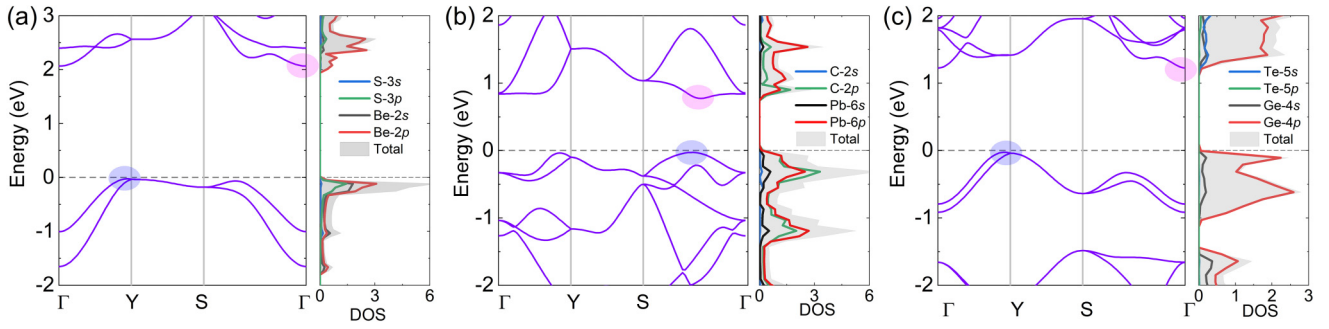


FIG. 3. Calculated electronic band structures and DOS of 2D $P\bar{4}2_1m$ (a) SBe_2 (10 VEs), (b) CPb_2 (12 VEs), and (c) $TeGe_2$ (14 VEs). The light blue and magenta ovals in the band structures indicate the valence band maximum and conduction band minimum, respectively.

magnetic properties of the 2D 11-VE (SbB_2 , AsB_2 , GaC_2 , InC_2 , and TiC_2) and 13-VE (LiO_2 and AlP_2) phases via spin-polarized first-principles calculations. The numerical results reveal that 2D $P\bar{4}2_1m$ SbB_2 , AsB_2 , and LiO_2 possess ferromagnetic ground states, while 2D $P\bar{4}2_1m$ GaC_2 , InC_2 , TiC_2 , and AlP_2 phases remain nonmagnetic even when spin polarization is considered. The total energies of the ferromagnetic, antiferromagnetic, and nonmagnetic states of 2D $P\bar{4}2_1m$ SbB_2 , AsB_2 , and LiO_2 phases are summarized in Table S5.

The calculated electronic band structures of 2D $P\bar{4}2_1m$ SbB_2 , AsB_2 , and LiO_2 phases using HSE06 functional are presented in Fig. 4, respectively. As shown in Fig. 4, these three ferromagnetic phases exhibit spin-polarized band structures and DOS with distinct asymmetry between the spin-up and spin-down channels, indicating potential applications in spintronic devices. Specifically, 2D $P\bar{4}2_1m$ SbB_2 is a ferromagnetic semiconductor with an indirect band gap of 1.06 eV within the HSE06 level of theory, as shown in Fig. 4(a). In the 2D $P\bar{4}2_1m$ SbB_2 , the spin-up and spin-down band gaps are 2.27 eV and 1.13 eV at the HSE06 level, respectively [Fig. 4(a)]. Similarly, 2D $P\bar{4}2_1m$ AsB_2 also exhibits a ferromagnetic ground state with an indirect band gap of 1.19 eV [Fig. 4(b)], while its spin-up and spin-down gaps are calculated as 2.15 eV and 2.16 eV, respectively, at the HSE06 level. In above both cases, the electronic states near the Fermi level predominantly originate from B $-2p$ orbitals. For the case of 2D $P\bar{4}2_1m$ LiO_2 , an indirect band gap of 2.75 eV is found within the HSE06 level of theory as shown in Fig. 4(c). Notably, in this phase, both the valence band maximum and conduction band minimum are dominated by

spin-down states of O $-2p$, further indicating spin-selective electronic behavior.

It is noted that these results identify 2D $P\bar{4}2_1m$ SbB_2 , AsB_2 , and LiO_2 as promising 2D magnetic semiconductors based on zero-temperature first-principles calculations. Nevertheless, their magnetic transition temperatures and finite-temperature magnetic stability remain to be established before their potential for practical spintronic applications can be fully assessed.

Last but not least, the band gap values of all 2D 11- and 13-VE phases are presented in Table S6. It is worth noting that 2D $P\bar{4}2_1m$ AlC_2 was previously reported as a nonmagnetic semiconductor [1.86 (1.19) eV by PBE (HSE06) functional] [31]. However, our spin-polarized PBE calculations reveal that 2D $P\bar{4}2_1m$ AlC_2 actually exhibits nonmagnetic metallic behavior (see Fig. S40a). These results highlight a systematic correlation between valence electron count, dimer bonding configuration, and the resulting electronic and magnetic properties. The tunable transition from semiconducting to metallic and magnetic behavior underscores the versatility of the 2D $P\bar{4}2_1m$ XY_2 structural prototype for electronic and spintronic applications.

D. In-plane mechanical property

The mechanical properties of materials, which relate structural deformation to externally applied forces, play a crucial role in determining their suitability for industrial applications. In the following, we systematically evaluate the in-plane Young's moduli, in-plane Poisson's ratios, and in-plane ideal

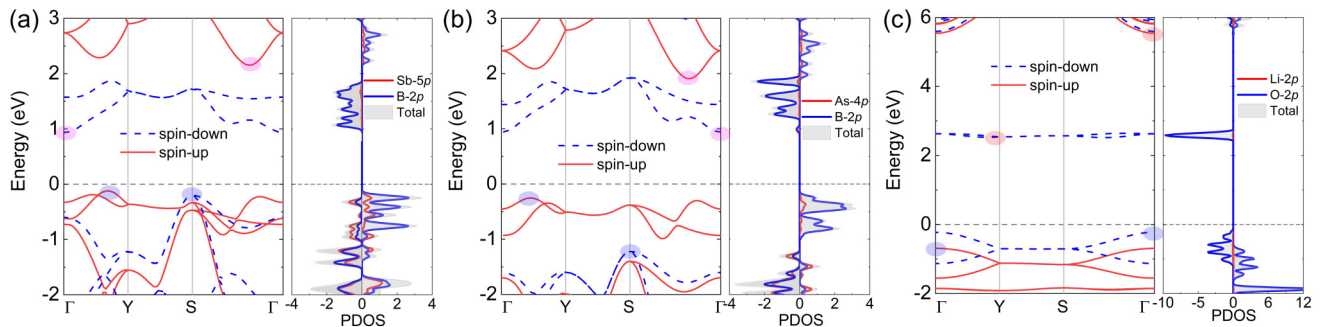


FIG. 4. Calculated electronic band structures and partial DOS of ferromagnetic 2D $P\bar{4}2_1m$ 11-VE and 13-VE XY_2 phases by the HSE06 functional: (a) SbB_2 , (b) AsB_2 , and (c) LiO_2 . The left (right) PDOS panel indicates the spin-down (spin-up) state.

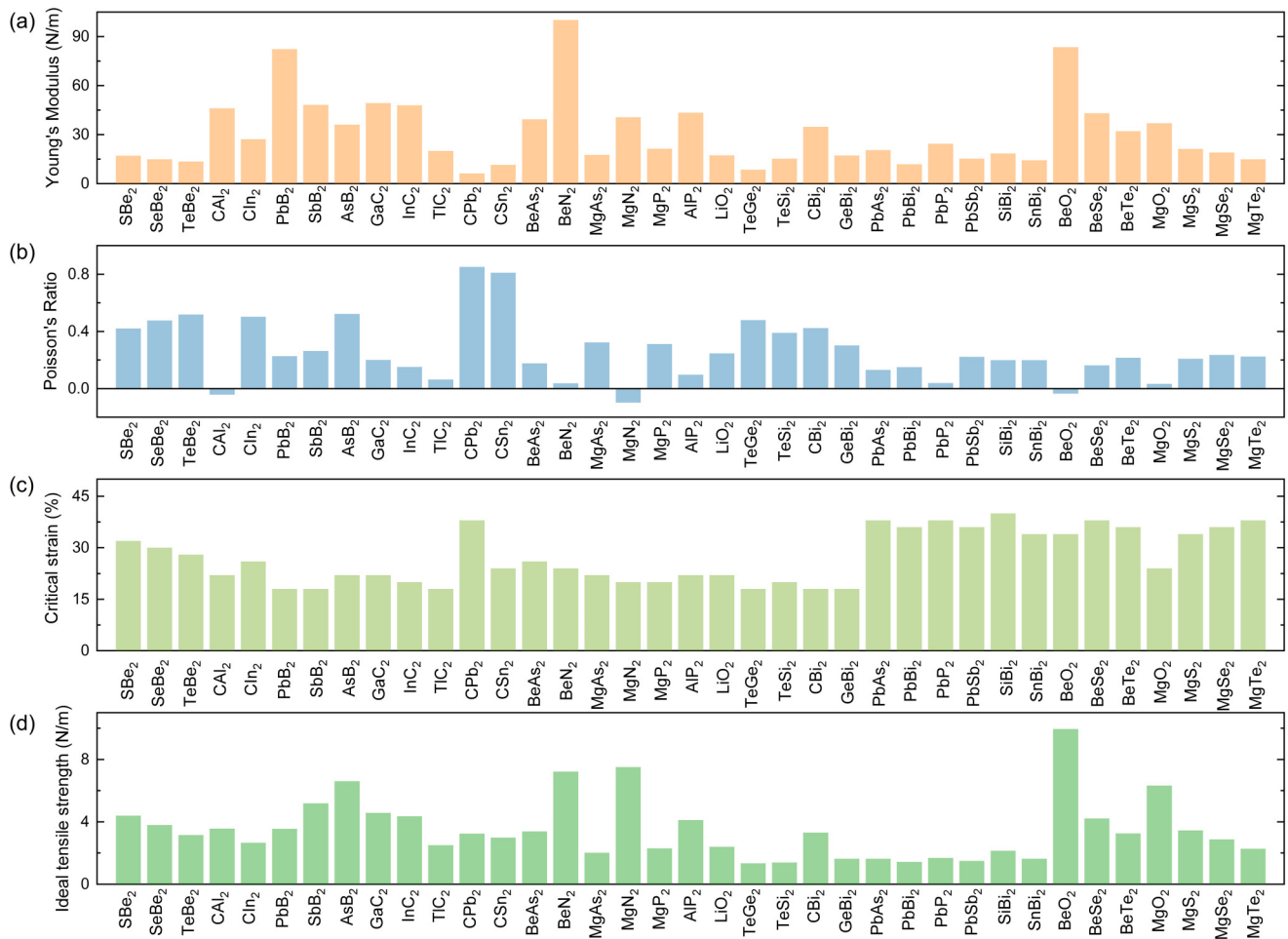


FIG. 5. Calculated in-plane mechanical properties of 37 2D $P\bar{4}2_1m$ XY_2 phases: (a) Young's modulus, (b) Poisson's ratios, (c) biaxial critical strain, and (d) ideal biaxial tensile strength.

tensile strengths of the newly predicted 37 pentagonal 2D $P\bar{4}2_1m$ XY_2 phases using first-principles calculations at the PBE level. The details of the computational method are provided in the SM.

The in-plane Young's modulus is a fundamental mechanical parameter reflecting the stiffness of a solid material and larger Young's modulus values indicate higher material stiffness. We calculate the in-plane Young's moduli along both the crystallographic a and b directions for these 37 2D $P\bar{4}2_1m$ XY_2 phases, as depicted in Fig. 5(a). The Young's moduli along the a and b axes are identical for all 2D phases, given the fourfold in-plane rotational symmetry of the $P\bar{4}2_1m$ space group (D_{2d} point group). Additionally, a comparative analysis shows that the Young's moduli of these 2D $P\bar{4}2_1m$ XY_2 phases generally range from 6 to 100 $N m^{-1}$, which is significantly lower than those of conventional 2D materials such as graphene ($\sim 340 N m^{-1}$) [84], h -BN ($\sim 290 N m^{-1}$) [85], and MoS_2 ($\sim 180 \pm 60 N m^{-1}$) [86,87]. Among these 37 phases, 2D $P\bar{4}2_1m$ PbB_2 , BeO_2 , and BeN_2 exhibit relatively higher in-plane Young's moduli of 82.38, 83.49, and 100.17 $N m^{-1}$, respectively, which can be attributed to strong B-B, O-O, and N-N covalent bonding within their structures. Moreover, the in-plane moduli of our proposed 2D $P\bar{4}2_1m$ XY_2 phases are also smaller than those of previously reported 2D $P\bar{4}2_1m$ XY_2

phases, i.e., BeN_2 (224 $N m^{-1}$ [88]), AlN_2 (115.70 $N m^{-1}$ [89]), CN_2 (324.87 $N m^{-1}$ [31]), PC_2 (175.22 $N m^{-1}$ [31]), and GeC_2 (126.04 $N m^{-1}$ [31]). The generally low in-plane Young's moduli across these 37 phases suggest promising potential for applications in flexible electronics, where moderate mechanical compliance is essential. Furthermore, anisotropic in-plane Young's moduli are observed in most of the 2D $P\bar{4}2_1m$ XY_2 phases, as illustrated in Figs. S42–S48. This anisotropy arises from directional variations in bonding strength and orientations of Y-X and X-X bonds within the 2D networks.

Poisson's ratio (ν) is another key mechanical descriptor that quantifies the extent to which a material contracts or expands laterally under longitudinal strain. Defined as the ratio of transverse strain to longitudinal strain, Poisson's ratio provides fundamental insight into the mechanical response of solids to external loads. The Poisson's ratios of these 37 2D $P\bar{4}2_1m$ XY_2 phases are presented in Fig. 5(b). Most of these phases exhibit positive and moderate in-plane Poisson's ratio values between 0 and 0.5, comparable to those observed in previously reported 2D $P\bar{4}2_1m$ XY_2 phases, CN_2 (0.02), CP_2 (0.35), CGa_2 (0.45), GeC_2 (0.05), and $CaAs_2$ (0.39) [31]. In addition, ultralow Poisson's ratios are identified in the 2D $P\bar{4}2_1m$ MgO_2 , BeO_2 , PbP_2 , and BeN_2 , with values of 0.03, 0.04, 0.04, and 0.04, respectively. Such small Poisson's ratios

along specific crystallographic directions suggest higher resistance to lateral deformation, which may be advantageous for applications such as strain-isolation layers or stretchable sensors. Conversely, large Poisson's ratios are found in 2D $P\bar{4}2_1m$ CPb₂ and CSn₂, with values of 0.85 and 0.81, respectively. These unusually high values can be attributed to highly anisotropic in-plane Young's modulus, as detailed in Fig. S44. For reference, in-plane Poisson's ratios greater than 0.5 have been also observed in other 2D materials, such as planar C₄ octagraphene (0.64) [90], P (0.93) [91], and α -silica (0.52) [92]. This comparison further highlights the diverse and tunable mechanical behavior in 2D $P\bar{4}2_1m$ XY₂ phases.

It is well established that most materials exhibit a positive Poisson's ratio, meaning they tend to expand (contract) in the direction perpendicular to an applied compressive (tensile) stress. Of particular interest is the identification of negative in-plane Poisson's ratio (NPR) behavior in several 2D $P\bar{4}2_1m$ XY₂ phases, specifically 2D $P\bar{4}2_1m$ CaI₂, MgN₂, and BeO₂, as shown in Fig. 5(b). These three materials display auxetic behavior, characterized by lateral expansion under uniaxial stretching along the in-plane *a* and *b* directions, with corresponding NPR values of -0.04 , -0.10 , and -0.04 , respectively. These values are comparable to previously reported NPR values in other 2D materials, such as 2D TiB₂ (-0.1) [93], borophene ($\nu_{12} = -0.04$ and $\nu_{21} = -0.02$) [94], and black phosphorene ($\nu_{32} = -0.03$) [91]. Additionally, NPR values were also predicted in previously reported 2D $P\bar{4}2_1m$ AlC₂ (-0.077) and PC₂ (-0.083) [31].

Subsequently, we also evaluate the ideal biaxial tensile strength of these 37 new 2D $P\bar{4}2_1m$ XY₂ phases by computing the stress as a function of biaxial tensile strain. In crystalline solids, the ideal tensile strength required to yield or fracture a perfect crystal reflects the intrinsic chemical bonding strength and elastic limit [95]. The stress-strain relationship of 2D $P\bar{4}2_1m$ SBe₂, taken as an example, is reported in Fig. S49. The maximum stress, representing the ideal tensile strength, reaches 4.39 N/m under a biaxial tensile strain of 32% (defined as the critical strain). The ideal biaxial tensile strength and corresponding critical strain values for all 37 2D $P\bar{4}2_1m$ XY₂ phases are depicted in Figs. 5(c) and 5(d) and the detailed data is presented in Table S7. As shown in Figs. 5(c) and 5(d), most 2D $P\bar{4}2_1m$ XY₂ phases exhibit critical strains exceeding 20%, with ideal tensile strengths ranging from 1.3 to 10 N/m. These strength values are notably lower than that of graphene (36.7 N/mm) [96]. This can be attributed to the relatively weak X-Y bonding in these compounds. The combination of relatively low in-plane Young's modulus, large critical strain, and moderate ideal tensile strength suggests that these 2D $P\bar{4}2_1m$ XY₂ phases possess promising mechanical properties suitable for flexible nanomechanical systems, as well as for applications in microelectronic and optoelectronic devices.

E. Piezoelectric property

In the noncentrosymmetric crystals, polarization changes can be induced by applied strain or stress and this phenomenon is described by the third-rank piezoelectric stress e_{ijk} and strain d_{ijk} tensors, which comprise both ionic and

electronic contributions [97,98]:

$$e_{ijk} = \frac{\partial P_i}{\partial \varepsilon_{jk}} = e_{ijk}^{\text{elec}} + e_{ijk}^{\text{ion}}, \quad (1)$$

$$d_{ijk} = \frac{\partial P_i}{\partial \sigma_{jk}} = d_{ijk}^{\text{elec}} + d_{ijk}^{\text{ion}}, \quad (2)$$

in which P_i , e_{jk} , and d_{jk} are the polarization vector, stress tensor, and strain tensor, respectively. Density functional perturbation theory, as implemented in the VASP package, is employed to calculate the relaxed-ion piezoelectric stress coefficients [99]. In the present work of 2D materials, only in-plane strain components using Voigt notation are considered and the d_{ij} can be derived by the following formula:

$$\begin{pmatrix} e_{11} & e_{12} & e_{16} \\ e_{21} & e_{22} & e_{26} \\ e_{61} & e_{62} & e_{36} \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{16} \\ d_{21} & d_{22} & d_{26} \\ d_{61} & d_{62} & d_{36} \end{pmatrix} \begin{pmatrix} C_{11} & C_{12} & C_{16} \\ C_{21} & C_{22} & C_{26} \\ C_{61} & C_{62} & C_{36} \end{pmatrix}. \quad (3)$$

Given the D_{2d} point group symmetry of the 2D pentagonal $P\bar{4}2_1m$ XY₂ phase, Eq. (3) can be further reduced as [100]

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & e_{36} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & d_{36} \end{pmatrix} \begin{pmatrix} C_{11} & C_{12} & 0 \\ C_{12} & C_{22} & 0 \\ 0 & 0 & C_{66} \end{pmatrix}. \quad (4)$$

This indicates that 2D pentagonal $P\bar{4}2_1m$ XY₂ structures exhibit only an out-of-plane piezoelectric response. The piezoelectric strain coefficient d_{36} quantifies the induced polarization per unit shear strain in the out-of-plane direction and is a key parameter for evaluating the performance of shear-mode piezoelectric devices based on 2D materials. According to Eq. (4), d_{36} is given by

$$d_{36} = e_{36}/C_{66}. \quad (5)$$

Subsequently, the out-of-plane piezoelectric properties of the newly predicted 2D $P\bar{4}2_1m$ XY₂ semiconductors are evaluated at the PBE level of theory. The calculated elastic constants C_{66} , piezoelectric stress coefficient e_{36} , and strain coefficient d_{36} are summarized in Table S8 and Fig. 6. As shown in Table S8, most of the 2D $P\bar{4}2_1m$ XY₂ semiconductors exhibit relatively small piezoelectric strain coefficient of d_{36} spanning the range of 0–5 pm/V, which can be attributed to their low piezoelectric stress tensor values e_{36} , typically less than 0.3×10^{-10} C/m.

Notably, five 2D $P\bar{4}2_1m$ XY₂ phases (SiBi₂, SnBi₂, GeBi₂, TeGe₂, and PbBi₂) exhibit significantly enhanced out-of-plane piezoelectric strain coefficients d_{36} , with values of 8.47, 22.62, 29.86, 17.96, and 59.81 pm/V, respectively, as shown in Fig. 6. Among these, 2D $P\bar{4}2_1m$ PbBi₂ shows the largest d_{36} . This is primarily due to the combination of a large piezoelectric stress coefficient e_{36} and a reduced shear elastic constant C_{66} . More precisely, the pronounced out-of-plane piezoelectric response of 2D $P\bar{4}2_1m$ PbBi₂ can be attributed to several intrinsic factors below. First, in the 2D $P\bar{4}2_1m$ PbBi₂, the comparable atomic polarizability between Pb and Bi renders the Pb–Bi bonds highly polarizable, which in turn enhances the polarization response under shear strain and thereby increases the e_{36} value. Second, the large atomic radii and high atomic masses of Pb and Bi contribute to a softer shear elastic constant C_{66} . Third, the stereochemically active lone pairs ($6s^2$) on both Bi

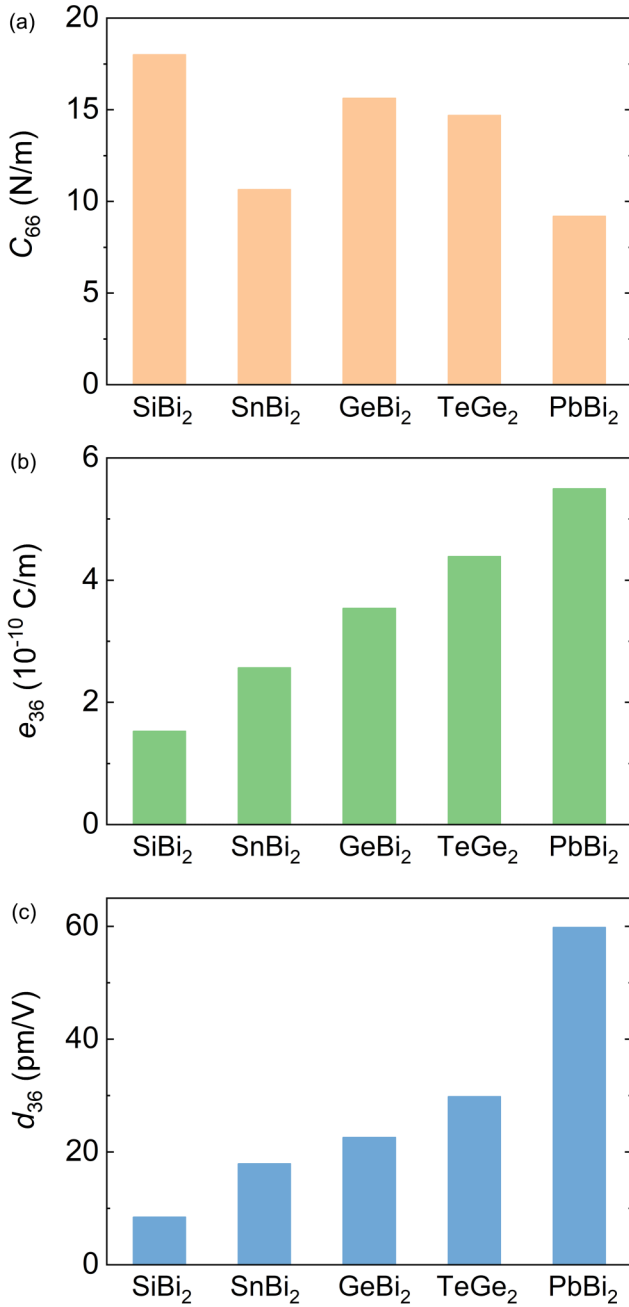


FIG. 6. Calculated (a) elastic constant C_{66} (N/m), (b) piezoelectric stress coefficient e_{36} (10^{-10} C/m), and (c) piezoelectric strain coefficient d_{36} (pm/V) of five 2D $P\bar{4}2_1m$ XY_2 semiconductors by the PBE functional.

and Pb atoms induce local structural distortions and facilitate spontaneous atomic displacements. Under shear deformation, these lone pairs can be easily reoriented or displaced, further amplifying the out-of-plane polarization and contributing substantially to a high d_{36} coefficient.

Importantly, the piezoelectric strain coefficients d_{36} of 2D $P\bar{4}2_1m$ GeBi₂, TeGe₂, SnBi₂, and PbBi₂ are higher than those of 2D pentagonal phases, such as penta-graphene (i.e., 2D $P\bar{4}2_1m$ CC₂, $d_{36} = -0.065$ pm/V) [100], penta-BCN ($P2_1$, $d_{36} = -0.076$ pm/V) [101], penta-CoSeS ($P2_1$, $d_{36} = -0.84$ pm/V) [28],

and CCB ($P\bar{4}2_1m$, $d_{36} = -0.418$ pm/V) [100], highlighting their potential for piezoelectric applications. The out-of-plane piezoelectric coefficient d_{36} plays a crucial role in determining the shear-mode electromechanical coupling in 2D materials, especially where in-plane piezoelectric effects are limited by symmetry constraints or atomic thickness. A high d_{36} value not only enables efficient shear-mode sensing, actuation, and energy harvesting in ultrathin and flexible 2D devices, but also provides unique opportunities for integrating 2D materials into next-generation wearable electronics, soft robotics, and tunable surface acoustic wave systems.

Finally, given the limited research focus on the piezoelectric properties of 2D $P\bar{4}2_1m$ XY_2 phases [100], in this work we also evaluate the out-of-plane piezoelectric responses of 26 previously reported 2D $P\bar{4}2_1m$ XY_2 semiconductors. The calculated values of C_{66} , e_{36} , and d_{36} are summarized in Table S9. Most of these phases exhibit relatively small d_{36} values below 1 pm/V. Our calculated result for 2D $P\bar{4}2_1m$ CC₂ (i.e., penta-graphene) aligns well with previous reports [100].

IV. CONCLUSIONS

In summary, 37 new 2D pentagonal $P\bar{4}2_1m$ XY_2 phases (X, Y are IA, IIA, IIIA, IVA, VA, VIA, and VIIA elements) are identified and their thermodynamic, mechanical, and dynamic stabilities are verified through first-principles high-throughput screening. These phases exhibit diverse electronic behaviors closely correlated with their valence electron counts per chemical formula: 10-VE (SBe₂, SeBe₂, TeBe₂, PbB₂, CaI₂, and ClIn₂), 12-VE (CPb₂, CSn₂, BeN₂, MgN₂, MgP₂, BeAs₂, and MgAs₂), and 14-VE (TeGe₂, TeSi₂, CBi₂, SiBi₂, GeBi₂, SnBi₂, PbP₂, PbAs₂, PbSb₂, PbBi₂, BeO₂, and BeSe₂; BeTe₂, MgO₂, MgS₂, MgSe₂, and MgTe₂) phases exhibit semiconducting behaviors, while 11-VE (SbB₂, AsB₂, GaC₂, InC₂, and TiC₂) and 13-VE (LiO₂ and AlP₂) phases present metallic or ferromagnetic semiconducting characteristics. We rationalize this behavior using a crystal-orbital approach. In particular, 2D $P\bar{4}2_1m$ SbB₂, AsB₂, and LiO₂ are ferromagnetic semiconductors with HSE06 band gaps of 1.06, 1.19, and 2.79 eV, respectively. Our calculations reveal that the 2D $P\bar{4}2_1m$ AlC₂ phase exhibits nonmagnetic metallic behavior, in contrast to the nonmagnetic semiconducting character reported in previous studies. In addition, 37 predicted phases display low in-plane Young's modulus ($\leq \sim 100$ N/m) and large critical strains (18%–40%), indicating excellent flexibility. Notably, large out-of-plane piezoelectric coefficients d_{36} of 18–60 pm/V are discovered in 2D $P\bar{4}2_1m$ SnBi₂, GeBi₂, TeGe₂, and PbBi₂, arising from its low shear modulus and strong polarization response. This work provides a comprehensive data set and fundamental understanding of 2D pentagonal $P\bar{4}2_1m$ structure prototypes, demonstrating their potential for applications in flexible electronics and shear-mode piezoelectric devices.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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