

Article

Coexistence of Large In-Plane and Out-of-Plane Piezoelectric Response in Group III–VI XMAY_2 ($\text{X} = \text{I}; \text{M} = \text{Ti, Zr}; \text{A} = \text{Al, Ga}; \text{Y} = \text{S, Se}$) Monolayers

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Abstract: Flexible materials with both in-plane and out-of-plane piezoelectric coefficients are needed in the development of advanced nanoelectromechanical systems. However, the challenge is to find flexible materials with the coexistence of in-plane and -out-of-plane piezoelectric responses, which hinders the progress of high-performance piezoelectric sensor development. In this paper, we propose the flexible XMAY_2 ($\text{X} = \text{I}; \text{M} = \text{Ti, Zr}; \text{A} = \text{Al, Ga}; \text{Y} = \text{S, Se}$) monolayers, which belong to the group III–VI XMAY_2 family, which showcase notable in-plane and out-of-plane piezoelectric coefficients. The in-plane (d_{11}) and out-of-plane (d_{31}) piezoelectric coefficients of the XMAY_2 monolayers vary from 5.20 to 7.04 pm/V and from -0.23 to 0.48 pm/V, respectively. The large in-plane and out-plane piezoelectric responses coexist ($d_{11} = 7.04$ pm/V; $d_{31} = 0.48$ pm/V) in the IZrGaS_2 monolayer, which is larger than other materials in the XMAY_2 family, such as SMoSiN_2 ($d_{11} = 2.51$; $d_{31} = 0.28$ pm/V). In addition, the mechanical and transport properties of XMAY_2 demonstrate its impressive flexibility characteristics as well as its efficient electrical conductivity. Due to inversion symmetry breaking in both atomic structure and charge distribution of XMAY_2 monolayers, the group III–VI XMAY_2 family exhibits a potentially rich scope of applications in the field of piezoelectricity.

Keywords: piezoelectric materials; 2D materials; first-principle calculation



Citation: Li, Z.; Zhou, Y.; Guo, X.; Peng, J.; Dong, H. Coexistence of Large In-Plane and Out-of-Plane Piezoelectric Response in Group III–VI XMAY_2 ($\text{X} = \text{I}; \text{M} = \text{Ti, Zr}; \text{A} = \text{Al, Ga}; \text{Y} = \text{S, Se}$) Monolayers. *Crystals* **2024**, *14*, 708. <https://doi.org/10.3390/cryst14080708>

Academic Editor: Yuui Yokota

Received: 13 July 2024

Revised: 26 July 2024

Accepted: 2 August 2024

Published: 5 August 2024



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1. Introduction

Flexible materials with large piezoelectric coefficients are commonly utilized in the advancement of advanced wearable nanosensors [1]. These high-performance piezoelectric materials efficiently transform mechanical energy into electrical energy. Consequently, they have found extensive application in nanomotors, actuation and energy harvesting sectors [2–4]. Since the discovery of piezoelectric properties in a MoS_2 monolayer [5], various two-dimensional materials have captured attention, such as graphene [6–8], phosphorene [9–11], germanene [12–14], transition metal dichalcogenides [15–17], hexagonal boron nitride [18,19], group IV monochalcogenides [20–23] and other 2D materials [24–28]. The experimentally measured in-plane piezoelectric coefficient e_{11} of the MoS_2 monolayer is in good agreement with the previous theoretical results, which shows the reliability of theoretical predictions [29]. Two-dimensional materials exhibit fine mechanical properties, with many flexible materials also demonstrating good piezoelectric properties. This suggests that mechanical properties play a crucial role in determining piezoelectric response. Two-dimensional materials possessing both in-plane and out-of-plane piezoelectric coefficients show promise for the development of energy harvesting and conversion devices. Despite this potential, the majority of 2D piezoelectric materials exhibit only in-plane piezoelectricity, restricting their usage to nanoscale devices with specific needs, like vertically integrated nanogenerator systems.

Therefore, 2D materials with out-of-plane piezoelectricity (as characterized by coefficient d_{31}) are being explored, especially the coexistence of out-of-plane and in-plane piezoelectricity [30]. To better explore piezoelectric properties, Janus structures are constructed which can enhance both the in-plane and out-of-plane polarization of materials by breaking mirror symmetry and inversion symmetry. Experimental synthesis of the Janus MoSSe monolayer has validated the effectiveness of this approach [31]. Additionally, two-dimensional materials with out-of-plane piezoelectric coefficients may exhibit a negative longitudinal piezoelectric (NLP) response, indicating promising prospects for enhancing piezoelectric sensor technology [32–35].

Recently, a new Janus XMAY_2 family material has been extensively researched for its properties [36–39]. Hong et al. synthesized a two-dimensional MoSi_2N_4 monolayer material using the chemical vapor deposition method and introduced the MA_2Y_4 family materials [40–42]. Sibator et al. [38] proposed, for the first time, asymmetric XMoSiN_2 ($\text{X} = \text{S, Se, Te}$) monolayers by replacing the Si-N layer on one side of MoSi_2N_4 with an X ($\text{X} = \text{S, Se, Te}$) layer belonging to the XMAY_2 family where letter X represents group VI element (S, Se), letter A represents group IV element (Si, Ge) and letter Y represents group V element (N, P, As). Liao et al. [43] reported the coexistence of in-plane (d_{11}) and out-of-plane (d_{31}) piezoelectric coefficients in XSSiN_2 monolayers, indicating that the XMAY_2 system may have excellent in-plane and out-of-plane piezoelectric properties.

In this paper, Janus XMAY_2 ($\text{X} = \text{I}; \text{M} = \text{Ti, Zr}; \text{A} = \text{Al, Ga}; \text{Y} = \text{S, Se}$) monolayers were proposed, which belong to the group III–VI XMAY_2 family. Using first-principles calculations, we observed that IZrGaS_2 monolayers exhibit the coexistence of the largest in-plane and out-of-plane piezoelectric coefficients among the XMAY_2 family materials. X, A and Y represent group VII elements (iodine), group III elements (Al, Ga) and group VI elements (S, Se) in the group III–VI XMAY_2 family, respectively. Compared to the previous XMAY_2 family materials, the modifications in X, A and Y make an improvement in the out-of-plane piezoelectric coefficients. Furthermore, the stability, electrical, mechanical and transport properties of the XMAY_2 monolayers were calculated and analyzed. The exceptional piezoelectric properties of XMAY_2 monolayers indicate promising potential in the field of piezoelectricity.

2. Methods

This study utilizes density functional theory (DFT) stimulation with the projected argument wave (PAW) method implemented in the VASP package [44,45]. The wave function is expanded using a plane wave with a cutoff energy [46] of 500 eV. The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) is employed for the exchange–correlation functional [47]. According to the intrinsic lattice feature of XMAY_2 ($\text{M} = \text{Ti, Zr}; \text{A} = \text{Al, Ga}; \text{Y} = \text{S, Se}$) monolayers, the Brillouin region is divided into a grid of k-points using a $16 \times 16 \times 1$ mesh, following the Monkhorst–Pack strategy. To ensure structural stability, the energy and force difference criteria of the plane wave are set at 10^{-8} eV and 0.01 eV/Å, respectively. Due to the thickness of the XAMY_2 monolayers being about 6 Å with five atomic layers, it is necessary to consider the weak van der Waals interactions. Here, the semi-empirical DFT-D3 method is adopted [48]. Additionally, a vacuum layer with a minimum thickness of 30 Å in the z-direction is included to prevent interactions between neighboring layers. Dynamic stability is verified by expanding the primitive cell into a supercell using Phonopy [49] and calculating the phonon spectrum with density functional perturbation theory (DFPT) [50,51]. Band structure calculations are performed using both PBE and HSE06 functionals [52]. Piezoelectric coefficients and elastic stiffness coefficients are calculated using DFPT and energy–strain methods [53], respectively.

3. Results and Discussions

3.1. Crystal Lattice and Stability

The optimized XMAY_2 ($X = \text{I}; M = \text{Ti, Zr}; A = \text{Al, Ga}; Y = \text{S, Se}$) monolayers are depicted in Figure 1, with the side view shown in Figure 1a and the top view in Figure 1b. The blue and yellow areas represent the primitive cell and rectangle cell, respectively. The XMAY_2 monolayer consists of four elements and five atomic layers, which belong to the $P3m1$ space group. The bond connection in the XMAY_2 monolayers follows the pattern of $Y-A-Y-M-X$. Table 1 summarizes the optimized lattice constants, thickness and bond lengths. Additionally, the bond angle θ ($^\circ$) of XMAY_2 monolayers is summarized in Table S1 and Figure S1.

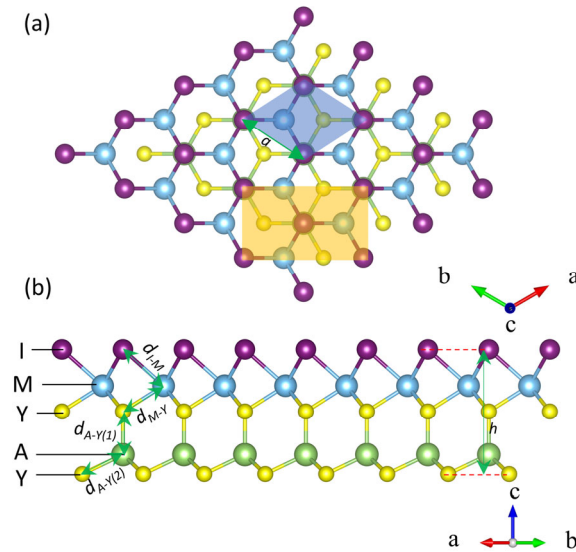


Figure 1. Top view (a) and side view (b) of the optimized structure of XMAY_2 monolayers. The primitive and orthogonal cells used are shown by the blue and yellow areas, respectively.

Table 1. Lattice constant a ($\text{\AA}$), bond length d ($\text{\AA}$), thickness h ($\text{\AA}$), cohesive energy E_{coh} and formation energy E_{form} of XMAY_2 monolayers.

Phase	a	h	d_{I-M}	d_{M-Y}	$d_{A-Y(1)}$	$d_{A-Y(2)}$	E_{coh}	E_{form}
ITiAlS ₂	3.64	6.32	2.82	2.50	2.20	2.32	−4.43	−0.97
ITiAlSe ₂	3.77	6.78	2.85	2.63	2.35	2.45	−3.95	−0.81
ITiGaS ₂	3.69	6.49	2.83	2.50	2.26	2.34	−3.98	−0.79
ITiGaSe ₂	3.79	6.84	2.86	2.62	2.41	2.47	−3.67	−0.69
IZrAlS ₂	3.70	6.57	2.93	2.61	2.20	2.33	−4.61	−1.09
IZrAlSe ₂	3.73	6.70	2.96	2.73	2.35	2.46	−4.31	−1.00
IZrGaS ₂	3.73	6.71	2.95	2.61	2.27	2.36	−4.27	−0.92
IZrGaSe ₂	3.84	7.06	2.97	2.72	2.42	2.48	−3.96	−0.82

In order to calculate the stability of XMAY_2 monolayers, the cohesive energy E_{coh} was calculated using the following formula:

$$E_{\text{coh}} = \frac{E_{\text{XMAY}_2} - E_X - E_M - E_A - 2E_Y}{N} \quad (1)$$

where E_{XMAY_2} is the total energy of XMAY_2 monolayers, E_X , E_M , E_A and E_Y are the energies of single X, M, A and Y atoms, respectively. N is the number of atoms in the primitive cell of XMAY_2 monolayers. The formation energy is calculated using the following formula:

$$E_{\text{coh}} = \frac{E_{\text{XMAY}_2} - E_X - E_M - E_A - 2E_Y}{N} \quad (2)$$

where E_{XMY_2} is the total energy of the XMY_2 monolayers and μ_X, μ_M, μ_A and μ_Y are the energies of X, M, A and Y in the bulk stable phase. The cohesive energy E_{coh} and the formation energy E_{form} value of XMY_2 monolayers are recorded in Table 1, respectively. The cohesive energy of XMY_2 monolayers is smaller than that of most previously reported two-dimensional monolayer materials, such as Al_2TeSeS monolayer (-2.89 eV per atom), Cu_2Si (-3.46 eV per atom), silene (-3.98 eV per atom) and germanene (-3.26 eV per atom) [54,55]. The negative values of formation energy and cohesive energy indicate that XMY_2 monolayers provide thermodynamic support for these materials compared to other materials in terms of energy.

Phonon spectrum calculations are performed to validate the dynamic stability of the XMY_2 monolayers. Figure 2 indicates the existence of a small virtual frequency near the Γ point, due to numerical error. These errors can be addressed using the Acoustic Summation Rule (ASR) and therefore can be ignored [56]. With five atoms in the XMY_2 monolayers, each phonon dispersion comprises 15 vibration branches, including 3 low-frequency acoustic branches and 12 high-frequency optical branches. Specifically, at the Γ point, the phonon mode of the XMY_2 monolayers can be decomposed into $G_{C3v} = 5A_1 + 5E$, where A_1/E represent the non-degenerate/doubly degenerate phonon modes at the Γ point, where correspond to out-of-plane optical (ZO) modes/in-plane transverse (TO) and longitudinal optical (LO) phonon modes [57]. The coexistence of acoustic and optical branches in the phonon spectrum validates the dynamic stability of the XMY_2 monolayers.

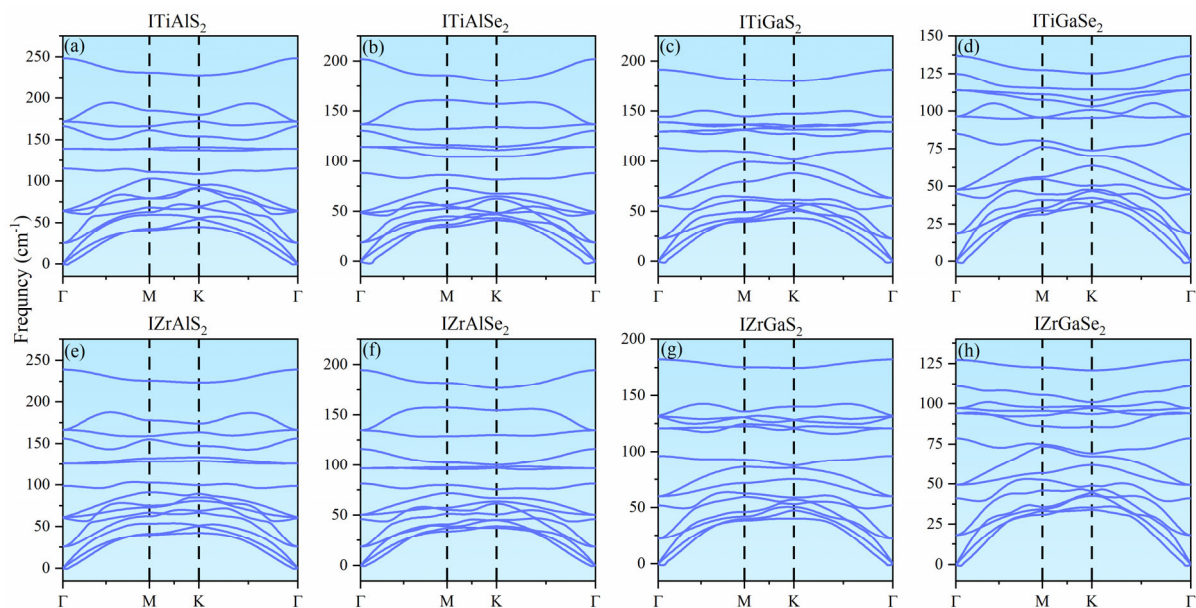


Figure 2. Phonon spectra of XMY_2 monolayers (a–h).

3.2. Piezoelectric Properties

The elastic stiffness coefficient C_{ij} is the crucial measure of a material's response to external stress and strain, reflecting its mechanical characteristics. The relaxed-ion [5] elastic stiffness coefficient is determined by the atom completely relaxed when the strain is applied, underscoring the electronic and ionic common contributions. Conversely, the clamped-ion [58] elastic stiffness coefficient is calculated by maintaining atomic positions after applying strain, highlighting the electronic contributions. Piezoelectricity is the interaction between external mechanical stress and intrinsic electrical polarization. The piezoelectric coefficients of clamped-ion represent the contribution of electronic parts, while relaxed-ion accounts for the combined effect of ionic and electronic parts.

Following on existing research, we calculate the in-plane elastic stiffness coefficient C_{ij} within the material as follows:

$$C_{ij} = \frac{1}{S_0} \frac{\partial E^2}{\partial \varepsilon_i \partial \varepsilon_j} \quad (3)$$

where ∂E , S_0 , $\partial \varepsilon_i$ and $\partial \varepsilon_j$ represent total energy, the area of the primitive cell and the strains along the x and y directions, respectively. The Young's modulus and Poisson's ratio of the XMay₂ monolayers can be calculated using the relaxed-ion elastic stiffness coefficient as follows [59]:

$$Y_{2D} = \frac{C_{11}^2 - C_{12}^2}{C_{11}}, \nu_{2D} = \frac{C_{12}}{C_{11}} \quad (4)$$

In the case of 2D materials, the relaxed-ion piezoelectric coefficient directly reflects the efficiency of electro-mechanical coupling. The piezoelectric stress coefficient e_{jk} and piezoelectric strain coefficient d_{ij} are essential coefficients for piezoelectric properties. According to the definition, the relaxed-ion piezoelectric stress coefficient is sum of electrons and ions. The piezoelectric strain coefficient d_{ij} can be calculated with the following formula:

$$e_{jk} = d_{ij} \cdot C_{jk} \quad (5)$$

The clamped-ion piezoelectric stress coefficient e_{11} is the polarization value contributed by the electrons, while the relaxed-ion piezoelectric stress coefficient e_{11} is the polarization value contributed by the electrons and ions. The piezoelectric strain coefficient d_{11} and d_{31} can be expressed as follows:

$$d_{11} = \frac{e_{11}}{C_{11} - C_{12}}, d_{31} = \frac{e_{31}}{C_{11} + C_{12}} \quad (6)$$

According to eq6, we can obtain the relaxed-ion and the clamped-ion piezoelectric strain coefficient d_{11} and d_{31} . Due to the symmetry of the XMay₂ monolayers $e_{11} = -e_{12}$ and $d_{11} = -d_{12}$. The calculation results are summarized in Table 2. For hexagonal 2D materials, the relaxed-ion elastic coefficients can better reflect the mechanical properties of the materials. The calculated elastic coefficients obey the Bonn–Huang stability criteria ($C_{11} - C_{12} > 0$ and $C_{66} > 0$).

Table 2. Elastic coefficient C_{11} and C_{12} (N/m), Young's modulus Y_{2D} (N/m), Poisson's ratio ν_{2D} , piezoelectric stress coefficients and piezoelectric strain coefficients of XMay₂ monolayers.

Phase	C_{11}	C_{12}	$C_{11} - C_{12}$	$C_{11} + C_{12}$	Y_{2D}	ν_{2D}	e_{11}	d_{11}	e_{31}	d_{31}
ITiAlS ₂	106.58	26.49	80.09	133.07	104.63	0.23	4.16	5.20	−0.03	−0.02
ITiAlSe ₂	89.56	22.77	66.79	112.33	85.64	0.25	3.97	5.95	−0.22	−0.19
ITiGaSe ₂	98.79	23.81	74.98	122.60	95.49	0.23	4.40	5.86	0.16	0.13
ITiGaSe ₂	79.42	18.50	60.92	97.92	80.00	0.24	4.17	6.84	−0.23	−0.23
IZrAlS ₂	96.71	26.92	69.79	123.63	98.44	0.21	3.73	5.35	0.33	0.26
IZrAlSe ₂	78.06	24.36	53.7	102.42	97.81	0.20	3.01	5.62	0.20	0.19
IZrGaSe ₂	81.57	26.72	54.85	108.29	86.59	0.21	3.86	7.04	0.52	0.48
IZrGaSe ₂	73.51	21.01	52.50	94.52	74.88	0.19	2.91	5.54	0.19	0.20

For XMay₂ monolayers, the C_{11} values range from 73.51 to 106.58 N/m, comparable to MoS₂ (130 N/m) [5] and graphene (336 N/m) [60]. The C_{11} value of the XMay₂ monolayers is equivalent to C_{22} , while C_{12} is approximately a quarter of C_{11} . As shown in Figure S3, the relationship between the Young's modulus and Poisson's ratio of XMay₂ monolayers exhibit isotropy. The Young's modulus of XMay₂ monolayers varies from 74.88 to 104.63 N/m, with ITiAlS₂ being the highest and IZrGaSe₂ being the lowest. The elastic constants of XMay₂ monolayers are closely linked to the bond length $d_{\text{Ti-S}} < d_{\text{Ti-Se}} < d_{\text{Zr-S}} < d_{\text{Zr-Se}}$. A shorter bond length results in a stronger influence between nearby atoms, making the materials show stiffness. Conversely, longer bond lengths lead to

more flexibility among atoms. The Young's modulus of the XMAY_2 monolayers is smaller than that of common two-dimensional materials, such as Janus MoSSe ($Y_{2D} = 113.61 \text{ N/m}$) monolayer, graphene ($Y_{2D} = 341 \text{ N/m}$) [61] and h-BN ($Y_{2D} = 275.9 \text{ N/m}$) [59]. XMAY_2 monolayers exhibit good flexibility, making them suitable for applications in flexible skin materials. Furthermore, the Poisson's ratio of the XMAY_2 monolayers ranges from 0.21 to 0.25, which is similar to the previously reported XMoSiP_2 (0.22–0.24) [62] monolayers with the same five-atom layers. Flexible mechanical properties indicate that the XMAY_2 monolayers may possess favorable piezoelectric properties and hold significant potential in the development of wearable flexible sensor devices.

The in-plane relaxed-ion piezoelectric strain coefficients d_{11} in 2D materials directly indicate the distortion-coupling ability of materials. Table 2 illustrates that the relaxed-ion in-plane piezoelectric strain coefficients d_{11} values range from 5.20 to 7.04 pm/V and the relaxed-ion out-of-plane piezoelectric strain coefficients d_{31} values range from -0.23 to 0.48 pm/V. The clamped-ion elastic coefficient and piezoelectric coefficients are summarized in Table S3. For the XMAY_2 monolayers, the clamped-ion and the relaxed-ion piezoelectric stress coefficient e_{11} values range from 431 to 562 pC/m and 291 to 440 pC/m, respectively. It is evident that the clamped-ion piezoelectric stress coefficients exceed the relaxed-ion piezoelectric stress coefficients for the same XMAY_2 monolayers. This difference is attributed to the competition between ionic and electronic polarization, resulting in a smaller piezoelectric stress coefficient e_{11} for the XMAY_2 monolayers. For a given M element, the values of e_{11} are related to the work function at the bottom, which is determined by the electrical properties of atoms A and Y. The larger the work function, the greater the values of e_{11} . Additionally, the low elastic coefficients C_{11} and C_{12} of the XMAY_2 monolayers contribute to its flexibility, ultimately leading to a larger piezoelectric coefficient for the XMAY_2 monolayers. In the XMAY_2 monolayers, the elastic stiffness coefficients ($C_{11} - C_{12}$) and ($C_{11} + C_{12}$) were analyzed, with values ranging from 52.50 to 80.09 N/m and from 92.52 to 133.07 N/m for $C_{11} - C_{12}$ and $C_{11} + C_{12}$, respectively. Due to the small elastic stiffness coefficients ($C_{11} - C_{12}$) and ($C_{11} + C_{12}$), as well as the large piezoelectric stress coefficient, large in-plane and expected out-of-plane piezoelectricity can be observed.

The piezoelectric stress coefficient e_{31} values of XMAY_2 monolayers range from -23 to 52 pC/m. Upon inspecting the absolute values, it is evident that, except for the ITiAlS_2 monolayer, all other XMAY_2 monolayers demonstrate large piezoelectric stress coefficients ($>20 \text{ pC/m}$). Notably, the IZrGaS_2 monolayer stands out, with a value as high as 52 pC/m, which contributes to its large out-of-plane piezoelectric coefficients within the group III-VI XMAY_2 family. In comparison to the IZrGaS_2 and IZrAlS_2 monolayers, both exhibit larger values of the piezoelectric stress coefficient e_{31} . However, due to a larger $d_{\text{S-Ga}}$ compared to $d_{\text{S-Al}}$, the elastic constants $C_{11} + C_{12}$ of IZrGaS_2 are smaller, ultimately leading to the piezoelectric strain coefficient d_{31} of IZrGaS_2 being twice that of IZrAlS_2 . Additionally, despite the relatively small piezoelectric stress coefficients of IZrGaSe_2 and IZrAlSe_2 monolayers, their elastic coefficients $C_{11} + C_{12}$ are also small, resulting in their out-of-plane piezoelectric coefficients (d_{31}) being comparable to those of IZrAlS_2 . This highlights the significant influence of mechanical properties on the piezoelectric properties of materials, with flexible materials showing promise as good piezoelectric materials.

Among them, the IZrGaS_2 monolayer exhibits the coexistence of large in-plane and out-of-plane piezoelectric coefficients at 7.03 pm/V and 0.48 pm/V, respectively. The values of d_{31} are similar to those of common two-dimensional materials like Janus HfSeTe ($d_{31} = 0.41 \text{ pm/V}$) and Janus group III monochalcogenides ($d_{31} = 0.07\text{--}0.46 \text{ pm/V}$) [63–65]. The large piezoelectric properties of the IZrGaS_2 monolayer are attributed to several factors: first, the large potential gradient indicates a large difference between the work function between the bottom and top, forming a large built-in electric field inside the materials which contributes to the large piezoelectric strain coefficients d_{11} and d_{31} . Furthermore, the IZrGaS_2 monolayer exhibits a smaller elastic coefficient, indicating that the material generates greater strain when subjected to the same external stress, resulting in a larger piezoelectric coefficient. A higher piezoelectric coefficient means that converting mechan-

ical energy into electrical energy promotes the application of piezoelectric materials in energy harvesting. Meanwhile, smaller elastic constants and larger piezoelectric strain coefficients also mean that when piezoelectric materials are used as pressure sensors, voltage will be generated, resulting in higher detection accuracy. At present, it is difficult for common piezoelectric materials to be suitable for use as flexible materials due to their brittleness. Therefore, piezoelectric materials with smaller elastic constants have a wider range of application scenarios. The IZrGaS₂ monolayer positions as a highly promising two-dimensional piezoelectric material with the coexistence of large in-plane and out-of-plane piezoelectric coefficients in the XMay₂ family.

3.3. Electronic Properties

To further analyze XMay₂ monolayers, the electronic properties are calculated. The band structure is calculated using PBE and HSE06 functionals, as shown in Figure 3. The bandgap energy values of XMay₂ monolayers range from 0.15 eV to 0.60 eV using the PBE functional. It is widely recognized that the PBE functional generally underestimates the bandgap, while the bandgap calculated by the HSE06 functional has acceptable accuracy. The bandgap energy calculated using the HSE06 functional range from 0.38 to 0.67 eV. The bandgap results calculated using both PBE and HSE06 functionals are summarized in Table 3. For the HSE06 functional, it was observed that the bandgaps of the ITiAlS₂, ITiAlSe₂, ITiGaS₂ and ITiGaSe₂ monolayers are direct bandgap semiconductors and the VBM and CBM of the ITiAlS₂, ITiAlSe₂, ITiGaS₂ and ITiGaSe₂ monolayers are located at K point. The IZrAlS₂, IZrAlSe₂, IZrGaS₂ and IZrGaSe₂ monolayers are indirect band gap semiconductors. The VBM of the IZrAlS₂, IZrGaS₂ and IZrGaSe₂ monolayers are located at M point, while the VBM of IZrAlSe₂ were at point Γ . The CBMs of the IZrAlS₂, IZrAlSe₂, IZrGaS₂ and IZrGaSe₂ monolayers are situated at K point. The projected band structure of XMay₂ monolayers is in Supplementary Materials Figures S4 and S5, using the HSE06 functional. The CBM and VBM of the ITiAlS₂, ITiAlSe₂, ITiGaS₂ and ITiGaSe₂ monolayers represent the d-orbital contribution of the Ti element. The CBM and VBM of the ITiAlS₂, ITiAlSe₂, ITiGaS₂ and ITiGaSe₂ monolayers represent the p-orbital contribution of the Al/Ga element and the d-orbital contribution of the Ti element, respectively. It is worth noting that the band gap of the stable XMay₂ monolayer exceeds 0.1 eV, which is the basis of its piezoelectric properties.

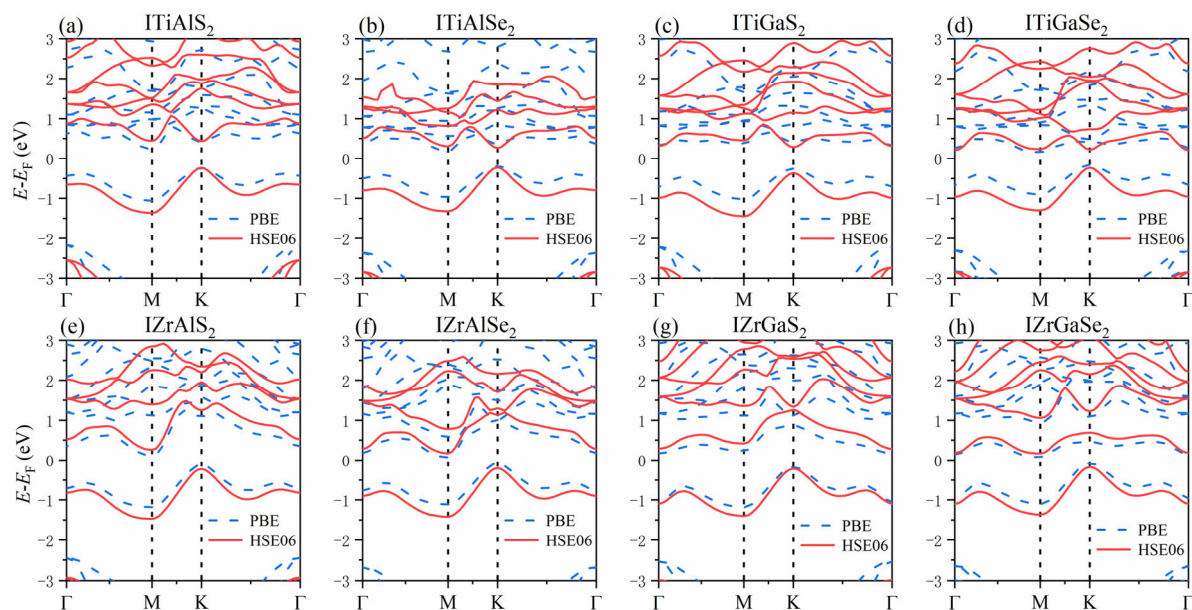


Figure 3. The band structures of the XMay₂ monolayers (a–h); the dashed blue and red lines are the results calculated using the PBE and HSE06 functionals, respectively.

Table 3. Band gap E_g with the PBE and HSE06 functionals, the fermi energy E_F , vacuum level difference $\Delta\Phi$ and top side Φ_2 and bottom side Φ_1 work function of XMAY_2 monolayers. All the units are eV.

	E_g^{PBE}	E_g^{HSE}	E_F	Φ_1	Φ_2	$\Delta\Phi$
ITiAlS ₂	0.48	0.67	−0.42	2.94	3.17	−0.23
ITiAlSe ₂	0.38	0.48	−0.70	2.52	2.99	−0.47
ITiGaS ₂	0.33	0.65	−0.80	3.07	2.86	0.21
ITiGaSe ₂	0.60	0.44	−1.03	2.70	2.63	0.07
IZrAlS ₂	0.23	0.48	−1.42	2.95	3.18	−0.23
IZrAlSe ₂	0.15	0.38	−0.42	2.59	2.99	−0.40
IZrGaS ₂	0.34	0.50	−0.34	3.13	2.82	0.31
IZrGaSe ₂	0.16	0.34	−0.74	2.78	2.66	0.12

Due to the difference in electronegativity between X, A and Y atoms in the Janus XMAY_2 monolayer, the bond lengths between atoms are different, resulting in the breaking of mirror symmetry and the generation of an internal electric field E_{in} . This internal electric field creates potential differences along the z-axis direction, necessitating a dipole correction when calculating the planar average potential of the two-dimensional Janus structure [66,67]. As shown in Figure 4, the work function of the XMAY_2 monolayers is denoted as $\Phi = E_{\text{vac}} - E_{\text{fermi}}$, where E_{vac} represents the vacuum energy level and E_{fermi} is the Fermi level. The work function and vacuum energy level difference between the top (Φ_2) and bottom (Φ_1) of the XMAY_2 monolayers are summarized in Table 3. A vacuum energy level difference between the top and bottom ranging from −0.47 to 0.31 eV was observed, establishing an intrinsic built-in electric field in the XMAY_2 monolayers that significantly affects the behavior of electrons and holes. ITiGaS₂, ITiGaSe₂, IZrGaS₂ and ITiGaSe₂ exhibit that the top side potential is higher than the bottom side, with the electric field direction from top to bottom promoting electron (hole) transition from the Y (X) layer to the X (Y) layer. Conversely, ITiAlS₂, ITiAlSe₂, IZrAlS₂ and ITiAlSe₂ exhibit that the bottom side potential is higher than the top side, with the electric field direction moving from the bottom to the top, facilitating electron (hole) transition from the X (Y) layer to the Y (X) layer. The highest built-in electric field E_{in} of the IZrGaS₂ monolayer is 0.31 eV, suggesting a possible correlation between the out-of-plane piezoelectric coefficient and the built-in electric field. Furthermore, charge density difference calculation was performed and analyzed using Bader Charge analysis [66]. (Supplementary Materials Table S2 and Figure S2). Both X and Y atoms acquire electrons, while M and A atoms lose electrons. The out-of-plane polarization is related to the values of electrons lost by the A atom and acquired by the Y atom.

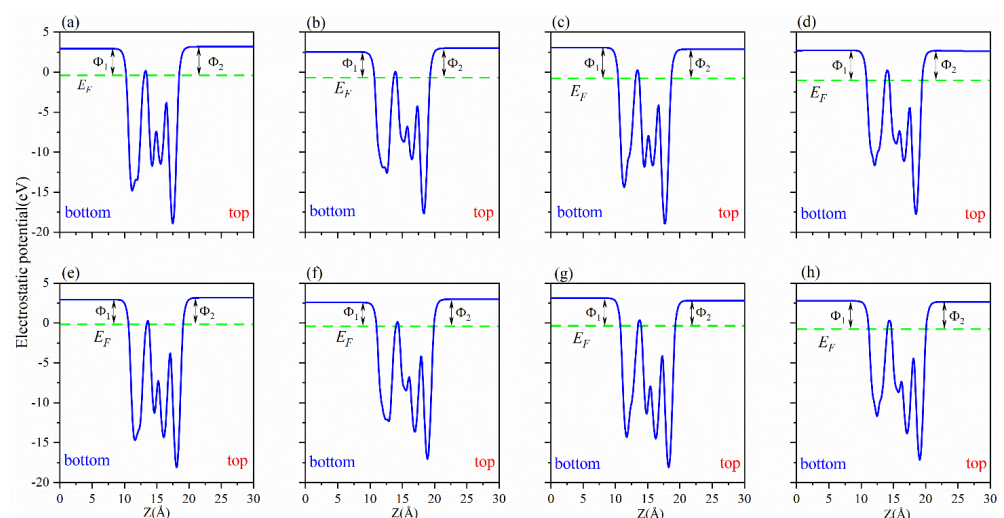


Figure 4. Plane-averaged electrostatic potential of the XMAY_2 monolayers (a–h).

3.4. Transport Properties

The carrier mobility, especially electronic, is vital for comprehending the transport properties of materials. The carrier mobilities of the XMAY₂ monolayers were analyzed using the deformation potential (DP) theory [68]. The carrier mobility of two-dimensional materials was calculated as follows:

$$\mu_{2D} = \frac{e\hbar^3 C_{2D}}{\kappa_B T m^* \bar{m} E_d^2} \quad (7)$$

where $e, \hbar^3, C_{2D}, \kappa_B, T, m^*, \bar{m}$ and E_d represent the electron charge, Planck constant, elastic modulus, Boltzmann constant, temperature, effective mass, average effective mass ($\bar{m} = \sqrt{m_x^* m_y^*}$) and deformation potential constant, respectively. The effective mass m^* of electrons and holes in two-dimensional materials are important parameter for calculating carrier mobility, which can be obtained through the parabolic functions of CBM and VBM, respectively.

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2} \quad (8)$$

where $E(k)$ is the energy corresponding to the wave vector k at the edge CBM and VBM positions. Therefore, the size of the effective mass m^* is related to the slope near CBM and VBM. A uniaxial strain of $-0.4\% \sim 0.4\%$ is applied to the x and y directions of the rectangle lattice of the XMAY₂ monolayers with an interval of 0.002 to fit the elastic modulus C_{2D} and the deformation potential constant E_d is expressed as follows, respectively.

$$C_{2D} = \frac{1}{S_0} \frac{\partial^2 E}{\partial \varepsilon^2}, E_d = \frac{\Delta E_{edge}}{\varepsilon} \quad (9)$$

where E is the total energy, S_0 is the area of the optimized unit cell, ε indicates the uniaxial strain along the x and y transport directions and ΔE_{edge} is the energy change in band edge of electrons and holes. From the calculated m^*, C_{2D} and E_d , the carrier mobility μ_{2D} of electrons and holes, can be calculated using Equation (7).

Materials with high electronic carrier mobility are believed to be applied for application in nanoelectronics devices. As shown in Table 4, the values of the elastic modulus C_{2D} are almost the same in the x and y directions and independent of the direction of uniaxial strain applied, which is attributed to the isotropy of the mechanical properties of the XMAY₂ monolayers. The deformation potential constant of electrons in the XMAY₂ monolayers is approximated in both the x and y directions and the effective mass of electrons shows differences in the x and y directions. Consequently, there is a notable difference in carrier mobility between electrons in the x and y directions, with higher mobility observed in the y direction. This is consistent with the lower effective mass of the structure along the y direction compared with the x direction.

Specifically, the high electronic carrier mobilities of ITiAlS₂ and ITiAlSe₂ in the y direction are 9546.23 and 9889.53 cm² s⁻¹ V⁻¹, respectively. Additionally, the carrier mobilities of the IZrAlS₂ and IZrAlSe₂ monolayers in the y -direction are 4364.81 and 5728.33 cm² s⁻¹ V⁻¹, respectively. Notably, the carrier mobility of the XMAY₂ monolayers surpasses that of common two-dimensional materials by one or two orders of magnitude, such as MoS₂ (~ 200 cm² s⁻¹ V⁻¹) [69] and GeP₃ (~ 190 cm² s⁻¹ V⁻¹) [17]. The electronic carrier mobility of ITiAlS₂ and ITiAlSe₂ is comparable to the newly discovered five-atom layers structures (Al₂STeSe $\sim 10,536$ cm² s⁻¹ V⁻¹ and STiGeAs₂ ~ 8175.66 cm² s⁻¹ V⁻¹) [36,54]. The high electronic carrier mobility observed in XMAY₂ monolayers, including ITiAlS₂, ITiAlSe₂, IZrAlS₂, IZrAlSe₂ and IZrGaSe₂, makes them promising for application in the development of electronic devices.

Table 4. The carrier effective mass m^* (m_0), elastic modulus C_{2D} ($N\ m^{-1}$), deformation potential constant E_d (eV) and carrier mobility μ_{2D} ($cm^2\ V^{-1}s^{-1}$) along the transport x and y directions for the $XMAY_2$ monolayers. m_0 is the mass of a free electron.

Phase	Type	m_x	m_y	C_{2Dx}	C_{2Dy}	E_{dx}	E_{dy}	μ_x	μ_y
ITiAlS ₂	Electron	0.99	0.24	108.5	107.22	9.42	1.43	53.97	9546.23
	Hole	0.51	0.52	108.5	107.22	5.07	5.30	331.77	313.24
ITiAlSe ₂	Electron	1.17	0.22	90.07	90.30	8.49	1.32	44.84	9889.53
	Hole	0.50	0.51	90.07	90.30	5.12	5.37	284.89	263.48
ITiGaS ₂	Electron	1.03	0.41	98.42	98.25	8.11	8.08	47.61	120.30
	Hole	0.60	0.63	98.42	98.25	5.69	5.88	166.87	164.36
ITiGaSe ₂	Electron	2.92	1.90	87.07	87.26	6.87	1.14	8.78	207.93
	Hole	0.60	0.60	87.07	87.26	5.03	5.29	204.05	184.08
IZrAlS ₂	Electron	1.06	0.22	102.42	102.52	9.21	2.17	50.24	4364.81
	Hole	0.37	0.40	102.42	102.52	4.93	5.24	583.83	558.15
IZrAlSe ₂	Electron	1.32	0.19	85.96	86.64	9.65	1.84	29.74	5728.33
	Hole	0.35	0.37	85.96	86.64	4.94	4.98	567.92	586.13
IZrGaS ₂	Electron	1.32	0.31	92.23	91.24	4.92	4.98	46.75	45.49
	Hole	0.41	0.45	92.23	91.24	5.76	5.85	303.03	325.94
IZrGaSe ₂	Electron	2.44	1.78	75.67	75.24	6.39	1.45	45.49	46.79
	Hole	0.35	0.42	75.67	75.24	5.00	4.80	7.76	1241.03

4. Conclusions

In summary, we systematically studied the stability and the electrical properties of 2D asymmetric $XMAY_2$ ($X = I$; $M = Ti, Zr$; $A = Ga, In$; $Y = S, Se$) monolayers. The cohesive energy, formation energy and phonon spectrum indicate that these structures are both thermodynamically and dynamically stable. All the $XMAY_2$ monolayers demonstrate flexible mechanical properties, with Young's modulus values ranging from 73.51 to 106.58 N/m. The in-plane (d_{11}) and out-of-plane (d_{31}) piezoelectric coefficients of $XMAY_2$ monolayers range from 5.20 to 7.04 pm/V and from -0.23 to 0.48 pm/V, respectively. The coexistence of in-plane and out-of-plane piezoelectric properties in these systems may be attributed to differences in atomic electronegativity and symmetry breaking. Additionally, the band structure of $XMAY_2$ monolayers is calculated using the HSE06 function, with bandgap values ranging from 0.34 to 0.67. ITiAlS₂, ITiAlSe₂, ITiGaS₂ and ITiGaSe₂ are direct bandgap semiconductors, while the others are indirect bandgap semiconductors. Furthermore, the $XMAY_2$ monolayers showcase remarkable carrier mobility, particularly with the ITiAlS₂ and ITiAlSe₂ monolayers having high electronic carrier mobility (9546.23 and 9889.53 $cm^2\ s^{-1}\ V^{-1}$). This study provides valuable insights into the potential applications of the $XMAY_2$ monolayers in the nanopiezoelectric field of devices and sensors.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst14080708/s1>, Figure S1: Side view of $XMAY_2$ monolayers. Figure S2: Top and side views of charge density difference for $XMAY_2$ monolayers (a–h). The red number are the results of Bader analysis. Figure S3: Young's modulus (N/m) (a) and Poisson's ratio (b) of $XMAY_2$ monolayers. Figure S4: The projected band structure of ITiAlS₂ (a), ITiAlSe₂ (b), ITiGaS₂ (c) and ITiGaSe₂ (d) monolayers. The blue dots represent the d-orbital contribution of Ti element. Figure S5: The projected band structure of IZrAlS₂ (a), IZrAlSe₂ (b), IZrGaS₂ (c) and IZrGaSe₂ (d) monolayers. The blue dots and orange dots represent the d-orbital contribution of Ti element and the p-orbital contribution of Al/Ga element, respectively; Table S1: The bond angle θ ($^\circ$) of $XMAY_2$ monolayers. Table S2: The results of Bader charge analysis for the charge transfer of $XMAY_2$ monolayers. A negative (positive) value indicates that the mentioned atom loses (gains) electrons. Table S3. Elastic coefficient, piezoelectric stress coefficients and piezoelectric strain coefficients of clamped-ion $XMAY_2$ monolayers.

Author Contributions: Conceptualization, Z.L.; data curation, Z.L. and Y.Z.; formal analysis, H.D.; funding acquisition, X.G.; investigation, Z.L. and Y.Z.; methodology, J.P.; project administration, H.D.;

software, Z.L. and X.G.; supervision, H.D.; writing—original draft, Z.L.; writing—review and editing, Z.L., J.P. and H.D. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the National Natural Science Foundation of China (Grants No. 11604056 and 11804057).

Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Materials, further inquiries can be directed to the corresponding author.

Acknowledgments: We thank the Center of Campus Network & Modern Educational Technology, Guangdong University of Technology, Guangdong, China for providing computational resources and technical support for this work.

Conflicts of Interest: The authors declare no conflict of interest.

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