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1. Introduction

Second harmonic generation (SHG) and piezoelectric properties caused by noncentrosymmetry in two-dimensional (2D) atomthick materials are sparking great interest. For instance, 2D MoS₂,^{1,2} GaSe,^{3,4} SiC,⁵ BN⁶ and GeC⁷ nanosheets display fascinating prospects in ultrathin SHG devices. However, these 2D materials only exhibit in-plane SHG properties as they embody out-of-plane centrosymmetric characters, i.e. out-of-plane SHG has not been discovered in these 2D materials. On the other hand, monolayer BN,8 MoS2,9 GaSe,10 GaSSe,11 buckled hexagonal compounds¹² and doped graphene,¹³ have a wide range of applications including in mechanical stress sensors, actuators and energy harvesting devices¹⁴ since they are piezoelectric. Even though a recent calculation has found strong out-of-plane piezoelectricity in multilayer MoSTe15 and a recent experiment has shown that out-of-plane piezoelectricity occurs in multilayer (10 nm-thick) α-In₂Se₃ flakes,¹⁶ the obtained out-of-plane

Peculiar electronic, strong in-plane and out-ofplane second harmonic generation and piezoelectric properties of atom-thick α -M₂X₃ (M = Ga, In; X = S, Se): role of spontaneous electric dipole orientations[†]

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Second harmonic generation (SHG) and piezoelectric properties of two-dimensional (2D) materials are sparking great interest. However, out-of-plane SHG in 2D materials has been rarely reported; the theoretical out-of-plane piezoelectric response in atom-thick 2D materials is very limited at the present stage. α -M₂X₃ monolayers exhibit out-of-plane spontaneous polarizations, promising out-of-plane SHG and piezoelectric properties of single- and few-layer α -M₂X₃. Results indicate the bandgaps of α -M₂X₃ monolayers are in the visible range, and become much narrower as the layer number goes up. Furthermore, the narrower bandgaps are broadened by more than 1.00 eV by switching the electric dipole orientation in few-layer α -M₂X₃ monolayers exhibit superior in-plane and out-of-plane SHG properties; in particular, their out-of-plane SHG coefficients are comparable with those of GaAs crystals. Furthermore, the out-of-plane SHG coefficients can be effectively tuned by switching the electric dipole orientation in α -M₂X₃ few-layers. α -M₂X₃ monolayers exhibit superior in-plane and considerable out-of-plane piezoelectricity, and the latter is significantly enhanced in bilayer α -M₂X₃ because of the built-in electric field originating from the parallel electric dipoles. Our work will stimulate research on the ultrathin 2D photo detection, SHG and piezoelectric devices.

piezoelectricity in atom-thick 2D materials such as monolayers¹¹⁻¹³ and bilayers is very limited. This makes it impossible to fabricate effective ultrathin 2D piezoelectric devices allowing out-of-plane mechanical–electrical energy conversions.

On the other hand, 2D nanosheets exfoliated from α - and β -In₂Se₃ bulk crystals are attracting great attention in the aspects of the thermal conductivity, phase transformation,17,18 photoresponsibility,19,20 sensitivity,21 dielectric22 and optical properties.²³ The electric field perpendicular to α - and β -In₂Se₃ monolayers induce a semiconductor to metal transition.24 Remarkably, the class of α-M2X3 ferroelectric monolayers exhibit in-plane and out-of-plane reversible spontaneous polarizations,25 promising in-plane and out-of-plane SHG and piezoelectric responses. Indeed, out-of-plane SHG has been recently discovered in monolayer α -In₂Se₃; however the features and magnitude of the SHG coefficients are still unknown.16 Moreover, monolayer multiferroics exhibit very small out-ofplane SHG coefficients $\chi^{(2)}_{zzy}$ and $\chi^{(2)}_{zyz}$.²⁶ This simulates us to explore the SHG and piezoelectricity of α -M₂X₃ monolayers using first-principles calculations, expecting to find strong outof-plane SHG and piezoelectricity.

Experiments indicate that the physical properties of In₂Se₃ multilayer nanosheets, such as optical bandgap²³ and thermal

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conductivity,¹⁷ show a strong layer-dependent behavior. These remind us to study the correlation between the layer thickness and the electronic, piezoelectric and SHG properties of atomicthick M_2X_3 nanosheets. It should be noted that the nanosheet in our theoretical calculations is much thinner than that in previous experiments.^{17,23} Moreover, the van der Waals heterostructure of α -In₂Se₃/WSe₂ shows a significant bandgap reduction when switching the electric dipole orientation of the In₂Se₃ layer. In essence, switching the electric orientation is changing stacking sequences. It has been shown SHG of few-layer GaSe nanosheets²⁷ and piezoelectricity of multilayer MoSTe¹⁵ can be effectively tuned by using various stacking sequences. Therefore, it is meaningful to explore how the electric dipole orientation affects the electronic, piezoelectric and SHG properties of few-layer M₂X₃.

2. Calculation models and details

Single- and few-layer β -M₂X₃ nanosheets are centrosymmetric, their piezoelectricity and SHG vanish. We thereby study the electronic, piezoelectric and SHG properties of monolayer α -M₂X₃ (M = Ga, In; X = S, Se), and their top and side views are displayed in Fig. 1. To study the layer-dependent behavior, the bilayer and trilayer exfoliated from α -Ga₂S₃ and α -In₂Se₃ bulk crystals are considered, which are respectively named as AA and AAA stacking. Furthermore, to investigate the effect of the electric dipole orientation, bilayer AB is achieved by switching the electric dipole orientation of the bottom layer in AA, while trilayer ABA is attained by switching the electric dipole orientation of the middle layer in AAA.

All calculations are on the basis of the density functional theory (DFT) using the projector-augmented wave (PAW)²⁸ method as implemented in the Vienna Ab initio Simulation Package (VASP).²⁹⁻³² The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE)³³ with van der Waals (vdW) correction proposed by Crimme (DFT-D2)³⁴ is employed. The single electron wave functions are expanded with a large wave cutoff energy of 500 eV. To minimize the periodic interaction along the z axis, the vacuum spacing between adjacent nanosheets is set to be at least 20 Å. A gammacentered k-point grid of $11 \times 11 \times 1$ is used to optimize geometry structures, and the convergence criteria for electronic and ionic relaxations are respectively set as 10^{-7} and 10^{-3} eV Å⁻¹. A *k*-point grid of $31 \times 31 \times 1$ is used to calculate piezoelectric coefficients of monolayers and few-layers. The more dense k-point grid of $60 \times 60 \times 1$ is used to obtain SHG coefficients of monolayers, while the *k*-point of $45 \times 45 \times 1$ is applied for few-layers.

3. Results and discussions

3.1. Structural properties

As shown in Fig. 1, α -M₂X₃ monolayers are five atoms thick, with atoms arranged in the sequence of X–M–X–M–X in the direction perpendicular to the layers. Table 1 summarizes the calculated in-plane constant *a* and effective thickness *h* of α -M₂X₃ monolayers. As the α -M₂X₃ bulk crystal contains three basic layers, the



Fig. 1 Schematics of top and side views of monolayer α -M₂X₃. The green atoms denote M (M = Ga, In) atoms, while the blue atoms denote X (X = S, Se) atoms. This figure represents bilayer AB is achieved by switching the electric dipole orientation of the bottom α -M₂X₃ layer in bilayer AA, and trilayer ABA is obtained by switching the electric dipole orientation of the middle α -M₂X₃ layer in trilayer AAA.

theoretical *h* of α -M₂X₃ monolayers is simply taken as 1/3 of the lattice constant *c* of optimized bulk crystals. The calculated *h* are larger than that of monolayer MX₂ (M = Mo, W; X = S, Se)³⁵ and GaX (X = S, Se, Te),²⁷ indicating a stronger SHG intensity in α -M₂X₃ monolayers than that in MoX₂ and GaX monolayers as the SHG intensity shows a quadratic dependence on the thickness, according to the dipole theory.⁴ It is very convenient to identify layer numbers of α -M₂X₃ nanosheets using the effective thickness value in further experiments, which will accelerate explorations of their properties.

Similar to previous calculations,³⁶ the formation energies of single- and few-layer α -M₂X₃ nanosheets are defined as $E_{\rm f} = E/N - E_{\rm ref}/N_{\rm ref}$, where *E* and $E_{\rm ref}$ are respectively the energies of nanosheets and corresponding bulk crystals. *N* and $N_{\rm ref}$ are the numbers of atoms in the respective unit cells. The calculated formation energies of monolayer α -M₂X₃, few-layer α -Ga₂S₃ and α -In₂Se₃ are shown in Fig. 2. The formation energies of α -M₂X₃ monolayers are comparable or even smaller than that of monolayer MoS₂. The formation energies of monolayer, bilayer

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Table 1 Calculated in-plane constants *a* (Å), effective thicknesses *h* (Å), PBE bandgaps E_g^{PBE} (eV), HSE06 bandgaps E_g^{HSE06} (eV), minimum direct energy gaps E_{min}^{HSE06} (eV) and SHG coefficients $\chi^{(2)}(0)$ (pm V⁻¹) of monolayer α -M₂X₃ (M = Ga, In; X = S, Se), few-layer α -Ga₂S₃ and α -In₂Se₃

	а	h	$E_{ m g}^{ m PBE}$	$E_{ m g}^{ m HSE06}$	E_{\min}^{HSE06}	$\chi^{(2)}_{xxy}(0)$	$\chi^{(2)}_{zxx}(0)$	$\chi^{(2)}_{ m zzz}(0)$
ML	3.59	8.94	1.79(I)	2.95(I)	3.25(G)	25.4	23.8	162.6
AA	3.59	17.88	0.65(I)	1.80(I)	2.05(G)	23.0	27.4	184.2
AB	3.59	17.88	1.64(I)	2.80(I)	3.04(G)	25.0	-0.3	0.8
ABA	3.59	26.82	1.52(I)	2.64(I)	2.81(G)	24.2	6.4	47.6
ML	3.77	9.40	1.06(I)	2.04(I)	2.30(G)	34.6	26.2	208.0
ML	3.83	9.18	1.29(I)	2.30(I)	2.36(G)	30.6	36.6	207.6
ML	3.99	9.68	0.88(I)	1.80(I)	1.83(G)	42.2	41.8	252.6
AB	3.99	19.36	0.57(I)	1.45(I)	1.46(G)	44.0	-1.80	-0.02
ABA	4.00	29.04	0.45(I)	1.25(I)	1.26(G)	48.2	8.2	61.4
	ML AA AB ABA ML ML AB ABA	a ML 3.59 AA 3.59 AB 3.59 ABA 3.59 ML 3.77 ML 3.83 ML 3.99 AB 3.99 AB 3.99 ABA 4.00	a h ML 3.59 8.94 AA 3.59 17.88 AB 3.59 17.88 ABA 3.59 26.82 ML 3.77 9.40 ML 3.83 9.18 ML 3.99 9.68 AB 3.99 19.36 ABA 4.00 29.04	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	ah E_g E_g ML 3.59 8.94 $1.79(I)$ $2.95(I)$ AA 3.59 17.88 $0.65(I)$ $1.80(I)$ AB 3.59 17.88 $1.64(I)$ $2.80(I)$ ABA 3.59 26.82 $1.52(I)$ $2.64(I)$ ML 3.77 9.40 $1.06(I)$ $2.04(I)$ ML 3.83 9.18 $1.29(I)$ $2.30(I)$ ML 3.99 9.68 $0.88(I)$ $1.80(I)$ AB 3.99 19.36 $0.57(I)$ $1.45(I)$ ABA 4.00 29.04 $0.45(I)$ $1.25(I)$	ah E_{g} E_{g} E_{min} ML 3.59 8.94 $1.79(I)$ $2.95(I)$ $3.25(G)$ AA 3.59 17.88 $0.65(I)$ $1.80(I)$ $2.05(G)$ AB 3.59 17.88 $1.64(I)$ $2.80(I)$ $3.04(G)$ ABA 3.59 26.82 $1.52(I)$ $2.64(I)$ $2.81(G)$ ML 3.77 9.40 $1.06(I)$ $2.04(I)$ $2.30(G)$ ML 3.83 9.18 $1.29(I)$ $2.30(I)$ $2.36(G)$ ML 3.99 9.68 $0.88(I)$ $1.80(I)$ $1.83(G)$ AB 3.99 19.36 $0.57(I)$ $1.45(I)$ $1.46(G)$ ABA 4.00 29.04 $0.45(I)$ $1.25(I)$ $1.26(G)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	a h E_g E_g E_{min} $\chi_{xxy}(0)$ $\chi_{zxx}(0)$ ML 3.59 8.94 $1.79(I)$ $2.95(I)$ $3.25(G)$ 25.4 23.8 AA 3.59 17.88 $0.65(I)$ $1.80(I)$ $2.05(G)$ 23.0 27.4 AB 3.59 17.88 $1.64(I)$ $2.80(I)$ $3.04(G)$ 25.0 -0.3 ABA 3.59 26.82 $1.52(I)$ $2.64(I)$ $2.81(G)$ 24.2 6.4 ML 3.77 9.40 $1.06(I)$ $2.04(I)$ $2.30(G)$ 34.6 26.2 ML 3.83 9.18 $1.29(I)$ $2.30(I)$ $2.36(G)$ 30.6 36.6 ML 3.99 9.68 $0.88(I)$ $1.80(I)$ $1.83(G)$ 42.2 41.8 AB 3.99 19.36 $0.57(I)$ $1.45(I)$ $1.46(G)$ 44.0 -1.80 ABA 4.00 29.04 $0.45(I)$ $1.25(I)$ $1.26(G)$ 48.2 8.2

AA, and trilayer AAA α -Ga₂S₃ (α -In₂Se₃) decrease as their layer numbers increase, suggesting it is more likely to successfully obtain α -Ga₂S₃ (α -In₂Se₃) nanosheets with larger layer numbers. Indeed, trilayer AAA α -In₂Se₃, *i.e.* 3.1 nm-thick α -In₂Se₃ nanosheets have been synthesized using mechanical exfoliation.²³ Moreover, the formation energy of α -Ga₂S₃ nanosheets is to some extent smaller than that of corresponding α -In₂Se₃ nanosheets. Furthermore, the difference of the formation energy can be negligible for AA (AAA) and AB (ABA), ensuring the feasibility to achieve AB (ABA) by switching the electric dipole orientation in AA (AAA) from the standpoint of energetics.

3.2. Electronic properties

In contrast to the previous bandgap calculation using the HSE06 functional with 25% exact exchange,²⁵ we calculated the band structure of single-layer α -M₂X₃ using 30% EE, *cf.* ESI (SI-1†). The calculated band structures are displayed in Fig. 3. α -M₂X₃ monolayers are indirect bandgap semiconductors with their valence band maximum (VBM) located between the *M* (0.0, 0.5, 0.0) and gamma (0.0, 0.0, 0.0) points. The conduction band minimum (CBM) is located at the *M* point for monolayer α -Ga₂S₃ and α -Ga₂Se₃, while for single-layer α -In₂S₃ and α -In₂Se₃ it is located at the gamma point. The top valence band of α -M₂X₃ monolayers is relatively flat, resulting in a high density of electronic states in the top valence band region as shown in Fig. 3(e), which is the origin of large SHG coefficients.⁷

Table 1 summarizes the PBE and HSE06 bandgaps of α -M₂X₃ monolayers. The PBE bandgap of 0.88 eV for monolayer α-In₂Se₃ gets very close to the calculated bandgap of 0.82 eV using PBE + SOC,²⁴ suggesting spin-orbital coupling (SOC) does not significantly modify the electronic property. The HSE06 bandgap of 1.80 eV for single-layer α -In₂Se₃ gets close to the calculated bandgap of 1.92 eV using the GW approximation,²⁴ but slightly larger than the bandgap of 1.45 eV calculated using HSE06 with 25% exact exchange.²⁵ The energy gaps of each monolayer at the gamma point are close to their respective indirect bandgaps, which is more evident for α -In₂S₃ and α -In₂Se₃ monolayers. It is expected the interband optical transition at the gamma point improves optical responses of α -M₂X₃ monolayers because no phonons are required for this optical transition to proceed. Additionally, the HSE06 bandgaps of α -M₂X₃ monolayers are large enough to avoid current leakages, and thereby they are promising in piezoelectric devices.

Fig. 4 displays the band structures of bilayer AA and AB, and trilayer ABA α -Ga₂S₃ calculated using HSE06. If there were no interlayer interaction, the band structure of bilayer AA α -Ga₂S₃ should be identical to that of monolayer α -Ga₂S₃. Nevertheless, the bands from different α -Ga₂S₃ layers in AA are pronouncedly splitted. Comparisons of Fig. 3(c) and 4(c) show the bottom valence bands from various α -Ga₂S₃ layers in AA are splitted by as large as 1.31 eV. Resultantly, the bandgap of AA significantly gets reduced by 1.15 eV in comparison with that of monolayer α -Ga₂S₃ as Table 1 shows, and that of trilayer AAA α -Ga₂S₃ further decreases as shown in Fig. 4(a). In brief, we find the bandgap of



Fig. 2 Calculated formation energies of monolayer α -M₂X₃, few-layer α -Ga₂S₃ and α -In₂Se₃. The formation energy of the synthesized MoS₂ monolayer is shown for comparison.



Fig. 3 Calculated band structure of (a) α -In₂S₃, (b) α -In₂Se₃, (c) α -Ga₂S₃ and (d) α -Ga₂Se₃ using HSE06 incorporating 30% EE. (e) Total and partial density of states of monolayer α -Ga₂S₃ calculated using PBE. (f) The high symmetry *k*-point path in the Brillouin Zone is chosen as: gamma (0, 0, 0) $\rightarrow k$ (-1/3, 2/3, 0) $\rightarrow M$ (0, 1/2, 0) \rightarrow gamma (0, 0, 0), and gamma is abbreviated as G.

few-layer α -Ga₂S₃ nanosheets becomes much narrower as their layer number increases. This bandgap reduction is also pronounced for few-layer α -In₂Se₃ nanosheets. Fig. 4(a) indicates the bandgap of trilayer AAA a-In₂Se₃ nearly vanishes. Similarly, optical absorption spectra show the bandgap decreases from 2.80 eV to 1.45 eV as the layer thickness increases from 3.1 nm to 20.1 nm.23 Considering the effective thickness of monolayer α -In₂Se₃ is \sim 1 nm, the optical bandgap of 1.45 eV for α -In₂Se₃ nanosheets with \sim 20 layers gets close to our theoretical value of 1.48 eV for α-In₂Se₃ bulk crystals. Nevertheless, the experimental bandgap of 2.8 eV for 3.1 nmthick (trilayer) a-In2Se3 nanosheets significantly varies from the zero bandgap of trilayer AAA α -In₂Se₃. Moreover, PBE calculations also find the bandgap of bilayer AA and trilayer AAA α-In₂Se₃ is closed.²⁵ It seems further bandgap measurements of few-layer α-In₂Se₃ are emergently needed to interpret the huge divergence between experimental and theoretical bandgaps. On the other hand, we note the band splitting in non-ferroelectric MoS_2 nanosheets is not so pronounced.³⁵ Single-layer MoS_2 embodies out-of-plane centrosymmetric characters and inplane non-centrosymmetric characters. Therefore, the pronounced band splitting in few-layer α -Ga₂S₃ (α -In₂Se₃) nanosheets is caused by the built-in electric field originated from the parallel out-of-plane electric polarizations (dipoles) of α -Ga₂S₃ (α -In₂Se₃) layers (*cf.* ESI-3†). This is further affirmed by semiconducting α -In₂Se₃ monolayers becoming metallic when an electric field perpendicular is applied.²⁴

The band splitting of bilayer AB α -Ga₂S₃ is not pronounced, and accordingly the bandgap difference between monolayer and bilayer AB α -Ga₂S₃ is very small. This is because the built-in electric field significantly decreases as the out-of-plane electric polarizations (dipoles) of α -Ga₂S₃ layers are antiparallelly



Fig. 4 (a) Bandgap variation of monolayer (ML), bilayer AA and AB, trilayer AAA and ABA α -Ga₂S₃ (α -In₂Se₃) nanosheets. Calculated Band structure of bilayer (c) AA and (d) AB, and (b) trilayer ABA α -Ga₂S₃ calculated using HSE06. Total and partial density of states (DOS) of bilayer (e) AA and (f) AB α -Ga₂S₃ calculated using HSE06. Total and partial density of states (DOS) of bilayer (e) AA and (f) AB α -Ga₂S₃ calculated using HSE06. Total and partial density of states (DOS) of bilayer (e) AA and (f) AB α -Ga₂S₃ calculated using HSE06.

aligned (cf. ESI-3[†]). Furthermore, the band splitting in Fig. 4(b) is minor in ABA α -Ga₂S₃ as expected. The divergence of electronic properties between AA and AB a-Ga2S3 is further emphasized in Fig. 4(e) and (f). The peaks in the conduction band region of bilayer AB α-Ga₂S₃ look similar to that of monolayer α -Ga₂S₃. Nevertheless, the peaks in AA α -Ga₂S₃ are significantly splitted, particularly for the peaks between -3 and -2 eV. Briefly, the bandgap in AA α -Ga₂S₃ is broadened by 1.00 eV in AB α -Ga₂S₃, which is very advantageous for applications as photodetectors since one can select the sensing photon energy window by switching electric dipole orientation. Additionally, the zero bandgap in AAA α-In₂Se₃ is opened in ABA α- In_2Se_3 , indicating the semiconducting nature can be achieved by switching the electric dipole orientation.

3.3. SHG properties

The length-gauge formulism at the independent-particle level derived by Aversa and Sipe37 and rearranged by Rashkeev et al.38 is used to calculate second-harmonic generation (SHG) coefficients (cf. ESI-2[†]), and its details are displayed in a previous work.39 Similar to previous works,7,27 the energy differences between HSE06 and PBE bandgaps are used for scissors corrections to reduce the errors caused by neglected many-body effects;40-42 the effective unit cell volume is applied to reduce underestimations caused by the large vacuum spacing. For α-M₂X₃ monolayers and few-layers, the effective volume is obtained by multiplying the area of in-plane unit cell and the effective thickness.

Because single- and few-layer α -M₂X₃ belong to C_{3v} symmetry, they have eleven static SHG coefficients and only three of them are independent dictated by Kleiman's symmetry: $\chi_{yyy}^{(2)}(0) = -\chi_{yxx}^{(2)}(0) = -\chi_{xyx}^{(2)}(0) = -\chi_{xyx}^{(2)}(0), \ \chi_{zzz}^{(2)}(0) \text{ and } \chi_{zxx}^{(2)}(0) = \chi_{zyy}^{(2)}(0) = \chi_{yyy}^{(2)}(0) = \chi_{yzy}^{(2)}(0) = \chi_{xzx}^{(2)}(0) = \chi_{xxz}^{(2)}(0).$ The static $\chi^{(2)}_{xxy}(0), \chi^{(2)}_{zxx}(0)$ and $\chi^{(2)}_{zzz}(0)$ are summarized in Table 1. The static $\chi^{(2)}_{xxy}(0)$ describes the in-plane SHG phenomenon, which has

been discovered in previous experiments of MoS₂,² GaSe⁴ and BN⁴³ monolayers. Even though the static $\chi^{(2)}_{xxy}(0)$ of α -M₂X₃ monolayers is much smaller than that of MoS_2 (ref. 35) and GaSe²⁷ monolayers, it is still comparable with $\chi^{(2)}_{779}(0)$ of 28.2 pm V^{-1} for an archetypical nonlinear optical crystal AgGaS₂,⁴⁴ ensuring α -M₂X₃ monolayers can be used as in-plane two-dimensional SHG devices. More importantly, α-M₂X₃ monolayers have additional SHG components $\chi^{(2)}_{777}(0)$ and $\chi^{(2)}_{zxx}(0)$ compared with MoS₂ and GaSe monolayers. Especially, the calculated $\chi^{(2)}_{zzz}(0)$ of α -M₂X₃ monolayers are comparable or even larger than the static SHG coefficient of 173.2 pm V^{-1} for GaAs crystals.⁴⁵ Therefore, α-M₂X₃ monolayers are of great importance in ultrathin two-dimensional devices allowing strong out-of-plane SHG occurs.

Fig. 5 represents the calculated real and imaginary parts of $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega),$ $\chi^{(2)}_{zxx}(-2\omega,\omega,\omega)$ SHG coefficients and $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ of α -M₂X₃ monolayers. The $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$ and $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ components are significant in the entire range of optical energy. The $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$ component is several times $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ and $\chi^{(2)}_{zxx}(-2\omega,\omega,\omega)$. For larger than $\chi^{(2)}_{zxx}(-2\omega,\omega,\omega)$, the electric field of both incoming and outgoing photons is parallel to the z axis, and thereby the electric depolarization vanishes. To analyze the prominent features in SHG spectra, the absolute values of imaginary part of $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$ and $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ for monolayer α -Ga₂S₃ are plotted in Fig. 6 and compared with the absorptive part of corresponding dielectric function ε'' . The first prominent peak between 1.7 and 3.8 eV in the $\chi^{(2)}_{777}(-2\omega,\omega,\omega)$ spectrum is caused by double-photon resonances (cf. Fig. 6(a) and (b)). In contrast, the double-peak structure between 3.8 and 5.6 eV in $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$ comes from single- and double-photon resonances. These single- and double-photon resonances only involve optical transitions for the electric filed vector \vec{E} parallel to the z axis $(\vec{E}||z)$. Fig. 6 further suggests the first prominent peak between 2.2 and 3.6 eV in the $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ spectrum is



Calculated real and imaginary parts of SHG coefficients $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega), \chi^{(2)}_{zxx}(-2\omega,\omega,\omega)$ and $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ of monolayer α -M₂X₃. Fia. 5

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Fig. 6 (a) Absolute value of the imaginary part of $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$, (b) imaginary part of the dielectric function ε''_z as a function of $\omega/2$ and ω , (c) absolute value of the imaginary part of $\chi^{(2)}_{xyy}(-2\omega,\omega,\omega)$, and (d) imaginary part of the dielectric function ε''_x as a function of $\omega/2$ and ω of monolayer α -Ga₂S₃.

caused by double-photon resonances with $\vec{E} || x$ (*cf.* Fig. 6(c) and (d)), while the peak between 3.9 and 5.4 eV in $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ comes from both single- and double-photon resonances with $\vec{E} || x$.

As shown in Table 1, the HSE06 bandgaps of few-layer α -Ga₂S₃ are in the visible range. In contrast, the HSE06 bandgaps of few-layer α-In₂Se₃ and AAA α-Ga₂S₃ are much narrower, which promises low laser damage thresholds. Therefore, we focus on SHG properties of bilayer AA and AB, and ABA α-Ga₂S₃, and their real and imaginary parts of $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$, $\chi^{(2)}_{zxx}(-2\omega,\omega,\omega)$ and $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ are displayed in Fig. 7. The line shape of the three SHG spectra of AA α -Ga₂S₃ is very similar to that of monolayer α -Ga₂S₃, and the SHG spectra of AA are significantly redshifted in comparison with that of monolayer α -Ga₂S₃ because of the sizable bandgap reduction. Moreover, the calculated $\chi^{(2)}_{zzz}(0), \chi^{(2)}_{zxx}(0)$ and $\chi^{(2)}_{xxy}(0)$ of AA α -Ga₂S₃ are very close to those of monolayer α -Ga₂S₃, respectively. These suggest that optical transitions occur within each α -Ga₂S₃ layer, namely the SHG property of each α-Ga₂S₃ layer is not modified by the built-in electric field of the neighboring α-Ga₂S₃ layer. According to the electric dipole theory, the SHG intensity shows a quadratic dependence on the SHG coefficient and the layer thickness,⁴ and thereby the non-resonant SHG intensity in bilayer AA is about four times that in monolayers.

The redshift of $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ for AB α -Ga₂S₃ is negligible as the bandgap difference of monolayers and AB is small. $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$ and $\chi^{(2)}_{zxx}(-2\omega,\omega,\omega)$ of AB α -Ga₂S₃ nearly vanishes, which is further corroborated by its vanishing static $\chi^{(2)}_{zzz}(0)$ and $\chi^{(2)}_{ran}(0)$. The electric dipole in the z(x) direction of the top and bottom a-Ga₂S₃ layers in bilayer AB points oppositely, and accordingly their contribution to the static $\chi^{(2)}_{777}(0)(\chi^{(2)}_{777}(0))$ cancels each other. The electric dipole in the z direction is the out-of-plane electric dipole, while the electric dipole in the x direction is the in-plane electric dipole. The $\chi^{(2)}_{777}(-2\omega,\omega,\omega)$ component of trilayer ABA α -Ga₂S₃ is 1/3 that of monolayer a-Ga2S3 as the contribution of the middle and bottom layers to $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega)$ in trilayer ABA cancels each other. Therefore, we propose that one can effectively tune the out-of-plane SHG coefficient by switching the electric dipole orientation in 2D nanosheets. Additionally, we summarize $\chi^{(2)}(0)$ of AB and ABA α -In₂Se₃ in Table 1, which indicates the obtained optical rules are valid for other α -M₂X₃ nanosheets. The SHG property of few-layer α -In₂Se₃ in recent experiments could be obtained by analogy.16

3.4. Piezoelectric properties

To obtain piezoelectric strain coefficients d_{ii} which measure mechanical-electrical energy conversion ratios, we calculate elastic constants Cii and piezoelectric stress coefficients eii using density functional perturbation theory (DFPT).46 The clampedion elastic and piezoelectric coefficients are obtained from purely electronic contributions, while the relaxed-ion coefficients are obtained from the sum of electronic and ionic contributions. The relaxed-ion elastic and piezoelectric coefficients are physically meaningful and can be directly compared with experimental results. As shown in Table 2, single- and fewlayer α -M₂X₃ have three independent elastic constants: C_{11} , C_{12} and C₆₆. The calculated clamped-ion and relaxed-ion elastic constants follow the correlation of $C_{66} \approx (C_{11} - C_{12})/2$. The relaxed-ion elastic constants fulfil the Born criteria of stability of 2D hexagonal structures, $^{47-49}$ *i.e.* $C_{11} > 0$ and $C_{11}-C_{12} > 0$, ensuing these monolayers and few-layers are mechanically stable. The calculated relaxed-ion Young's moduli $(Y = (C_{11}^2 - C_{12}^2)/C_{11})$ of single-layer a-M2X3 are smaller than that of graphene (341 N m⁻¹) and monolayer BN (275.9 N m⁻¹),⁵⁰ and comparable with that of monolayer TMDCs.⁵¹ Therefore, α-M₂X₃ monolayers are much softer than graphene and monolayer BN, and their stiffness is comparable with that of monolayer TMDCs. Moreover, the calculated Young's moduli of bilayer (trilayer) α -Ga₂S₃ are about two (three) times that of monolayer α-Ga₂S₃. This is because, of the same strain, the force needed for bilayers (trilayers) is two (three) times that of monolayers.

Single- and few-layer α -M₂X₃ have two independent piezoelectric stress coefficients e_{11} and e_{31} dictated by C_{3v} symmetry. The piezoelectric strain coefficients d_{11} and d_{31} , which respectively measure the mechanical-electrical energy conversion ratios in *x* and *z* directions, are expressed as $d_{11} = e_{11}/(C_{11} - C_{12})$ and $d_{31} = e_{31}/(C_{11} + C_{12})$.¹² The relaxed-ion e_{11} values of monolayer α -Ga₂S₃ and α -Ga₂Se₃ in Fig. 8(a) are even larger than that of monolayer 2H-CrTe₂, which has the largest e_{11} of 654 pC m⁻¹ among TMDCs.¹² The relaxed-ion d_{11} values of single-layer α -Ga₂Se₃ and α -In₂Se₃ in Fig. 8(c) are comparable with the maximum d_{11} of 13.45 pm V⁻¹ for monolayer TMDCs, and



Fig. 7 Calculated real and imaginary parts of SHG coefficients $\chi^{(2)}_{zzz}(-2\omega,\omega,\omega), \chi^{(2)}_{zxx}(-2\omega,\omega,\omega)$ and $\chi^{(2)}_{xxy}(-2\omega,\omega,\omega)$ of bilayer AA, AB, and trilayer ABA α-Ga₂S₃.

larger than the maximum d_{11} of 8.47 pm V⁻¹ for Janus group-III chalcogenide monolayers.¹¹ The relaxed-ion d_{11} values of α -In₂S₃ and α -In₂S₃ monolayers are comparable with the maximum d_{11} of 2.30 pm V⁻¹ for group-III chalcogenides.¹⁰ Therefore, α -M₂X₃ monolayers are promising in ultrathin piezoelectric sensors and nano-generators. Fig. 8(a) and (c) further suggest the electronic and ionic polarizations of α -Ga₂S₃ and α-Ga₂Se₃ monolayers both positively contribute to relaxedion piezoelectric coefficients e_{11} and d_{11} , resulting in significant in-plane piezoelectricity. In contrast, the electronic and ionic polarizations of α -In₂S₃ and α -In₂Se₃ monolayers oppositely contribute to relaxed-ion e_{11} and d_{11} , resulting in smaller inplane piezoelectricity. Our calculation also generates relaxedion e_{11} and d_{11} are respectively 369 pC m⁻¹ and 3.72 pm V⁻¹ for monolayer MoS₂, in good agreement with previous theoretical values of 364 pC m⁻¹ and 3.73 pm V⁻¹,⁸ indicating our theoretical results are numerically reliable.

Fig. 8(b) and (d) suggest α -M₂X₃ monolayers have nonzero out-of-plane piezoelectric coefficients e_{31} and d_{31} . The electronic

Table 2 Theoretical elastic constants C_{ij} and Yang moduli Y (N m⁻¹) in both clamped- and relaxed-ion cases of monolayer α -M₂X₃ and fewlayer α -Ga₂S₃

		Clamped-ion				Relaxed-ion			
		C_{11}	C_{12}	C_{66}	Y	C_{11}	C_{12}	C_{66}	Y
α-Ga ₂ S ₃	ML	146.7	48.6	48.9	130.5	115.5	45.0	35.1	104.3
	AA	293.3	97.6	97.6	261.0	228.2	83.3	72.4	197.7
	AB	292.3	96.2	97.6	260.6	224.3	85.4	69.3	191.7
	ABA	439.2	145.8	146.7	390.7	348.7	134.5	106.6	296.8
	AB								
	ab								
α -Ga ₂ Se ₃	ML	120.9	39.9	40.2	107.7	91.8	42.0	24.6	72.5
α -In ₂ S ₃	ML	117.0	43.2	36.6	101.0	75.6	36.6	19.2	57.8
α-In ₂ Se ₃	ML	96.3	35.1	30.6	83.5	68.4	24.0	21.9	59.9

and ionic polarizations of all α -M₂X₃ monolayers both negatively contribute to e_{31} and d_{31} . The d_{31} values of α -M₂X₃ monolayers are comparable with the maximum d_{31} of 0.46 pm V⁻¹ for monolayer Janus group-III chalcogenides¹¹ and the maximum d_{31} of 0.658 pm V⁻¹ for bucked hexagonal compounds.12 However, the bucked hexagonal compounds are energetically metastable. In contrast, α -M₂X₃ monolayers are energetically, dynamically²⁵ and mechanically stable, ensuing they are experimentally feasible.

The calculated piezoelectric coefficients e_{11} and e_{31} of AA and AB α -Ga₂S₃ are summarized in Fig. 8(e), while their d_{11} and d_{31} coefficients are displayed in Fig. 8(f). Comparisons of Fig. 8(a) and (e) show the clamped-ion (relaxed-ion) e_{11} of AB α -Ga₂S₃ is exactly twice that of monolayer α-Ga₂S₃. This is because, of the same strain, the change of polarization charges in the x direction of bilayer AB α -Ga₂S₃ is twice that of monolayer α -Ga₂S₃. Therefore, the piezoelectric effect occurs within each α -Ga₂S₃ layer in AB, namely the piezoelectricity of each α-Ga₂S₃ layer is not modified by the built-in electric field of the neighboring α - Ga_2S_3 layer. This is further affirmed by the relaxed-ion d_{11} of 10.4 pm V^{-1} for AB α -Ga₂S₃ being very close to that (10.7 pm V⁻¹) for monolayer α -Ga₂S₃. The relaxed-ion d_{31} of bilayer AB nearly vanishes since the piezoelectric contribution to d_{31} of each α -Ga₂S₃ layer cancels each other.

Fig. 8(a) and (e) further suggest the clamped-ion e_{11} of 485.1 pC m⁻¹ for bilayer AA α -Ga₂S₃ is exactly twice that (243.6 pC m⁻¹) of monolayer α -Ga₂S₃, while the relaxed-ion e_{11} of 1350.3 pC m⁻¹ for AA α -Ga₂S₃ is to some extent smaller than twice that (755.6 pC m⁻¹) of monolayer α -Ga₂S₃. The clampedion e_{31} of -240.2 pC m⁻¹ for AA α -Ga₂S₃ is much larger than that $(-11.4 \text{ pC m}^{-1})$ of monolayer α -Ga₂S₃, namely the clampedion e_{31} of AA α -Ga₂S₃ is much enhanced by the strong built-in electric field originated from the parallel out-of-plane electric polarizations of α -Ga₂S₃ layers. The relaxed-ion d_{31} of -0.91 pm V^{-1} for AA α -Ga₂S₃ is accordingly several times larger

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Fig. 8 Piezoelectric coefficients (a) e_{11} , (b) e_{31} , (c) d_{11} and (d) d_{31} of monolayer α -M₂X₃ in clamped- and relaxed-ion cases. (e) Clamped- and relaxed-ion e_{11} and e_{31} of bilayer AA and AB α -Ga₂S₃. (f) Relaxed-ion d_{11} and d_{31} (pm V⁻¹) of AA and AB α -Ga₂S₃.

than that $(-0.248 \text{ pm V}^{-1})$ of monolayer α -Ga₂S₃, suggesting AA α -Ga₂S₃ is much more easily polarized than monolayer α -Ga₂S₃. Similarly, the electric dipole (0.165 eÅ) of AA α -In₂Se₃ is much larger than that (0.07 eÅ) of monolayer α -Ga₂S₃.

Briefly, we find AA α -Ga₂S₃ has the largest out-of-plane d_{31} among all atomic-thick 2D materials up to date. More importantly, the built-in electric field can induce strong outof-plane piezoelectricity in atomic-thick 2D materials, which is corroborated by a recent calculation which finds large d_{31} of -1.234 pm V⁻¹ and d_{33} of -13.517 pm V⁻¹ in multilayer MoSTe.¹⁵ However, the large $d_{33}(\partial P_3/\partial \sigma_3, P$ is the electric polarization and σ is the stress) in multilayer MoSTe will vanish in atomic-thick 2D MoSTe such as monolayer¹⁵ and bilayer MoSTe (cf. ESI-4[†]). This reflects it is very difficult to impose stresses along the z direction for atomic-thick 2D materials since their effective thickness is far smaller than their flake size. For instance, the effective thickness of monolayer MoSSe is about 6.3 Å while its flake size is more than 5 µm.52 The effective thickness of monolayer MoSSe is considered as the average of that of MoS₂ and MoSe₂ monolayers.³⁵ In contrast, it is easy to impose stresses along the xdirection to achieve large $d_{31}(\partial P_3/\partial \sigma_1)$ because of the large size of atomic-thick 2D materials. Therefore, it is more reasonable to induce out-of-plane piezoelectricity by imposing stresses along the x direction within atomic-thick 2D materials. Moreover, the d_{31} coefficient of -1.234 pm V⁻¹ for multilayer MoSTe decreases to -0.417 pm V⁻¹ of bilayer MoSTe (cf. ESI-4^{\dagger}), being smaller than that of AA Ga₂S₃. The small bandgap of AAA α-Ga₂S₃ is disadvantageous to avoid current leakages. The piezoelectric coefficient d_{11} of ABA α -Ga₂S₃ should be close to that of monolayer α -Ga₂S₃, while its d_{31}

coefficient is around 1/3 that of monolayer $\alpha\text{-}Ga_2S_3$ since the piezoelectric response occurs within each $\alpha\text{-}Ga_2S_3$ layer.

4. Summaries

We have carried out first-principles calculations of structural, electronic, SHG and piezoelectric properties of single- and fewlayer α -M₂X₃ (M = Ga, In; X = S, Se). Firstly, α -M₂X₃ few-layers are energetically favorable and mechanically stable, ensuring bilayer AA and trilayer AAA can be successfully attained by mechanical exfoliation and bilaver AB and trilaver ABA can be achieved by switching the electric dipole orientation. Secondly, the relative flat top valence band of α-M₂X₃ monolayer promises large SHG coefficients, and their large bandgaps are helpful to avoid current leakages in piezoelectric devices. The splitting of energy bands in few-layer AA and AAA is very pronounced because of the built-in electric field originated from the parallel out-of-plane electric dipoles, while in contrast, that of AB and ABA is not pronounced because the built-in electric field significantly diminishes as the out-of-plane electric dipoles are antiparallelly aligned. Therefore, we propose a completely new method, *i.e.* switching the electric dipole orientation to tune electronic structures and bandgaps, which is very advantageous to tune the sensing photon energy window and achieve the semiconducting nature. Thirdly, the in-plane SHG coefficients of α -M₂X₃ monolayers are comparable with that of AgGaS₂ crystals. More importantly, we find out-of-plane SHG in α -M₂X₃ monolayers and their out-of-plane SHG coefficients are comparable with that of GaAs crystals. Furthermore, SHG occurs within each α-M₂X₃ layers in AA and AB, and accordingly one can achieve an enhanced out-of-plane SHG intensity in AA

and eliminate the out-of-plane SHG in AB. Fourthly, the stiffness of α -M₂X₃ monolayers is comparable that with monolayer TMDCs. α -M₂X₃ monolayers exhibit strong in-plane and considerable out-of-plane piezoelectricity. Furthermore, out-of-plane piezoelectricity vanishes in AB α -Ga₂S₃, and it is greatly enhanced in AA α -Ga₂S₃ as the electric dipoles are parallelly aligned. To our knowledge, out-of-plane SHG in 2D materials has been rarely reported, while the out-of-plane piezoelectricity is very limited in ultrathin 2D materials. Here we have presented strong out-of-plane SHG and piezoelectricity in ultrathin 2D materials. In general, our research will stimulate researches on the ultrathin 2D photo detection, SHG and piezoelectric devices.

Conflicts of interest

There are no conflicts to declare.

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