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Second-harmonic generation in quaternary atomically thin layered AgInP₂S₆ crystals

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Nonlinear effects in two-dimensional (2D) atomic layered materials have attracted increasing interest. Here, we report the observation of optical second-harmonic generation (SHG) in two-dimensional atomically thin silver indium phosphorus sulfide (AgInP₂S₆) crystals, with odd layer thickness. The nonlinear signal facilitates the use of thickness-dependent SHG intensity to investigate the stacking type of this material, while the crystal-orientation dependent SHG intensity of the monolayer sample reveals the rotational symmetry of the AgInP₂S₆ lattice in plane. Our studies expand the 2D crystal family in nonlinear effect field, which opened considerable promise to the functionalities and potential applications of 2D materials. *Published by AIP Publishing.*
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The exploration of functional 2D materials beyond graphene has quickly expanded recently driven by the variety of new materials and functionalities.^{1–10} The main interest is primarily focused on the unique electronic and optical properties to the bulk counterpart, such as indirect–direct bandgap transition and inversion symmetry breaking.^{11–16} Compared with graphene and transition metal dichalcogenides (TMDs), metal phosphorus trichalcogenides (MPTs) are newcomers to this field, especially for the quaternary MPTs which were recently synthesized in our team (M^I_{1/2}M^{III}_{1/2}PX₃ or M^IM^{III}P₂X₆, M^I=Cu and Ag; M^{III}=Cr, V, Al, Ga, In, Bi, Sc, Er, and Tm; X=S and Se).¹⁷

In general, it is not trivial to form a stable lattice structure when the materials are doped by elements with the valence state different from the original one. Therefore, compared with the common 2D crystals, such as TMDs, h-BN and GaSe, the MPTs offer a more artistic platform to manipulate artificial layered materials by providing more available positions for doping, as they contain metal elements with multiple valence states, e.g., mono- or tri-valence states in quaternary compounds and bi-valence state in ternary compounds. For example, besides the traditional X elements in M^IM^{III}P₂X₆, we can make the doping in the M^I position as compound Ag_{0.1}Cu_{0.9}InP₂S₆ or M^{III} position as compounds Ag_{1/2}Cr_(1/2–x)In_xPS₃.^{18,19} This would greatly improve the functionality of 2D materials with additional properties, including tunable bandgap, magnetism, and ferroelectricity in the MPTs.^{20,21} Furthermore, the crystal structure and symmetry may be different among MPTs in both the bulk and monolayer form. This point would set the uniqueness of this material from TMDs and makes the metal doping interesting,

particularly in the few-layer cases.²² In addition, the nonlinear effects in the atomically thin region including second harmonic generation (SHG) and chiral electroluminescence have expanded the functionalities and potential applications of 2D materials, which may disappear in the centrosymmetric bulk counterpart.^{13–15,21,23,24} In addition, the broken inversion symmetry in monolayer 2D materials has shown the viability of optical valley control.^{25,26} The external modulation opens a path to explore the physical and technological applications furthermore.

In this work, we have observed the inversion symmetry breaking of atomically thin quaternary AgInP₂S₆ with odd-layer thickness by detecting SHG. The absence of SHG in the even layer and bulk AgInP₂S₆ can be attributed to the AB stacking of neighboring layers. With this method, the symmetry variations were probed in few-layer AgInP₂S₆ by the layer-number dependent SHG intensity. Crystal oriented dependence of SHG intensity indicated the three-fold lattice symmetry of flakes with the odd-number layer.

The AgInP₂S₆ crystals have been synthesized by physical vapor transport (PVT) in a two-zone furnace.²⁷ Stoichiometric amounts of high-purity elements (mole ratio Ag:In:P:S=1:1:2:6, around 1 g in total) were sealed into a quartz ampoule with the pressure of 1×10^{-4} Torr inside the ampoule. The length of the quartz ampoule was about 15–18 cm with the 13 mm external diameter. The ampoule was kept in a two-zone furnace (680 → 600 °C) for 1 week. After the furnace was cooled down to room temperature, the flexible plate crystals could be found inside the ampoule (Figure 1(a)). The experimental powder X-ray diffraction (PXRD) of AgInP₂S₆ agrees with the simulated one from the crystal structure of ICSD 202185 well with the $P\bar{3}_1c$ space group (Figure 1(b)). Selected area electron diffraction (SAED) also confirmed the crystal symmetry (Figure 1(c)).

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FIG. 1. (a) The optical image of the as-grown AgInP_2S_6 crystal. (b) PXRD of the AgInP_2S_6 crystal. (c) Transmission electronic microscopy (TEM) image of AgInP_2S_6 flakes. The inset is the selective area electron diffraction (SAED) patterns of AgInP_2S_6 . (d) Raman spectra of the AgInP_2S_6 bulk crystal in room temperature excited by a 532-nm continue-wave (CW) laser.

Raman spectroscopy of bulk AgInP_2S_6 samples at room temperature (293 K) was investigated. The Raman measurements were carried out on a triple-grating micro-Raman spectrometer (Horiba-JY T64000). A solid state laser ($\lambda = 532$ nm) was used to excite the sample. The backscattered signal was collected through a $100\times$ objective and dispersed with a 1800 g/mm grating. To avoid sample heating by the laser beam, only few hundreds of microwatts were used in the experiments. As shown in Figure 1(d), ten Raman peaks could be resolved in AgInP_2S_6 , which showed a similar spectrum to CuInP_2S_6 and some ternary metal phosphorous sulfides, especially in the range of 200 to 500 cm^{-1} .^{17,28–30} The modes of metal phosphorus sulfides in the high frequency region are mainly attributed to the inner vibrations of the $[\text{P}_2\text{S}_6]$ unit, while few minor difference can still be observed among different compounds.²⁸ For instance, probably due to the different crystal structure, a weak peak located around 450 cm^{-1} , which has been attributed to the stretch vibration of the P-P bond, can be observed in the Raman spectrum for AgInP_2S_6 , while it can only be observed in the infrared spectrum for ternary compounds.²⁸ The Raman spectra show a larger difference in the low frequency part ($<200\text{ cm}^{-1}$), where the Raman modes are largely affected by the vibration of metal atoms. For example, no Raman peak could be resolved below 50 cm^{-1} in AgInP_2S_6 ; while a peak around 25 cm^{-1} was observed in the spectrum of CuInP_2S_6 .³⁰ This phenomenon implied a possibility that the distribution of metal atoms and related bonds in these two materials was largely different.

As a layered material, AgInP_2S_6 offers us an opportunity to distinguish the ab plane and c axis in the study of the crystal structure by fabricating atomically thin samples. For the study of the atomically thin sample of AgInP_2S_6 , mechanical exfoliation would be a convenient method to prepare the sample, as people usually performed on graphene and TMDs. The mono- and few-layer AgInP_2S_6 flakes on 100 nm SiO_2/Si substrates were mechanically exfoliated from the bulk crystal by Scotch tape. As shown in Fig. 2, the AgInP_2S_6 flakes from

mono- to four-layer were characterized by using optical microscopy (Olympus BX51) and atomic force microscopy (AFM, Bruker Dimension Icon) in a tapping mode. The thickness of the monolayer is ~ 0.80 nm, which is similar to the value of other metal phosphorus sulfides in previous reports.¹⁷ The optical contrast of thin samples with different thicknesses is distinct on the surface of 100 nm SiO_2 .

The SHG of AgInP_2S_6 was investigated in both bulk crystal and exfoliated flakes (Figure 3(a)). The SHG measurements were performed in a reflection geometry using normal incidence excitation. A mode-locked Ti/Sapphire oscillator was used as the pumping source at 800 nm wavelength (Spectra-Physics, 80 MHz, ~ 100 fs). With a $100\times$ objective, the pumping light was focused to a spot size of $\sim 3\text{ }\mu\text{m}$ in diameter on the sample. The laser power was limited to around 1 mW to avoid sample heating and burning (except the power dependent experiment). Different from the SHG spectrum of the CuInP_2S_6 crystal, which is proved to be non-centrosymmetric at room temperature, the absence of the SHG signal from the bulk AgInP_2S_6 crystal suggests that the lattice structure is centrosymmetric, thus leading to the disappearance of second-order optical nonlinearity.³¹ The contrast on SHG spectra of AgInP_2S_6 and CuInP_2S_6 distinctly points out the variation of crystal symmetry when the metal atoms are substituted in the bulk case. Therefore, it is significant to acquire more detailed information about the lattice structure in this family of materials. In this letter, our investigation is focused on AgInP_2S_6 , which is rarely explored in previous reports. The physical properties can also be investigated when the system transits from three- to two-dimensional.

FIG. 2. (a) The optical microscopy photograph of exfoliated AgInP_2S_6 flakes on 100-nm SiO_2/Si substrates. The optical contrast shows the different thickness of AgInP_2S_6 flakes. (b) AFM image of exfoliated AgInP_2S_6 flakes, corresponding to the area of the red frame in (a). (c) Height profiles of exfoliated AgInP_2S_6 flakes from bi- to four-layer with corresponding lines indicated in (b). (d) The AFM image of monolayer AgInP_2S_6 flakes. The insets are the optical microscopy photograph and height profile of the monolayer sample.

FIG. 3. (a) SHG spectra from the AgInP₂S₆ bulk crystal and exfoliated monolayer counterpart in room temperature excited by the 800-nm fs laser. (b) The power dependent SHG intensity from the AgInP₂S₆ monolayer sample. (c) The azimuthal angle θ dependent SHG intensity. (d) The in-plane configuration of monolayer AgInP₂S₆ along the *c* axis. (e) The relative in-plane position of Ag and In atoms. (f) In-plane schematic of six P-S bonds from a [P₂] pair. The neighboring angles θ_1 and θ_2 are different.

Typical optical spectra of monolayer AgInP₂S₆ flakes under excitation of 800-nm femtosecond laser are also shown in Figure 3(a). A conspicuous peak, which is centered at 400 nm, can be exactly assigned to the SHG signal. The dependence of SHG intensity on the excited femtosecond laser power was investigated. The electric dipole theory predicts that SHG intensity I_{SHG} is determined by the following formula under the first-order perturbation:³²

$$I_{\text{SHG}} \propto |E(2\omega)|^2 \propto |P(\omega)|^2, \quad (1)$$

where $E(2\omega)$ and $P(\omega)$ are the SHG electric field vector and excited laser power, respectively. As a consequence, the SHG intensity should be quadratically dependent on the excitation power. In Figure 3(b), the SHG intensity of the monolayer sample was plotted as the function of excitation power in log scale. The fitting line shows that the exponent is around 2.1, roughly consistent with the theoretical value. The consistency indicates that the measured signal at 400 nm is indeed originated from the second-order nonlinear process in monolayer AgInP₂S₆, which can be well described by the electric dipole theory.

The SHG intensity from monolayer AgInP₂S₆ exhibited a strong dependence on the azimuthal angle θ , which is defined as the angle between the polarization of the excitation beam and one of the armchairs (as shown in Figures 3(c) and 3(d)). Figure 3(d) indicates the lattice symmetry and orientation of monolayer AgInP₂S₆. The monolayer polarization P_i can be explained by a bond charge model.³³ The potential difference between two different ions in each bond $\hat{b}_n$ will cause a position shift of center of the bond charge. The shifting of the bond center gives rise to a second-order bond hyperpolarizability $\beta_n^{(2)}$ related to the second-order nonlinear susceptibility $\chi^{(2)}$ of the whole structure. When light incidents along the sample surface normal, the second-order dipole moment $p_{2\omega,n} = \beta_n^{(2)}(E_\omega \cdot \hat{b}_n)^2$ is generated in each bond. Based on

this, the non-inversional symmetric distribution of bond charges leads to the arising of monolayer polarization. In detail, the non-inversional symmetry of the lattice structure in the *ab* plane is mainly attributed to the triangle distribution of In atoms, as well as that of Ag atoms and [P₂] pairs (Figure 3(e)). The relative in-plane positions of any two kinds of atoms are comparable with the atom distribution of B and N in monolayer h-BN.^{14,15} Besides that, the distribution of S atoms, which is not exactly hexagonal, also introduces a non-inversional symmetric bond charge in the monolayer lattice structure. For example, the neighboring in-plane angles of P-S bonds from a [P₂] pair are 54.2° and 65.8°, due to the bond twisting between upper and lower P atoms (Figure 3(f)). Therefore, monolayer AgInP₂S₆ has 3-fold symmetry in plane, where the SHG intensity is expected to exhibit a 6-fold rotational symmetric response when rotating the sample about its surface normal. The angle resolved SHG intensity exhibits a symmetric pattern with 6 petals, which can be described as $I = I_0 \cos^2(3\theta)$, where I and I_0 are the SHG intensity and the maximum SHG intensity, respectively. According to the in-plane lattice structure, the direction parallel to a mirror plane of the crystal line has the maximum of dipole moment, leading to the maximum SHG intensity.

In monolayer crystals, the second-order nonlinear susceptibility $\chi^{(2)}$ could be estimated by³⁴

$$I_{2\omega} = [\chi^{(2)}]^2 I_\omega^2 \times \frac{\omega^2 d^2}{n_{2\omega} n_\omega^2}, \quad (2)$$

where I_ω is the intensity of the excitation laser; $I_{2\omega}$ is the SHG intensity; n_ω and $n_{2\omega}$ are the refractive indices of the material at frequencies ω and 2ω , respectively; d is the thickness of the monolayer. In order to estimate the second-order nonlinear susceptibility of the AgInP₂S₆ monolayer, the SHG measurement was conducted on monolayer MoS₂, which is exfoliated on the same substrate and excited with

the same excitation power. The SHG intensity of the MoS₂ monolayer is around 100 times larger than that of the AgInP₂S₆ monolayer. Regardless of the related minor difference from the refractive index and the sample thickness, the difference is mainly originated from the second-order nonlinear susceptibility $\chi^{(2)}$, which is about one order of magnitude smaller in the AgInP₂S₆ monolayer than that in the MoS₂ counterpart.^{34–36}

Further investigation is conducted on the dependence of SHG spectra on the layer-number. The SHG spectra of AgInP₂S₆ from mono- to four-layer under excitation of the 800-nm laser are shown in Figure 4(a). In the SHG spectra of monolayer and tri-layer AgInP₂S₆, the SHG peak was distinctly observed at 400 nm. However, no SHG signal can be resolved in the spectrum of bilayer and four-layer AgInP₂S₆ samples. Since the SHG response of the materials can be treated as an optical method to probe the symmetry lattice structure, the contrast of the SHG signal reflects the different lattice symmetry of AgInP₂S₆ between the odd and even layer number.

As shown in Figure 4(b), monolayer AgInP₂S₆ belongs to the non-centrosymmetric structure, which is supposed to have nonzero SHG signal. Ag and In atoms are six coordinated with S atoms. P atoms are tetrahedral coordinated to form a binuclear [P₂S₆]⁴⁻ cluster ([P₂]), which are located in the center of hexagon composed by alternative three Ag atoms and three In atoms. Besides that, the metal (Ag and In) layers are sandwiched by two layers of S atoms, while the [P₂] pairs act as stanchions inside the layer. However, in the bulk and multilayer samples, the neighboring layers are coupled by van der Waals interactions. The [P₂] pairs and Ag atoms stack alternately in the nearby two layers, leading to the AB stacking order of the adjacent layers. In the even-

layer number sample, the bonds in one layer have the opposite symmetry with respect to the bonds in the adjacent layer in the *ab* plane, leading to the cancellation of total dipole moment. Therefore, the even layer number and bulk AgInP₂S₆ indeed exhibit inversion symmetry, where no SHG signal should be observed. Nonetheless, a weak SHG signal, which can be observed in the bulk AgInP₂S₆ crystal at a large excitation power and long integral time, is attributed to the lattice reconstruction on the surface of the bulk crystal.³⁷ This similarity to TMDs on lattice symmetry implies the various potential functions in AgInP₂S₆, such as valleytronic properties in the monolayer.

The SHG spectrum has several advantages in the study of atomically thin AgInP₂S₆ materials. First, the prominent difference of SHG intensity between the odd-layer and even-layer number sample shows a potential to easily determine the layer number of the AgInP₂S₆ sample assisted with the optical contrast of the sample. An optical method is widely used to determine the thickness of the different exfoliated 2D materials. For example, the layer number of MoS₂ can be determined by the central wavelength and intensity of the photoluminescence^{12,38} and the wavenumber of interlayer Raman modes.⁷ However, for few-layer AgInP₂S₆ flakes (<20 nm), the Raman signal is too weak to be detected in the thin sample, while no photoluminescence can be observed probably due to its indirect bandgap. Therefore, the SHG becomes an excellent optical tool to clearly probe the layer number of AgInP₂S₆. Second, the SHG intensity varies with the crystal orientation rotating in odd layer number AgInP₂S₆. This phenomenon provides a pure optical method to precisely probe the crystallographic axes of the local sample without chemical damage. Third, the SHG measurement in AgInP₂S₆ reveals the potential to precisely detect the local crystal symmetry, including the orientation symmetry in *ab* plane and stacking order, of doping MPTs in further investigation. Although AgInP₂S₆ is not magnetic or ferroelectric, its stable structure of atomically thin flakes offers a platform to manipulate the artificial atomically thin magnetic or ferroelectric sample by doping relevant elements. During this process, the variation of the lattice symmetry of the material can be also detected by the SHG signal.

In summary, the mono- and few-layer quaternary MPTs, AgInP₂S₆, were prepared by mechanical exfoliation from the bulk crystal, and the SHG on monolayer AgInP₂S₆ was reported. The layer-number dependent SHG measurement was conducted to probe the crystal symmetry. The distinct contrast of SHG intensity between odd- and even-number layers indicates that the even-layer number samples have inversion symmetry, which is broken for the odd-layer number counterpart. The orientation dependent SHG intensity of monolayer AgInP₂S₆ reveals the 3-fold rotational symmetry of the lattice. The SHG spectrum offers a potential method to probe the grain boundary of monolayer AgInP₂S₆ in the *ab* plane. Our study of nonlinear optics on AgInP₂S₆ provides a platform to explore the crystal structure of metal phosphorus sulfides and opens a path to manipulate artificial and stable 2D materials with various properties by doping metal atoms.

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FIG. 4. (a) SHG spectra of exfoliated AgInP₂S₆ flakes from mono- to four-layer. (b) The packing configuration of the lattice structure of AgInP₂S₆ from mono- to tri-layer. The stacking sequence of the AgInP₂S₆ crystal shows different lattice symmetry between odd- and even-layer samples.

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