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Second-harmonic generation in quaternary atomically thin layered AgInP$_2$S$_6$ 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 (AgInP$_2$S$_6$) 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 AgInP$_2$S$_6$ 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. 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. 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$_{1/2}$M$_{1/2}$PX$_3$ or M$_1$M$_{10}$P$_2$X$_6$, M$^I$=Cu and Ag; M$^{III}$=Cr, V, Al, Ga, In, Bi, Sc, Er, and Tm; X=S and Se).

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$_1$M$_{10}$P$_2$X$_6$, we can make the doping in the M$^I$ position as compound Ag$_{0.1}$Cu$_{0.9}$InP$_2$S$_6$ or M$_{III}$ position as compounds Ag$_{1/2}$Cr$_{1/2-3}$In$_2$P$_3$. This would greatly improve the functionality of 2D materials with additional properties, including tunable bandgap, magnetism, and ferroelectricity in the MPTs. 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.

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. In addition, the broken inversion symmetry in monolayer 2D materials has shown the viability of optical valley control. 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 AgInP$_2$S$_6$ with odd-layer thickness by detecting SHG. The absence of SHG in the even layer and bulk AgInP$_2$S$_6$ can be attributed to the AB stacking of neighboring layers. With this method, the symmetry variations were probed in few-layer AgInP$_2$S$_6$ 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 AgInP$_2$S$_6$ crystals have been synthesized by physical vapor transport (PVT) in a two-zone furnace. 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 (XRD) of AgInP$_2$S$_6$ agrees with the simulated one from the crystal structure of ICSD 202185 well with the P$_{31c}$ space group (Figure 1(b)). Selected area electron diffraction (SAED) also confirmed the crystal symmetry (Figure 1(c)).
Raman spectroscopy of bulk AgInP$_2$S$_6$ 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$_2$S$_6$, which showed a similar spectrum to CuInP$_2$S$_6$ and some ternary metal phosphorus sulfides, especially in the range of 200 to 500 cm$^{-1}$.\textsuperscript{1,17,28–30} The modes of metal phosphorus sulfides in the high frequency region are mainly attributed to the inner vibrations of the [P$_2$S$_6$] unit, while few minor difference can still be observed among different compounds.\textsuperscript{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$_2$S$_6$, while it can only be observed in the infrared spectrum for ternary compounds.\textsuperscript{28} The Raman spectra show a larger difference in the low frequency part ($<200$ 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$_2$S$_6$; while a peak around 25 cm$^{-1}$ was observed in the spectrum of CuInP$_2$S$_6$.\textsuperscript{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$_2$S$_6$ 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$_2$S$_6$, 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$_2$S$_6$ 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$_2$S$_6$ 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 $\sim 0.80$ nm, which is similar to the value of other metal phosphorus sulfides in previous reports.\textsuperscript{17} The optical contrast of thin samples with different thicknesses is distinct on the surface of 100 nm SiO$_2$.

The SHG of AgInP$_2$S$_6$ 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, $\sim 100$ fs). With a $100 \times$ objective, the pumping light was focused to a spot size of $\sim 3$ $\mu$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$_2$S$_6$ crystal, which is proved to be non-centrosymmetric at room temperature, the absence of the SHG signal from the bulk AgInP$_2$S$_6$ crystal suggests that the lattice structure is centrosymmetric, thus leading to the disappearance of second-order optical nonlinearity.\textsuperscript{31} The contrast on SHG spectra of AgInP$_2$S$_6$ and CuInP$_2$S$_6$ 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$_2$S$_6$, which is rarely explored in previous reports. The physical properties can also be investigated when the system transits from three- to two-dimensional.
Typical optical spectra of monolayer AgInP$_2$S$_6$ 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 $I_{\text{SHG}}$ is determined by the following formula under the first-order perturbation: \(^3^2\)

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

(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 AgInP$_2$S$_6$, which can be well described by the electric dipole theory.

The SHG intensity from monolayer AgInP$_2$S$_6$ exhibited a strong dependence on the azimuthal angle $\theta$, 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 AgInP$_2$S$_6$. The monolayer polarization $P_i$ can be explained by a bond charge model. \(^3^3\) The potential difference between two different ions in each bond $b_i$ 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 $\beta_{b_i}^{(2)}$, 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 $p_{2\omega, n} = \beta_{b_i}^{(2)}(E_{\omega} \cdot \hat{b}_i)^2$ 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 [P$_2$] 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. \(^1^4, ^1^5\) 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 [P$_2$] pair are 54.2$\degree$ and 65.8$\degree$, due to the bond twisting between upper and lower P atoms (Figure 3(f)). Therefore, monolayer AgInP$_2$S$_6$ 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 by \(^3^4\)

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

(2)

where $I_\omega$ is the intensity of the excitation laser; $I_{2\omega}$ is the SHG intensity; $n_\omega$ and $n_{2\omega}$ are the refractive indices of the material at frequencies $\omega$ and $2\omega$, respectively; $d$ is the thickness of the monolayer. In order to estimate the second-order nonlinear susceptibility of the AgInP$_2$S$_6$ monolayer, the SHG measurement was conducted on monolayer MoS$_2$, which is exfoliated on the same substrate and excited with...
the same excitation power. The SHG intensity of the MoS$_2$ monolayer is around 100 times larger than that of the AgInP$_2$S$_6$ monolayer. Regardless of the related minor difference from the refractive index and the sample thickness, the difference is mainly originated from the second-order non-linear susceptibility $\chi^{(2)}$, which is about one order of magnitude smaller in the AgInP$_2$S$_6$ monolayer than that in the MoS$_2$ counterpart.

Further investigation is conducted on the dependence of SHG spectra on the layer-number. The SHG spectra of AgInP$_2$S$_6$ 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 AgInP$_2$S$_6$, the SHG peak was distinctly observed at 400 nm. However, no SHG signal can be resolved in the spectrum of bilayer and four-layer AgInP$_2$S$_6$ 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 AgInP$_2$S$_6$ between the odd and even layer number.

As shown in Figure 4(b), monolayer AgInP$_2$S$_6$ 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 $[\text{P}_2\text{S}_6]^{4-}$ cluster ($[\text{P}_2]$), 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 $[\text{P}_2]$ 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 $[\text{P}_2]$ 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 AgInP$_2$S$_6$ indeed exhibit inversion symmetry, where no SHG signal should be observed. Nonetheless, a weak SHG signal, which can be observed in the bulk AgInP$_2$S$_6$ crystal at a large excitation power and long integral time, is attributed to the lattice reconstruction on the surface of the bulk crystal. This similarity to TMDs on lattice symmetry implies the various potential functions in AgInP$_2$S$_6$, such as valleytron properties in the monolayer.

The SHG spectrum has several advantages in the study of atomically thin AgInP$_2$S$_6$ 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 AgInP$_2$S$_6$ 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 MoS$_2$ can be determined by the central wavelength and intensity of the photoluminescence and the wavenumber of interlayer Raman modes. However, for few-layer AgInP$_2$S$_6$ 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 AgInP$_2$S$_6$. Second, the SHG intensity varies with the crystal orientation rotating in odd layer number AgInP$_2$S$_6$. 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 AgInP$_2$S$_6$ 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 AgInP$_2$S$_6$ 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, AgInP$_2$S$_6$, were prepared by mechanical exfoliation from the bulk crystal, and the SHG on monolayer AgInP$_2$S$_6$ 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 AgInP$_2$S$_6$ reveals the 3-fold rotational symmetry of the lattice. The SHG spectrum offers a potential method to probe the grain boundary of monolayer AgInP$_2$S$_6$ in the $ab$ plane. Our study of nonlinear optics on AgInP$_2$S$_6$ 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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