New Frontiers on van der Waals Layered Metal Phosphorus Trichalcogenides

Fengmei Wang, Tofik A. Shifa, Peng Yu, Peng He, Yang Liu, Feng Wang, Zhenxing Wang, Xueying Zhan, Xiaoding Lou,* Fan Xia,* and Jun He*

The exponentially growing works on 2D materials have resulted in both high scientific interest and huge potential applications in nanocatalysis, optoelectronics, and spintronics. Of especial note is that the newly emerged and promising family of metal phosphorus trichalcogenides (MPX₃) contains semiconductors, metals, and insulators with intriguing layered structures and architectures. The bandgaps of the members in this family range from 1.3 to 3.5 eV, significantly enriching the application of 2D materials in the broad wavelength spectrum. In this review, emphasizing their remarkable structural, physicochemical, and magnetic properties, as well as the numerous applications in various fields, the innovative progress on layered MPX₃ crystals is summarized. Different from other layered materials, these crystals will advance a fascinating frontier in magnetism and spintronics devices with their especially featured atomic layered nanosheets. Thus, their crystal and electronic structures, along with some related researches in magnetism, are discussed in detail. The assortments of growth methods are then summarized. Considering their potential applications, the prominent utilization of these 2D MPX₃ nanocrystals in catalysis, batteries, and optoelectronics is also discussed. Finally, the outlook of these kinds of layered nanomaterials is provided.

1. Introduction

van der Waals layered materials, including graphene,[1] transition metal dichalcogenides (TMDs),[2,3] black phosphorus,[4,5] and boron nitride (BN),[6] dominate the current era of 2D crystals. Given their unique physical and chemical properties, which do not appear in 3D structures, they are widely utilized as electronic and structural materials.[7] Especially, the fabrication of heterostructures and optoelectronic nanodevices using 2D materials has been studied, resulting in extraordinary findings in various fields of study. The electron confinement in the 2D feature endows them with some specific properties, such as charge density wave occurrence,[8] anisotropic magnetic behavior,[9] and conductivity.[2,4] anisotropy of photoluminescence,[10] and large surface area. In this regard, TMD materials represent a strikingly indispensable series of 2D crystals. As far as their structure is concerned, strong covalent bonded layers, constituting a cationic plane (M⁺) enclosed by two planes of anionic (S²⁻, Se²⁻, or Te²⁻), enlarge into infinite sheets. The arrangement of such S(Se)–M–S(Se) sandwiches provides an empty space, in which two adjacent layers are weakly bonded to each other via the van der Waals (vdW) force.[11,12] Their optical and electronic properties could be controlled by changing the components and the thickness.[13,14] For instance, the bandgap of MoS₂ (a typical TMD) can be enlarged from 1.29 to 1.9 eV via reducing the thickness from multilayers to a monolayer.[13,15] Although their bandgaps can be tuned, TMDs are generally characterized by small bandgaps (smaller than 2.02 eV),[16] which limits their application in devices requiring values beyond this range. Thus, 2D materials exhibiting bandgaps ranging from 2.02 to 4.0 eV are extensively sought to meet the application requirements in the broad wavelength spectrum.

Nowadays, a burgeoning research direction goes toward the newly emerged van der Waals layered materials known as metal phosphorus trichalcogenides (MPX₃). The metal cations (M⁺ or M⁺M⁺) stabilize [P₂S₄]²⁻ or [P₂Se₄]²⁻ framework layers weakly bonding each other via vdW interactions. This family contains a variety of transition metal phases, ranging from vanadium to zinc (M = V, Mn, Fe, Co, Ni, Zn, etc.) in the first row, partial alkaline metal in group-II, and some other metal...
ions. Friedel[17] and Ferrand[18,19] discovered them in the late 1800s. Based on the interesting structure of these materials, significant research works were reported in the early 2000s. As expected, 2D MPX$_3$ phases share most of the abovementioned specific properties of 2D TMDs. According to the theoretical and experimental results, MPX$_3$ compounds are the most sought functional materials for their intermediate bandgaps ranging from 1.3 to 3.5 eV,[20,21] indicating their enhanced light absorption efficiency as compared to the TMD materials. In addition, their unusual intercalation-substitution or intercalation-reduction behavior as well as the incipient ionic conductivity promote their usage in Li-ion batteries,[22,23] gas storage,[24] and photo-electrochemical reactions.[25] Unlike TMDs, several MPX$_3$ materials show intrinsic anti-ferromagnetism below the Neel temperatures of 78 K for MnPS$_3$, 116 K for FePS$_3$, and 155 K for NiPS$_3$. Recently, Li et al.[26] predicted that transformation from the anti-ferromagnetism to ferromagnetism for exfoliated MnPSe$_3$ nanosheet will be reduced by carrier doping. And the Monte Carlo simulation reveals the Curie temperature of the doped MnPSe$_3$ nanosheets can reach 206 K, rendering it with potential for utilizations in spintronic devices at high temperature. Therefore, the members in the MPX$_3$ family have the abovementioned properties along with structural flexibility stemming from their van der Waals nature; thus, it is reasonable to assume that they will contribute to the next major frontier in 2D vdW layered materials.

Herein, we emphasize on reviewing the impressive recent progress and thoughts on physical and chemical characteristics, specific properties, growth methods, and potential applications of 2D MPX$_3$ crystals. The structure of MPX$_3$ is comprehensively described and compared with the common TMD’s structure. According to the variety of cations (M) and their corresponding valence states, they are categorized into M$^{2+}$, M$^{3+}$ and other component-based MPX$_3$ materials. The bandgaps, crystal structures, and stacking of layers are summarized for tangible deduction on the materials functionality and specific properties. Furthermore, the material functionality and specific properties of MPX$_3$ are also discussed. Up to now, the synthesis of 2D ultrathin MPX$_3$ crystals has been a big challenge. Therefore, we are inclined to summarize the growth of atomic layered MPX$_3$ crystals. Considering the feature-based application of this type of layered crystals, we also introduce some applications. The final section of this review contains future perspectives of these types of 2D layered materials.

### 1.1. Composition and Crystal Structures

All the members in the family of MPX$_3$ materials share a defining common structural feature such that $(P_xS_x)_n^4-$ or $(P_xSe_x)_n^4-$ anion sublattice appears within each layered crystal. The honeycomb arrangement of the transition metal ions is distributed around the $(P_xX_y)_n^4-$ bipyramids. Thus, these compounds are usually described as $M_2P_xS_y$. A structural comparison between typical layered MoS$_2$ and MPX$_3$ is shown in Figure 1. In general, the vdW gap (shortest distance between the S layers) distance of the MPX$_3$ crystals with the first row transition metal elements is around 3.22–3.24 Å, much wider than that of MS$_2$ ones. Various atomic radii cations can be
located in the MPX₃ along with the change of the slab size. As to the P₂S₆⁻ structural modification, the flat pyramid constituting S²⁻ ions remains invariable but the P−P distance is somewhat elongated to accommodate the different metal cations. There is a shift, regardless of the type of M cations, from 2.148 Å (NiPS₃) to 2.222 Å (CdPS₃) for P−P distance in MPS₃ crystals.[29] However, the layer thickness is positively related to the value of the P−P distances for MPX₃ crystals. [30] The component of MPX₃ can be tuned by changing the M and X atoms. On the anion side, P₂S₆⁴⁻ and P₂Se₆⁴⁻ anions can be alloyed in the M₁₂P₂X₆ structure. Mixed chalcogen, in which the various atoms (i.e., S or Se) are alloyed with each other, is adopted. Some alloys, such as Ni₂P₂S₆−ₓSeₓ,[31] CuInP₂S₆−ₓSeₓ,[27,32] MnPS₃Se₁−ₓ[33] and Sn₂P₂S₆−ₓSeₓ[34] have been studied. On the cation side, MPX₃ can accommodate group II elements (e.g., Mg), group IV elements (e.g., Sn), transition metals (i.e., Sc, Mn, Fe, Co, Pd, Ag, and Cd, etc.), or a combination thereof. Until now, the most studied materials are Mn, Fe, and Ni based MPX₃ compounds due to their magnetic ordering and applications in electrochemistry and catalysis.[20,35,36] From the component point of view, it constitutes a potentially broad material class.

Figure 1. Comparison of crystal structures, including the top view (top), side view with two layers (middle), and crystal phase, of a) MoS₂ with hexagonal crystal, b) M⁰PX₃ with hexagonal (left) and monoclinic(right) crystals, and c) M⁰M⁰⁰PX₃ with monoclinic crystal. Here, the 2H phase of MoS₂ is taken as an example.

1.1.1. M⁰ Based MPX₃ Crystals

Divalent metal atom-based M⁰PX₃ crystals are common and intensively studied presently. Notably, this aspect is one of particularities to distinguish M⁰PX₃ from M⁰X₃ (e.g., MoS₂) compounds. The MPS₃ phases are taken as layered MS₂ crystals with one third of the M sites substituted by P−P pairs (Pⱼ), i.e., M₂/₃(Pⱼ)¹/₃S₂. The sulfur atoms comprise the surfaces within individual lamella. From Figure 3a, an octahedrally coordinated configuration can be visualized in which the 2/3 is filled by M⁰ cations and the remaining 1/3 is occupied by P−P dimers. The P−P dimers are covalently bonded to six sulfur atoms to form an ethane-like (P₂S₆)⁴⁻ unit, where each P atom is tetrahedrally coordinated with three S atoms. Meanwhile, a sulfur atom is covalently bonded to one P atom.

Generally, the overall structure of the individual lamella is similar across the MPX₃ family members, but their stacking arrangements in bulk vary depending on the cations and anions constituting the crystals. Their symmetry and lamellar stacking are summarized in Table 1. There is an obvious distinction between the sulfides and selenides encountered in their symmetry and crystal structures. The widest symmetry of M⁰PS₃ is C2/m with monoclinic crystal structure, but HgPS₃ crystallizes into a space group of P₁[37] along with distorted tetrahedrally coordinated Hg ions.[38] In the C2/m space group, the structure is constructed from sulfur cubic close-packed arrays with the octahedral sites in each layer completely filled by M⁰ and P−P pairs at a 2/1 ratio. One observes that the value of monoclinic angle β, varying from 106.97° for MgPS₃ to 107.35° for MnPS₃, is different based on M cations (Figure 3b). For an undistorted monoclinic cell, the value of β is calculated to be 107.16°, suggesting that CoPS₃ and FePS₃ possess a perfect cell.[38] All M⁰PX₃ materials with the C2/m space show a layers stacking sequence of “AA” (Table 1).

For M¹PSe₃ (e.g., CdPSe₃, MgPSe₃, FePSe₃, ZnPSe₃), owing to the enlarged P−Se bond distance and Se−P−Se bond angles, their space group has been reported as R3(−h).[39−41] The distortions exhibited in the PSe₃ groups on the bottom halves of one layer result in the lack of an inversion center for these MPSe₃ crystals. Otherwise, NiPSe₃ has the same symmetry as that of
NiPS₃ (C2/m). Based on the above descriptions, most selenides crystallize into monoclinic or trigonal crystallographic structures. The M IIPSe₃ crystals with R3(-)h symmetry demonstrate the lamellar stacking sequence of “ABC” (Table 1). Hg₂P₂Se₆ adopts a unique structure with tilting of P₂Se₆ dimers, distorting the octahedral cages between the P₂Se₆ units, and its stacking sequence is “ABAB.”

For layered MPX₃ crystals, their interlayer distances (d, i.e., distance between two layers) vary from 6.3 to 6.7 Å (Figure 3c). The ordering of d, namely, dₓMnPSe₃ > dₓFePS₃ > dₓNiPS₃, is same as that of the M radius (r) (rₓMn > rₓFe > rₓNi). Additionally, selenides possess a larger interlayer distance than that of the corresponding sulfides, like dₓMnPSe₃ > dₓMnPS₃.

1.1.2. Polymetallic MPX₃ Compounds

The “M” atoms in MPX₃ crystals could be substituted by other metal atoms, including homocharge and heterocharge substitution. If the size of M₁⁺ and M₂⁺ cations is almost the same, the homocharge substitution will be realized easily. For example, a series of Zn₁₋ₓFeₓPS₃, Zn₁₋ₓNiₓPS₃ (0 ≤ x ≤ 1),[29] and CdₓFe₁₋ₓP₂S₆ (0 ≤ x ≤ 1) [42] has been obtained. Significantly, the MPX₃ structural type also shows that one M₂⁺ could be replaced by a couple of heterocharge metal atoms, namely, 1/2 M₁⁺ and 1/2 M₃⁺. M₁ includes Ag⁺, Cu⁺, and M₃⁺ contains In₃⁺, V³⁺, Sc⁺, and Cr³⁺, etc. The structure of the mixed-cation M₁M₃[Pi₄P₂S₆]₄⁻ compounds is easily tuned. In the 1980s, the synthesized AgInP₂S₆[43] and AgScP₂S₆[42] crystals were identified as trigonal (P1(-)3c) and centrosymmetric structures at room temperature. Of special note is that the Cu⁺ cations based Cu₃M₃[P₂S₆]₄⁻ compounds are unique. For instance, there are three possible Cu⁺
sites in CuInP$_2$S$_6$ and the temperature could affect the occupancy.$^{[44]}$ The Cu atom hopping motions have indirectly been proved with single-crystal X-ray diffraction. When the temperature is above 315 K, the Cu$^+$ occupancy splits evenly into the upper and lower sites. Otherwise, the upper site is preferentially filled at $T < 315$ K. Compared to the midplane of the lamella, the Cu$^+$ cations were shifted upward by 1.58 Å, while the In$^{III}$ shifted in the opposite direction by 0.2 Å. Two polar sublattices, which are formed by partial compensation of the two different cations, produce ferrielectric materials due to the huge spontaneous polarization in the stacking direction. However, in CuCrP$_2$S$_6$ and CuVP$_2$S$_6$ crystals, the shifts and transitions are different.$^{[45,46]}$ Of the M$^{II}$P$_2$S$_6$ crystals, most of them exhibit an ABAB stacking sequence with various space groups. Notably, AgVP$_2$S$_6$ and AgCrP$_2$S$_6$ compounds have buckled crystal structures, likely resulting from the much larger Ag$^{+}$ (1.15 Å) ions than the Cr$^{3+}$ (0.62 Å) and V$^{3+}$ (0.64 Å).$^{[47]}$ Thus, Ag atoms do not vary their locations within the sulfur-defined octahedral but they are limited to the center of the layers. Similarly, M$^{III}$P$_2$Se$_6$ shows the structures that are depicted in Figure 1. The compounds of CuAlP$_2$Se$_6$, AgAlP$_2$Se$_6$, and AgCrP$_2$Se$_6$ are reported to exhibit random cation ordering, which does not exist in the other alloyed compounds. Their crystal structure and stacking sequences are shown in Table 2. Exceptionally, the existence of three temperature phases (Figure 4) occur in CuBiP$_2$Se$_6$.$^{[48]}$ Their stacking sequences are ABAB (298 K, P3$\overline{1}$-hc), ABCDEF (173 K, R3$\overline{1}$-hh), and ABCDEFGHJKLM (97 K, R3$\overline{1}$-hc), respectively, suggesting the extended stacking of six to twelve layers before the observed translational symmetry at low temperature.

### 1.2. Unique Properties of MPX$_3$ Compounds

Owing to the special crystal structure of MPX$_3$ compounds, many important features, including electrical, magnetic, and optical properties, are demonstrated.$^{[10]}$ On the one hand, the number of electrons in the outermost shell or d orbital of the metal elements constituted in MPX$_3$ contributes to their unique properties. On the other hand, the $[P_2X_6]^{4-}$ provides a weak ligand field, resulting in a high spin state of the metal atoms.$^{[49,50]}$ Accordingly, a plethora of results about the magnetism of these materials are published from the perspective of experiments and calculations. The electronic configuration varies corresponding to the different cations. These features will be discussed in the following section.

#### 1.2.1. Electronic Structure

The fascinating electronic band model of MPX$_3$ layered compounds aroused extensive attention in 1980s.$^{[51]}$ The electronic energy-band scheme of the MPX$_3$ family, e.g., MnPS$_3$, FePS$_3$, and NiPS$_3$, has been studied through the vacuum ultraviolet reflectivity spectra and X-ray absorption spectra. In terms of the molecular orbital and crystal-field theories, Khumalo and Hughes$^{[51]}$ found that high-spin divalent M ions are octahedrally coordinated, and the octahedral ligand of $[P_2S_6]$ field splits the $d^5$ (Mn$^{2+}$) orbitals into $t_{2g}^3$ and $e_g^2$, $d^6$ (Fe$^{2+}$) orbitals into $t_{2g}^4$ and $e_g^2$, and $d^6$ (Ni$^{2+}$) orbitals into $t_{2g}^6$ and $e_g^2$. The energy level scheme shown in Figure 5a$^{[50]}$ demonstrates the energy level of $[P_2S_6]^{4-}$ clusters and the localized 3d levels of M$^{III}$ ions. Irrespective of the metal 3d levels, the valence band and conduction band edges consist of the bonding and the antibonding levels derived from the P–P bonds. In the ionic band-model scheme with divalent metal cations, the P–P pair possesses a valence of +8, suggesting that one electron in P atom contributed to the formation of chemical bond between two P atoms.$^{[52]}$ This electronic structure calculated from the ionic extreme of the Wilson–Yoffe band model was adopted to explain the unusual optical absorption spectra, which reveals that the MPS$_3$ compounds exhibit semiconducting

---

**Table 1. Structural information for the 2D layered M$^{III}$PX$_3$ crystals.**

| Components | S based | Components | Se based |
|------------|---------|------------|----------|
|            | Crystal structures | Space group | Stacking | Ref. | Crystal structures | Space group | Stacking | Ref. |
| ZnPS$_3$   | Monoclinic | C2/m | AAA | [117] | ZnPSe$_3$ | Rhombohedral | r$_3$ | ABC | [89] |
| CdPS$_3$   | Monoclinic | C2/m | AAA | [118] | CdPSe$_3$ | Rhombohedral | r$_3$ | ABC | [41] |
| MnPS$_3$   | Monoclinic | C2/m | AAA | [118] | MnPSe$_3$ | Rhombohedral | r$_3$ | ABC | [39] |
| FePS$_3$   | Monoclinic | C2/m | AAA | [118] | FePSe$_3$ | Rhombohedral | r$_3$ | ABC | [39] |
| NiPS$_3$   | Monoclinic | C2/m | AAA | [41] | NiPSe$_3$ | Monoclinic | C2/m | AAA | [41] |
| VPS$_3$    | Monoclinic | C2/m | AAA | [89] | VPSe$_3$ | – | – | – | – |
| CoPS$_3$   | – | – | – | – | CrPSe$_3$ | Monoclinic | C2/m | AAA | [41] |
| CoF$_3$    | Monoclinic | C2/m | AAA | [89] | CoF$_3$ | – | – | – | – |
| MgPS$_3$   | Monoclinic | C2/m | AAA | [89] | MgPSe$_3$ | Rhombohedral | r$_3$ | ABC | [89] |
| PdPS$_3$   | Monoclinic | C2/m | AAA | [89] | PdPSe$_3$ | – | – | – | – |
| SnPS$_3$   | Monoclinic | C2/m | AAA | [118] | SnPSe$_3$ | – | – | – | – |
| HgP$_3$    | Triclinic | – | AAA | [37] | HgPSe$_3$ | Monoclinic | C2/c | ABAB | [37] |

*The c stacking direction; – denotes data not mentioned in the publications.*
behavior. Further refined Wilson–Yoffe model and extended Huckel model[52] were utilized to estimate a band structure. These MIIIPX3 (M II: first raw series transition metals) compounds possess similar electronic band structures. Some of the known semiconducting MPX3 compounds have been surveyed and collected in Table 3. The value of their bandgaps ranges from 1.3 eV for FePS3 to 3.5 eV for CdPS3.[49] Compared with the bandgaps of sulfides, those of selenides are smaller due to the relative electronegativity of S and Se atoms. It can be seen that the value of the bandgap is closely related to the metal cations present in the compound. Additionally, in 1996, Zhukov et al.[53] calculated and discussed the relation between the electronic structure and the spin polarization in metal ions. The linear muffin-tin method with the atomic sphere approximation was utilized. The 3d regions of the density of state (DOS) of MPS3, including MnPS3, FePS3, and NiPS3, are displayed in Figure 5b, demonstrating the relative energies of t2g and eg bands and their occupations with the shaded areas. The spin-up states are more stable with lower energy than the spin-down ones, indicating they are at a high-spin configuration, consistent with the results based on experiments.[18,50]

| Components | Crystal structures | Space group | Stacking[a] | Ref. |
|------------|-------------------|-------------|-------------|-----|
| CuInP2S6   | Monoclinic        | C2/c        | ABAB        | [45]|
| AgInP2S6   | Trigonal          | P31c        | ABAB        | [43]|
| CuCrP2S6   | Monoclinic        | C2/c        | ABAB        | [120]|
| CuVP2S6    | Monoclinic        | C2          | AAA         | [46]|
| AgScP2S6   | Trigonal          | P31c        | ABAB        | [42]|
| AgErP2S6   | –                 | –           | –           | –   |
| AgTmP2S6   | –                 | –           | –           | –   |
| AgVP2S6    | Trigonal          | P31c        | AAA         | [122]|
| AgCrP2S6   | –                 | –           | –           | –   |
| CuAlP2S6   | –                 | –           | –           | –   |
| CuBiP2S6   | –                 | –           | –           | –   |
| AgBiP2S6   | –                 | –           | –           | –   |
| AgGaP2S6   | –                 | –           | –           | –   |

[a] The c stacking direction; – denotes data not mentioned in the publications.

Table 2. Structural information for the 2D layered M’MIIIPX3 crystals.

| Components | Crystal structures | Space group | Stacking[a] | Ref. |
|------------|-------------------|-------------|-------------|-----|
| CuInP2Se6  | Trigonal          | P31c        | ABAB        | [119]|
| AgInP2Se6  | Trigonal          | P31c        | ABAB        | [119]|
| CuCrP2Se6  | Monoclinic        | C2/m        | AAA         | [119]|
| CuVP2Se6   | –                 | –           | –           | –   |
| AgScP2Se6  | Trigonal          | P31c        | ABAB        | [119]|
| AgErP2Se6  | –                 | –           | –           | –   |
| AgTmP2Se6  | –                 | –           | –           | –   |
| AgVP2Se6   | Monoclinic        | C2          | AAA         | [123]|
| AgCrP2Se6  | –                 | –           | –           | –   |
| CuAlP2Se6  | –                 | –           | –           | –   |
| CuBiP2Se6  | –                 | –           | –           | –   |
| AgBiP2Se6  | –                 | –           | –           | –   |
| AgGaP2Se6  | –                 | –           | –           | –   |

[a] The c stacking direction; – denotes data not mentioned in the publications.

Figure 4. a) View of a single CuBiP2Se6 layer down the c-axis [(001) direction] showing the ordered arrangement of the metal ions (top) and the immediate coordination environment of Cu+ and Bi3+ in CuBiP2Se6 at room temperature. b) 298 K, c) 173 K, and d) 97 K structures of CuBiP2Se6 viewed down the[110] direction. Reproduced with permission.[48] Copyright 2005, American Chemical Society.
From the perspective of band theory, the orbital projected partial DOS of single-layer MnPS$_3$, FePS$_3$, and NiPS$_3$ are demonstrated in Figure 6,[54] revealing that the $s$ and $p$ orbitals of the P atoms mainly contribute to the conduction-band edges, while the top of valence band is significantly contributed by the chalcogen’s atomic orbitals. Notably, considering the specific composition and magnetic configuration of these MPX$_3$ materials, the edges of valence band and conduction band are dominated by metal, phosphorus, or chalcogen atoms. The crystal field splitting of the $d$-orbitals and the filling fractions affect their electronic structures near the Fermi level.[54] The ab initio calculations conducted by Chittari et al.[54] predict that most bandgaps of the anti-ferromagnetic MPX$_3$ crystals decrease with the increase of the atomic number of the chalcogen. Thus, half-metallic structure with ferromagnetic states or nonmagnetic metallic states is properly obtained in some cases.

Regarding other metals, e.g., Mg and Zn based MPX$_3$ structures, their electronic DOS and orbital contribution are somehow different. MgPS$_3$ contains no $d$ electrons. Its valence band consists primarily of S and Mg states, and S and P states dominate its conduction band.[55] Recently, the band diagram for CuInP$_2$S$_6$ was calculated by using density functional theory (DFT)-based ab initio theory to simulate the Jahn–Teller effect, which would make a contribution to the ferroelectric ordering of CuInP$_2$S$_6$.[56]

### Table 3. Reported calculated and experimental bandgaps for various MPX$_3$ compounds.

| Components | Bandgaps$^{[20]}$ | Experimental | Type | Indirect/Direct |
|------------|------------------|--------------|------|-----------------|
| ZnPS$_3$   | 3.30 ML (HSE06)$^{[93]}$ | –3.34 –6.64 | $E_g$ | Indirect |
| CdPS$_3$   | 3.03 ML (HSE06)$^{[93]}$ | –3.70 –6.73 | $E_g$ | Indirect |
| MnPS$_3$   | 3.05 ML (HSE06)$^{[54]}$ | – – | $E_g$ | Direct |
| FePS$_3$   | 2.54 ML (HSE06)$^{[21]}$ | – – | $E_g$ | Indirect |
| NiPS$_3$   | 3.01 ML (HSE06)$^{[21]}$ | – – | $E_g$ | Indirect |
| VPS$_3$    | 2.50 ML (HSE06)$^{[64]}$ | – – | $E_g$ | Indirect |
| CuPS$_3$   | 1.76 ML (HSE06)$^{[64]}$ | – – | $E_g$ | Indirect |
| MgPS$_3$   | 3.94 ML (HSE06)$^{[93]}$ | –3.07 –7.01 | $E_g$ | Direct |
| CuInP$_2$S$_6$ | – – | 2.9$^{[125]}$ | $E_g$ | Direct |
| AgScP$_2$Se$_6$ | 3.16 ML (HSE06)$^{[93]}$ | –3.55 –6.71 | $E_g$ | Direct |
| AgBiP$_2$Se$_6$ | – – | 1.2$^{[125]}$ | $E_g$ | Indirect |
| AgInP$_2$Se$_6$ | 2.41 ML (HSE06)$^{[93]}$ | –3.65 –6.06 | $E_g$ | Indirect |
| CdPSe$_3$  | 3.03 ML (HSE06)$^{[54]}$ | –3.70 –6.73 | $E_g$ | Indirect |
| ZnPSe$_3$  | 2.32 ML (HSE06)$^{[93]}$ | –3.71 –6.02 | $E_g$ | Indirect |
| FePSe$_3$  | 1.48 ML (HSE06)$^{[54]}$ | – – | $E_g$ | Indirect |
| MnPSe$_3$  | 2.24 ML (HSE06)$^{[54]}$ | – – | $E_g$ | Indirect |
| VPS$_3$    | 2.10 ML (HSE06)$^{[54]}$ | – – | $E_g$ | Indirect |
| NiP$_2$Se$_3$ | 2.22 ML (HSE06)$^{[21]}$ | – – | $E_g$ | Indirect |
| CuP$_2$Se$_3$ | 0.56 ML (HSE06)$^{[54]}$ | – – | $E_g$ | Indirect |
| MgP$_2$Se$_3$ | 2.97 ML (HSE06)$^{[93]}$ | –3.38 –6.35 | $E_g$ | Direct |
| CuBiP$_2$Se$_6$ | – – | 1.2$^{[64]}$ | $E_g$ | Indirect |
| AgBiP$_2$Se$_6$ | – – | 1.4$^{[64]}$ | $E_g$ | Indirect |
| AgScP$_2$Se$_6$ | 2.66 ML (HSE06)$^{[93]}$ | –3.79 –6.45 | $E_g$ | Direct |
| AgInP$_2$Se$_6$ | 1.77 ML (HSE06)$^{[93]}$ | –4.03 –5.80 | $E_g$ | Indirect |

ML denotes the “monolayer” of MPX$_3$. B denotes the “bulk crystal” of MPX$_3$.

**1.2.2. Optical Properties**

The research on the optical properties of layered MPX$_3$ crystals started in the early 1880s.[57] Piacentini et al.[57] collected the optical absorption spectra in the energy range 0–5.4 eV for NiPS$_3$ at different temperatures (300, 78, and 4.2 K). The features observed in the spectrum were interpreted to explain the transitions within the different Ni$^{3+}$ 3d levels and transitions between the S $3p_d$ valence states and the Ni$^{3+}$ 3d empty states ($e_g$ orbital) (Figure 5a). Furthermore, the study about the Raman spectra of
various layered 2D materials is a hot topic. As a popular characterization tool, the features present in the Raman spectra are helpful to estimate the thickness of nanosheets, such as graphene and TMDs. Du et al. studied the Raman spectra of FePS$_3$ nanosheets with different thicknesses, revealing the strong interlayer vibrations in three-layered FePS$_3$ and stable structure of monolayer FePS$_3$ under ambient conditions (Figure 7a). The comprehensive investigation of the layer-number and temperature dependent Raman spectra shows a magnetic persistence in FePS$_3$ nanosheets with different layers, including single layered FePS$_3$ nanosheet. But the Neel temperature of the anti-ferromagnetic FePS$_3$ sample reduces from 117 K in bulk to 104 K in the monolayer. Some more works on the Raman spectroscopic study reveal a similar trend for NiPS$_3$ nanosheet which also exhibits a substantially varying feature depending on the number of layers. A remarkable linear relation is found between the Raman intensity of the peak for A$_g$ mode of NiPS$_3$ on a sapphire substrate and the thickness in Figure 7b,c which provides a simple way to estimate their thickness.

1.2.3. Magnetism

Recently, the discovery and characterization of magnetism of novel 2D crystals have been a major research direction. Ultimately, the magnetic functionality of these 2D materials is employed for fabricating spintronic or magnetoelectronic applications. MPX$_3$ members, being an important family of layered 2D materials, have potential application in low-dimensional magnetic and spintronic devices. Until now, experimental studies and theoretical calculations of the magnetic properties of MPX$_3$ have been widely performed. The experimental studies on magnetic properties were mainly focused on the MPX$_3$ with bulk crystals, while the theoretical calculations of the spin-state were concentrated on single-layered MPX$_3$ nanosheets. There are three types of magnetic moments-distributions that were proposed for the MPX$_3$ crystals in 1900s. In NiPS$_3$ and CoPS$_3$ monolayers, double parallel ferromagnetic chains are anti-ferromagnetically coupled (type I) with each other. For MnPS$_3$ layers, a magnetic ion anti-ferromagnetically coupled with the three nearest neighbors

---

Figure 6. Orbitally projected partial density of the states (PDOS) of a) MnPS$_3$, b) FePS$_3$, and c) NiPS$_3$ calculated for self-consistently converged ground-state magnetic configurations. Reproduced with permission. Copyright 2016, American Physical Society.

Figure 7. a) Raman spectra of bulk and monolayer FePS$_3$ obtained with a 532 nm laser at ≈77 K. Reproduced with permission. Copyright 2015, American Chemical Society. b) Raman spectra of nanosheets on sapphire substrate with varying thickness from 2.1 to 45.5 nm. c) The thickness dependence of relative intensity (red curve) and Raman shift (blue curve) of selected modes in (b). Reproduced with permission. Copyright, 2017, Wiley-VCH.
in the layer (type II) and their net magnetic moments pointing vertically to the basal planes. In FePS$_3$, each Fe$^{2+}$ ion is ferromagnetically coupled with two of the three nearest neighbors in single layer. Meanwhile, each plane is anti-ferromagnetically coupled to adjacent interplanar ones, which is contrary to the type I structure (type III). Meanwhile, FePS$_3$ has been of interest for its realization of the anti-ferromagnetic 2D Ising model on a honeycomb lattice.$^{[64,69]}$ As temperature decreases across $\approx$118 K, FePS$_3$ undergoes a conversion from the paramagnetic to the antimagnetic phase.$^{[59]}$ Magnetic measurement shows that bulk Ni, Fe, Mn, and Co based MPS$_3$ or MPSe$_3$ have been found to be anti-ferromagnetic with Neel temperatures ($T_N$) at a range of 82–155 K.$^{[29,39,70]}$ Additionally, the magnetic properties of the MPX$_3$ crystal are affected by the test conditions and magnetic field intensity. Taking the NiPS$_3$ crystal as an example, some previous results demonstrate$^{[64,71]}$ that the susceptibility was a function of temperature and it was anisotropic above $T_N$. Conversely, Wildes et al.$^{[72]}$ found that the susceptibility is isotropic above the $T_N$ ($T_N = 155$ K) while it becomes anisotropic below the $T_N$ with an applied field of 0.1 T along three high symmetry directions, a, b, and c (Figure 8b).

Most bulk MPS$_3$ (M = Ni, Fe, Co, and Mn) compounds are anti-ferromagnetic below their $T_N$ and are paramagnetic above the $T_N$. As is shown in Figure 8c,$^{[29,66]}$ their magnetic susceptibility was conducted at a field of 1000 Oe. Parameters such as apparent total spin S assuming zero orbital moment, the magnetic moment, Neel temperature, and Weiss constant could be evaluated from the susceptibility data. The Weiss constant of MnPS$_3$ ($-245$ K), CoPS$_3$ ($-223$ K), and NiPS$_3$ ($-712$ K) is negative while it is a positive value for FePS$_3$ (16 K), indicating the existence of ferromagnetic correlations. However, some compounds, such as CdPS$_3$, ZnPS$_3$, and SnPS$_3$, in this family exhibit diamagnetism under any temperature because of the core electrons. The magnetic parameters of these bulk MPX$_3$ compounds are illustrated in Table 4.

The magnetism of the MPX$_3$ crystals in the 2D limit has attracted tremendous attention recently. In this regard, MPX$_3$ monolayers are studied by theoretical calculations except for FePS$_3$ which has an experimental evidence as well. These

| Compound  | Type of magnetism | Neel temperature [K] | Magnetic moment [µB] |
|-----------|-------------------|----------------------|---------------------|
| NiPS$_3$  | AFM$^{[27]}$       | 155$^{[27]}$          | 3.9$^{[49]}$        |
| MnPS$_3$  | AFM$^{[27]}$       | 78$^{[27]}$           | 3.1$^{[73]}$        |
| MnPSe$_3$ | AFM$^{[39]}$       | 74 ± 2$^{[19]}$       | 4.74$^{[27]}$       |
| FePS$_3$  | AFM$^{[19]}$       | 118$^{[11]}$          | 5.0$^{[27]}$        |
| FePSe$_3$ | AFM$^{[19]}$       | 119 ± 1$^{[11]}$      | 4.9$^{[27]}$        |
| CoPS$_3$  | AFM$^{[49]}$       | 137$^{[11]}$          | –                   |
| AgVP$_2$S$_6$ | AFM$^{[19]}$       | 10–15$^{[12]}$       | –                   |
| AgCoP$_2$S$_6$ | AFM$^{[23]}$   | 20$^{[11]}$           | –                   |
| CuCoP$_2$S$_6$ | AFM$^{[11]}$ | 42$^{[11]}$           | –                   |
| CuCoP$_2$Se$_6$ | AFM$^{[11]}$ | 40$^{[11]}$           | –                   |

$^{[49]}$The experimental data based on bulk MPX$_3$ crystals.
studies mainly focus on monolayer magnetic ordering, the relationship between band structure and magnetic phase, and modulation techniques. Chittari et al. \cite{54} studied the electronic and magnetic properties of single-layer MPX$_3$ ($M = V, Cr, Mn, Fe, Co, Ni, Cu, and Zn; X = S, Se, Te}$) via first-principles calculations. For the MPX$_3$ monolayer, there are four magnetic orderings (illustrated in Figure 9a–d) which include ferromagnetism (FM), Neel anti-ferromagnetism (AFM), zigzag AFM (zAFM), and stripy AFM. As to the FM ordering, all the spin-states of the metal atoms have the same orientation. In addition, the spin-states in the nearest neighbor metal atoms have an opposite orientation for the Neel anti-ferromagnetic ordering. The zigzag AFM ordering, where the spin-state of the adjacent metal atom chains along the zigzag direction has an opposite orientation, is different from the previous two. However, the spin-state of the adjacent metal atoms for the stripy anti-ferromagnetic ordering chain along the armchair direction has an opposite orientation. According to the DFT results,\cite{54} monolayers VPX$_3$, MnPX$_3$, and NiPX$_3$ ($X = S, Se, and Te$) prefer the AFM ordering, while the nonmagnetic state of monolayer CoPX$_3$, CuPX$_3$, ZnPX$_3$, and FePX$_3$ is more stable than the others, except for FePS$_3$, which prefers the zAFM ordering. Beyond that, monolayers CrPS$_3$ and CrPSe$_3$ are ferromagnetic. Recently, several studies on spin properties using Raman spectroscopy have reported on spin–phonon coupling and quasielastic scattering owing to the difficulty in directly measuring the magnetic behaviors of atomically thin 2D crystals.\cite{35,73} In the Raman spectra of magnetic crystals, the appearance of two magnon scattering and change of the Raman peak positions or intensities suggest ordered spin states.\cite{35,73} Particularly, the changes in the Raman spectrum of anti-ferromagnetic materials concomitant with a magnetic transition are good signals for monitoring their magnetic ordering. Based on this method, Wang et al.\cite{35} verify the magnetic persistence in monolayer FePS$_3$ nanosheets, revealing that the intralayer spin arrangement dominates the magnetic structure. The FePS$_3$ nanosheets with different layers were studied by monitoring the intensity of the Raman peaks ($P_{1a}$), which result from zone folding because of AFM ordering at the transition temperature.\cite{35} Lee et al. found that it exhibits an Ising type AFM ordering when its thickness reduces to the monolayer (0.7 nm) (Figure 9e–g). Moreover, the transition temperature ($T_N \approx 118$ K) remains irrelevant to the thickness of FePS$_3$. This result indicates that the weak interlayer interaction plays a negligible role on the anti-ferromagnetic ordering.

Notably, there is a certain correlation between band and magnetic structure of monolayer MPX$_3$,\cite{54} proved by the first principle calculation. Monolayer MPX$_3$ nanosheets are generally metallic with ferromagnetic ordering. Particularly, monolayer CoPX$_3$ turned out to be nonmagnetic. The band structures of various monolayer MPX$_3$ (Figure 10a) show that the nonmagnetic ones (with green bands) can be metal (Co-based and Cu-based MPX$_3$ compounds), semiconductor (FePX$_3$), or insulator (ZnPX$_3$). The semiconducting ones, such as VPX$_3$, MnPX$_3$, NiPX$_3$, and FePX$_3$ exhibit anti-ferromagnetic ordering, while, Cr-based compounds show ferromagnetic ordering with a metallic phase.

![Figure 9. Top view of different magnetic ordering arrangements: a) ferromagnetic, b) Neel anti-ferromagnetic, c) zigzag anti-ferromagnetic, and d) stripy anti-ferromagnetic. The black and white spheres represent up and down spins, respectively. The red circles identify the nearest neighbors (NN) of the central metal site, the navy blue circles (dashed–dotted) identify the second-nearest neighbors, and the light blue circles identify the third-nearest neighbors. (a)–(d) Reproduced with permission.\cite{54} Copyright 2016, American Physical Society. e) $a$–$b$ plane of monolayer FePS$_3$. Definitions of the incident ($\alpha$) and scattered ($\beta$) polarization angles are shown. f) Polarized Raman spectra of bulk FePS$_3$ at 80 and 300 K in parallel polarization configurations ($\alpha = \beta$), for $\alpha = 45^\circ$ and $90^\circ$, respectively. g) Temperature dependence of the $P_{1a}$ peak height at different thicknesses. (e)–(g) Reproduced with permission.\cite{35} Copyright 2016, American Chemical Society.](image-url)
The magnetic phase transition can also be realized through applying stress or modulating the carrier concentration. Chittari et al.\cite{54} found that applied strains can act as switchers to give rise to transitions or change in the stability of the magnetic phases. The compressive and expansive biaxial strains can be obtained through enlarging rectangular unit cell. Similarly, scaling either in the zigzag or armchair directions is used to obtain the uniaxial strains (Figure 10b). Theoretically, huge strains are required to tune the magnetic behavior of MnPS$_3$. However, for other systems, such as CrPS$_3$, FePS$_3$, FePSe$_3$, and NiPS$_3$, the transitions of magnetic properties can be realized when a small strain is applied. Moreover, Yang and co-workers\cite{28} predicted that controlling the carrier concentration will lead to a magnetic phase transition from the AFM phase at the ground state to the FM phase after the observation is made via increasing the density of the carriers ($1.4 \times 10^{14}$ cm$^{-2}$) on the MnPSe$_3$ nanosheet (Figure 10c).

Alloying is also an approach to alter the magnetic properties for these MPX$_3$ materials. The nonmagnetic metal element (Mn) is alloyed with ZnPS$_3$ to obtain the Mn$_{x}$Zn$_{1-x}$PS$_3$ crystal.\cite{75} The alloying extent, namely, the value of $x$, usually has an influence on the value of $T_N$ and the magnetic phase of the alloyed MPX$_3$. The study of the Mn$_{x}$Zn$_{1-x}$P$_2$S$_6$ crystal demonstrates that its $T_N$ value is related to the concentration of Zn atoms. It decreases concomitantly when the concentration of the nonmagnetic cation species increases. A $T_N$/applied-field(Hz)/dilution magnetic phase diagram for Mn$_{x}$Zn$_{1-x}$P$_2$S$_6$ is shown in Figure 11a. In this diagram, the enclosed region is the AFM region with a percolation threshold of $x = 0.7$. A high-order paramagnetic phase and a disordered paramagnetic phase will appear with a large magnetic field and high temperature, respectively. Likewise, the low percentage ($x < 0.7$) of Mn atoms also introduces the paramagnetic phase. Above the top surface of the AFM region, the spin-flop phase dominates the diagram. The other is alloying MPX$_3$ with magnetic metal for Mn$_{1-x}$Fe$_x$PS$_3$\cite{76} and Fe$_{0.5}$Ni$_{0.5}$PS$_3$\cite{68}. The substitutive magnetic metal atom, like Mn and Fe atoms, in alloyed MPX$_3$ is more likely to bring about a magnetic glass phase or a spin glass phase. The alloyed Mn$_{1-x}$Fe$_x$PS$_3$ exhibits a spin glass state when a portion of the Mn atoms are substituted by other magnetic Fe atoms (Figure 11b).\cite{76} It is clear that the magnetic phase of Mn$_{1-x}$Fe$_x$PS$_3$ changes with the increase of the iron concentration. Obviously, the anti-ferromagnetic phases exist in the ranges of $0.0 \leq x \leq 0.2$ and $0.8 \leq x \leq 1.0$. The spin glass state is in the range of $0.5 \leq x \leq 0.6$ and the reentrant spin glass state is confined to the ranges of $0.3 \leq x \leq 0.45$ or $0.6 \leq x \leq 0.7$ at a low temperature. Apart from the spin glass state, a magnetic glass state may appear in a magnetically substituted MPX$_3$ system. Goossens et al.\cite{68} found that this alloyed system shows obvious hysteresis for Fe$_{0.5}$Ni$_{0.5}$PS$_3$ in the transition temperature and
The temperature/applied-field ($H = H_z$)/dilution phase diagram for Mn$_{1-x}$Zn$_x$PS$_3$. Reproduced with permission. Copyright 1998, IOP Publishing.

Figure 11. a) The temperature/applied-field ($H = H_z$)/dilution phase diagram for Mn$_{1-x}$Zn$_x$PS$_3$. SF, AF, and P stand for the spin-flop, anti-ferromagnetic, and paramagnetic phases, respectively. Reproduced with permission. Copyright 1998, IOP Publishing. b) Magnetic phase diagram of the Mn$_{1-x}$Fe$_x$PS$_3$. The notations SC, RSG, AF, and Para show a spin glass, a re-entrant spin glass, an anti-ferromagnetic ordered, and a paramagnetic phase, respectively. Reproduced with permission. Copyright 2007, Elsevier B.V. c) Magnetic susceptibility of a Fe$_0.5$Ni$_0.5$PS$_3$ powder, measured in a field of 1 T under a range of conditions. The directions of temperature change were as follows: (1) warming after cooling in the zero field (ZFCW); (2) cooling in a field (FCC); and finally (3) warming after cooling in a field (FCW). Reproduced with permission. Copyright 2013, Elsevier B.V.

One of the interesting phenomena in metal thiophosphates or selenophosphates is the presence of ferroelectric ordering.

1.2.4. Ferroelectricity

One of the interesting phenomena in metal thiophosphates or selenophosphates is the presence of ferroelectric ordering. Usually, the ferroelectric ordering only appears on M$_1$M$_2$P$_2$X$_6$ crystals, such as CuInP$_2$Se$_6$, CuInP$_2$S$_6$, CuBiP$_2$Se$_6$, and AgBiP$_2$S$_6$. A list of all M$_1$M$_2$P$_2$X$_6$ compounds and their ferroelectric ordering is illustrated in Table 5. Especially, the ferroelectric ordering of CuInP$_2$S$_6$ has been widely studied. The structure of CuInP$_2$S$_6$ is shown in Figure 12a. Cu$^+$ atoms can move among three sites, as follows: first site is closest to the center of the octahedron (Cu1), the second site is further off-center (Cu2), and the third site is in the interlayer space (Cu3).

The transition from order to disorder occurs at 315 K and the symmetry of the CuInP$_2$S$_6$ phase is apparent because the first site has two positions, i.e., “up” and “down” positions (Figure 12b), and the third site shows an equal position of both “up” and “down”. When the CuInP$_2$S$_6$ is cooled below 315 K (Figure 12c), the motion of the inter-site Cu is restricted to the Cu$_{1s}$ sublattice in the “up” position with a compensatory shift of the In$_3^+$ sublattice to the opposite polarity, leading to the formation of a non-centrosymmetric ferroelectric phase.

In addition, hydrostatic pressure is also applied to realize the structural phase transition of CuInP$_2$S$_6$. Its ferroelectric transition temperature ($T_c$), demonstrating the linear increment along with the strength of pressure ($\partial T_c/\partial P = 210$ K GPa$^{-1}$), can be tuned with pressure. This result indicates the transition from order to disorder nature and the coupling effect of ferroelectric dipoles across the vdW gap. Notably, the ferroelectric polarization can occur in CuInP$_2$S$_6$ crystal when the temperature is above the room temperature. This is unique for the vdW layered crystals. The domain structure, switchable polarization, and hysteresis loops in the ambient and ultrahigh vacuum scanning probe microscopy spectra, studied by Belianinov et al., directly reveal stable, ferroelectric polarization of this crystal. They also found that the domain structure of flakes, whose thickness is $>100$ nm, is similar to the cleaved bulk surfaces, whereas polarization disappears when its thickness is below 50 nm, which is originated from the instability of polarization under the depolarization field. The piezoresponse force microscopy studies show that the polarization switching at high bias is also related to the ionic mobility and the ferroelectric domains are persistent across several hundreds of layers. The ferroelectric properties are also shown in the MP$_2$S$_6$ class. The P$_2$S$_6$ bond possesses a weaker degree of covalence than that in P$_2$S$_6$ bonds. Thus, the Cu$^+$ ion displacement occurs at the lower temperature.
temperature phase.\textsuperscript{[44,29]} Phase transitions in the CuInP\textsubscript{2}Se\textsubscript{6} compound contain a second-order phase transition at 248 K (T\textsubscript{c}) and a first order transition at 236 K (T\textsubscript{1}), which is lower than that (T\textsubscript{c} = 315 K) in CuInP\textsubscript{2}S\textsubscript{6}.\textsuperscript{[44]}

1.2.5. Intercalation Effect

Intercalation is a reversible chemical process to insert foreign species, including molecules and ions, into the crystal gap. The remarkably wide van der Waals gaps existing in MPX\textsubscript{3} compounds create a suitable platform for practical realization of intercalation chemistry. For instance, alkali metals are shown to chemically and electrochemically intercalate into the MPX\textsubscript{3} crystals.\textsuperscript{[85]} Among them, NiPS\textsubscript{3}, FePS\textsubscript{3}, and CoPS\textsubscript{3} can easily react with butyl-lithium, whereas CdPS\textsubscript{3}, ZnPS\textsubscript{3}, and MnPS\textsubscript{3} do not. Considering the structure of MPS\textsubscript{3} crystals, filling of all the octahedral sites in the vdW gaps by the lithium cations should lead to the formation of product Li\textsubscript{1.5}MPS\textsubscript{3} (i.e., Li\textsubscript{3}M\textsubscript{2}P\textsubscript{2}S\textsubscript{6}). At the same time, their magnetic, optical, and electrical properties after lithium intercalation were investigated in detail.\textsuperscript{[49]} The intercalation can result in the occurrence of negative free carriers and a decrement of magnetic susceptibility in Li\textsubscript{i}NiPS\textsubscript{3}. In addition to these fundamental interests, they can be used in lithium batteries.\textsuperscript{[23,86]} A high formation energy, which is related to the difference between the Li\textsuperscript{+}/Li potential and the accepting d level, for the intercalation trigger, a high potential of the host compound.\textsuperscript{[87,88]} Thus, the nickel phase was proved to be best candidate used in Li batteries. On the one hand, the ideal size of vdW gap presents the appropriate space to accommodate the Li\textsuperscript{+} ions without expansion. The unchanged cell volume is a strong advantage of the MPS\textsubscript{3} materials used as a cathode. On the other hand, the chemistry of MPX\textsubscript{3} compounds has an ionic nature and, hence, they can be viewed as ionic salts with the metal ions being connecting together by [P\textsubscript{2}S\textsubscript{6}]\textsuperscript{4−} bridging ligands.\textsuperscript{[29]} Therefore, the high mobility of the metal cations in the ion-exchange mechanism describes the intercalation.

2. Synthesis Methods

The fundamental exploration of functional materials with respect to their properties and applications greatly depends on the development of facile and reliable synthesis methods. Particularly, regarding the case of 2D layered materials, the achievement of an atomic thickness with a lateral size of up to micrometers is sought to realize the interesting properties, especially the unique magnetic and electronic properties. Historically, the attempt to synthesize MPX\textsubscript{3} materials can be traced back to the late 19th century, which was reported by Friedel\textsuperscript{[37]} who obtained FePS\textsubscript{3} by heating a weighed amount of phosphorus pentasulfide with iron. Later, Ferrand\textsuperscript{[79]} was then able to extend this technique for growing ZnPS\textsubscript{3}, CdPS\textsubscript{3}, and NiPS\textsubscript{3} materials. Though investigation of MPX\textsubscript{3} was held back till the introduction of the vapor growth method by Klingeb et al. in the mid1960s.\textsuperscript{[80]} Yet, the obtained products using the vapor phase or hydrothermal growth methods\textsuperscript{[89]} had micro size. Very recently, techniques such as chemical vapor deposition and exfoliation were introduced in which ultrathin materials of this family were communicated with interesting applications. In the subsequent section, we present the strategies and progress made for growing MPX\textsubscript{3} materials.

2.1. Exfoliation and Intercalation

Micromechanical cleavage is usually used in fabricating ultrathin nanosheets by exfoliating layered bulk crystals by using Scoch tape or force-assisted liquid exfoliation.\textsuperscript{[56,91,92]} In this regard, the cleavage energies of layered MPX\textsubscript{3} and the formation energies of single-layer MPX\textsubscript{1} are essential properties that need to be considered. Du et al. and Liu et al.\textsuperscript{[20,93]} have calculated the cleavage and the formation energies of some 2D layered MPX\textsubscript{3} materials, respectively. The cleavage energies have been calculated by determining the separation between the fractured layer (d) and the original layer (d\textsubscript{0}). As shown in Figure 13a, the trend of increasing cleavage energy is associated with the enlargement of the interlayer separation and ultimately reaches the maximum level. Of note, the cleavage energy of these layered MPX\textsubscript{1} materials, except for FePS\textsubscript{3}, is smaller than that of graphite (\textasciitilde 0.36 J m\textsuperscript{−2}),\textsuperscript{[29]} indicating the suitability of layered MPX\textsubscript{3} materials for exfoliation (Figure 13b). Additionally, the formation energy of layered MPX\textsubscript{1} material is much lower than that of a single-layer MoS\textsubscript{2} (\textasciitilde 0.14 J m\textsuperscript{−2}), that is to say, less formation energy is needed in the process of exfoliation from the bulk materials to single-layer nanosheets (Figure 13c).
Therefore, both the small values of cleavage and formation energies of layered MPX$_3$ materials determine the success in exfoliation of bulk MPX$_3$ crystals to single layered ones.

The successful preparation of graphene by the "Scotch Tape" method[91] has prompted researchers to comprehensively study lots of layered materials. Inspired by this, the micromechanical cleavage technique has been widely utilized to obtain various types of ultrathin nanosheets from the corresponding layered bulk crystals, including TMD (e.g., MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$, etc.),[94] MPX$_3$ (e.g., MnPS$_3$, FePS$_3$, NiPS$_3$, etc.),[20,21,54,95] topological insulators (e.g., Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$, etc.),[96] antimonene,[97] and h-BN.[98] Among the 2D materials preparation routes, this method can be regarded as a nondestructive technique due to the mere physical phenomena (no chemical reaction) occurring during exfoliation. Therefore, successfully exfoliated 2D materials exhibit a clean surface, maintaining the "perfect" crystal quality with little defect site. Moreover, the exfoliations can be made in such a way that the lateral size of the obtained material can be up to dozens of micrometers. Recently, the micromechanical exfoliations of MPX$_3$ materials have been widely reported. As shown in Figure 14a,b, Du et al.[20,93] successfully exfoliated bulk FePS$_3$ crystal to few-layered nanosheets by the "cotch Tape" method. This result can be further confirmed with an optical microscopy photograph and the corresponding AFM topography (Figure 14c,d). Unfortunately, the production yield from micromechanical cleavage technique is quite low with inferior precision and there is restricted controllability for practical application. Additionally, liquid exfoliation has been widely adopted to produce MPX$_3$ nanosheets. Typically, it requires the addition of some small molecules, such as acetone, lithium ions, and surfactants,[99–101] to assist the process of exfoliation. These types of molecules are able to percolate into the interlayer matrix to expand the van der Waals gaps. Figure 14e depicts a schematic illustration of the small molecule assisted liquid exfoliation of MPX$_3$ bulk crystals. The scanning electron microscopy (SEM) image of FePS$_3$ bulk crystals and exfoliated FePS$_3$ nanosheets (Figure 14f,g) corroborate the thinning effect of solvent exfoliation.[102] However, impurities and more defective edge sites would be introduced into the MPX$_3$ nanosheets. This method is not an optimal one for fabricating (photo)electronic devices based on MPX$_3$ semiconductors where impurities and defects are detrimental for realizing of excellent performance.

![Figure 13](image13.png)

**Figure 13.** a) Cleavage energy versus the separation distance. b) Comparison of the saturated cleavage energy between graphite and the compounds MPS$_3$ (pink squares) and MPSe$_3$ (blue stars). Reproduced with permission.[20] Copyright 2015, American Chemical Society. c) Calculated formation energies of single-layer MPX$_3$ as a functional of the corresponding lattice constants (Å), compared with that of MoS$_2$. The blue dashed line indicates the formation energy of MoS$_2$. Reproduced with permission.[93] Copyright 2014, AIP Publishing LLC.

![Figure 14](image14.png)

**Figure 14.** a) Schematic illustration of the typical process with Scotch tape. Reproduced with permission.[129] Copyright 2015, American Chemical Society. b) TEM image and SAED pattern of FePS$_3$. c,d) Optical microscopy photograph and the corresponding AFM topography of FePS$_3$. Reproduced with permission.[100] Copyright 2015, American Chemical Society. e) Schematic illustration of liquid exfoliation of MPX$_3$ bulk crystals. f,g) SEM image of FePS$_3$ bulk crystals and exfoliated FePS$_3$ nanosheets. Reproduced with permission.[102] Copyright 2016, American Chemical Society.
performance. In the field of catalysts, the controllable introduction of impurities and defect sites are believed to enhance the catalytic activity. It, therefore, appears reasonable to suggest that if high yield fabrication of the catalyst via solvent exfoliation is assured, it may lead to excellent catalytic activity.

2.2. Chemical Vapor Growth

A vast majority of MPX₃ compounds with large enough crystals to enable adequate physical characterizations were synthesized through a vapor phase growth technique, i.e., chemical vapor transport (CVT). Stoichiometric amounts of sources, including metal, chalcogen, and phosphorus powders, are located in quartz ampoule along with a transport agent (e.g., iodine) and heated at certain temperature required for the formation of the desired MPX₃. The ampoule is made in such a way that it could host a temperature gradient system, such as T₁ and T₂ (T₁ < T₂), as shown in Figure 15a. In the hotter region (T₂), the precursors form vapors to be transported to the cooler region (T₁) for undergoing reaction. The temperature of the cooler region should be thermodynamically efficient for making the growth of MPX₃ possible, thereby forming a large plate of crystals (Figure 15b). The heating rate is an important parameter in CVT to widen the interlayer distances and control how well the crystallinity is ordered. Ismail et al. adopted the heating rates of 1 and 40 °C min⁻¹ to grow FePS₃ at 650 °C through the CVT. It was found that a slow heating rate is useful to get the FePS₃ with single crystalline phase while the fast heating rate was not. Thus, the slow heating rate induces better crystallinity. As seen from the scanning electron microscopic image (Figure 15c–f), this technique generally gives bulk materials with compact layers of irregular thicknesses. A comprehensive investigation of layered metal phosphorus trisulfides/selenides was recently made by Pumera and co-workers. It can be seen that the growth of different members (with varying the metal or the chalcogen) in the MPX₃ family requires separate optimization of the temperature and heating rate. Figure 15g depicts the Raman spectra as a confirmation tool for the formation of the desired product through the CVT method with appropriate heating rates. The CVT grown MPS₃ phases are featured by prominent Raman modes from P₃S₆ units with D₃d symmetry (3A₁g and 5E₉ Raman active modes). In some cases, a pregrown metal oxide/hydroxide precursor is used as a metal source, which is then mixed with a stoichiometric amount of phosphorus and slight in excess of chalcogen in a quartz ampoule. Liang et al. made use of this method to grow FePS₃, CoPS₃, and NiPS₃. The corresponding precursors of metal hydroxide nanosheets were first synthesized via the hydrothermal method then eventually converted to the MPX₃ form at 520 °C after being mixed with red phosphorus and sulfur powders. Accordingly, the products of FePS₃, CoPS₃, and NiPS₃ with high crystalline nanosheets, having average thickness and lateral sizes of ≈18 and ≈200 nm, respectively, were obtained. The main drawback of CVT is the long duration of the synthesis process. This can be associated with the slow heterogeneous chemical reaction between the metal, chalcogen, and phosphorus atoms. If exactly the stoichiometric amount is taken at the initial stage, the formation kinetics for MPX₃ slows down when the pressure of the gaseous product becomes slow.

Figure 15. a) Schematics of typical chemical vapor transport (CVT) set-up. b) Photos of bulk 2D crystals obtained via the CVT method. Reproduced with permission. Copyright 2016, American chemical society. c–f) SEM images and g) Raman spectra of various samples grown via the CVT method. Reproduced with permission. Copyright 2017, American chemical society.
The equilibrium condition for the product dissociation can also be reached, which limits the practical completion of the reaction. Thus, merely raising the temperature cannot lead to a faster growth route.

A more strategic approach in vapor phase growth is the chemical vapor deposition (CVD) method, in which the chemical constituents first heated to vapor phase and then reacted. The desired product is obtained through controlled reaction of one or more volatile precursors on the surface of suitable substrate. In this situation, volatile by-products are also frequently formed and they can be removed by flowing gas in the reaction, chamber as shown in Figure 16 (top). As far as the growth of MPX₃ materials is concerned, CVD is a very recent technique that enabled the controllable synthesis for various members to fit to the desired applications. A pregrown metal oxide/hydroxide precursor as a metal source is placed at the back zone to meet the incoming vapors of phosphorus and chalcogen from the front zone. The temperature in the front zone requires careful optimization to assure simultaneous vaporization of both P and S/Se sources, which otherwise results in the introduction of impure phases. The temperature is held constant for ≈10 min, as shown in Figure 16a (bottom), for this purpose. Very recently, He and co-workers reported the synthesis of ultrathin NiPS₃ nanosheets on a carbon fiber substrate from Ni(OH)₂ nanosheets, red phosphorous, and sulfur using this approach. Reaction time and temperature play substantial roles in tuning the morphology of the incoming product. Initially, small and irregular sheets with sizes below 500 nm were formed. With the increasing of the reaction time, the product increased in lateral size and the nanosheets were formed. Moreover, the low temperature (below 400 °C) was found to be inefficient to complete the reaction and, hence, ruminants of unreacted hydroxides were observed, whereas a high temperature (above 500 °C) caused etching on the surface of the nanosheet. Given the optimized temperature and time of reaction, the obtained nanosheet has the thickness of ≤3.5 nm with the lateral size of larger than 15 µm. And all the elements (Ni, P, and S) distributed uniformly throughout the material (Figure 16b,d). It is also obvious that the X-ray diffraction peaks match the standard NiPS₃ crystallographic pattern, as is depicted in Figure 16c. Using this approach, the independent growth of metal chalcogenide may occur along with the growth of the desired MPX₃, in some cases. This problem introduces impure phases and defies the realization of controllable growth. A preheating strategy, which assures the formation of fused mixture of chalcogen and phosphorous, can tackle this problem. After preheating, the mixed vapor can subsequently be carried to the back zone to meet the metal precursors, as depicted in the temperature profile of the growth route (Figure 16a, bottom). The growth made through this approach yielded high crystal quality of MnPSe₃ and MnPS₃ nanosheets (Figure 16f). Thus, careful optimization of the temperature profile in CVD confers a facile and successful conversion of oxide/hydroxide precursor to phospho-trichalcogenide with phase purity and high crystal quality.

3. Potential Applications of MPX₃ Compounds

3.1. Catalysis

The MPX₃ materials have received significant attention because of their unique physical and chemical characteristics, which are mainly originated from their energy band model and electronic structure. This peculiar structure endows the MPX₃ materials with excellent magnetic, electronic, optical, and catalytic
properties.\textsuperscript{[21,30,107]} The wide bandgaps (1.3–3.5 eV) and supercolossal specific surface area of MPX$_3$ materials can result in the wide spectrum light absorption, outstanding interfacial reaction activity in photoelectronic properties, and photocatalytic activities. Considering these fascinating properties, the attention of different research groups has been devoted to the rational design of photo(electro)catalysts based on MPX$_3$ compounds. The experimental realization for photo-electrochemical property of SnPS$_3$, FePS$_3$, and NiPS$_3$ was made in early 1980s on their bulk states.\textsuperscript{[25,108]} Recently, Wang et al. successfully synthesized high crystalline quality 2D structured NiPS$_3$ nanosheets with thickness of a few atomic layers and large lateral sizes up to tens of micrometers (Figures 16b–d and 17a–c).\textsuperscript{[36]} The atom resolved high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image shows that sulfur vacancies (7.6\%) are observed in favor of creating more defective catalytic sites. Interestingly, the NiPS$_3$ nanosheets can realize water-splitting without sacrificial agent to produce hydrogen gas. In this system, the H$_2$ evolution rates are $\approx 26.42$ and $6.46\, \mu$mol g$^{-1}$ h$^{-1}$ under Xe light and simulated solar light, respectively (Figure 17d). Furthermore, a proper bandgap is of primary importance for photocatalytic reactions. Based on the optical absorption spectrum, Mott–Schottky plots, and ultraviolet photoelectron spectroscopy, the conduction band energy ($-5.57$ eV vs E$_{\text{vacuum}}$) of the NiPS$_3$ nanosheets is placed above the water reduction (H$_2$/H$_2$O) potential (Figure 17e), which is in a thermodynamically efficient position to generate H$_2$ gas from water. The valence band energy ($-3.61$ eV) is slightly below the oxidation level of H$_2$O to O$_2$ and the presence of sulfur vacancies will suppress the generation of O$_2$ gas via forming strong adsorption with an oxygen intermediate species (Figure 17f). These intermediates can be traced by a spin trapping experiment based on electron spin resonance spectroscopy, which detects the surface hydroxyl radicals.\textsuperscript{[106]} This finding reveals that photogenerated holes would oxidize the H$_2$O molecules adsorbed on the surface of the photocatalysts to hydroxyl radicals, and the road to O=O covalent bond formation for oxygen molecules has not been completed. Thus, much more research on the photocatalytic properties of MPX$_3$ nanosheets should be conducted to realize the overall water splitting activity with excellent performance.

2D MPX$_3$ materials are also utilized as electrocatalysts in hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction, presently.\textsuperscript{[66,100,105]} Their electrocatalytic activity results from the appreciable conductivity and abundant active sites at room temperature.\textsuperscript{[99,105]} More significantly, the atomic-level thickness of the MPX$_3$ materials not only enlarges the specific surface area to expose more active sites but also increases the intrinsic catalytic activity. Song et al.\textsuperscript{[105]} synthesized the bulk materials and corresponding 2D ultrathin nanosheets of Ni$_{1-x}$Fe$_x$PS$_3$ ($x = 0, 0.05, 0.1, 0.15, 1$) via ultrasonication-assisted exfoliation. The SEM and transmission electron microscopy (TEM) images of exfoliated Ni$_{0.9}$Fe$_{0.1}$PS$_3$ nanosheets show several micrometers in the lateral size and clear lattice fringes (Figure 18a–c). The average thickness of the exfoliated Ni$_{0.9}$Fe$_{0.1}$PS$_3$ nanosheets is found to be 4 nm (Figure 18d), indicating that a single nanosheet consists of approximately five layers. The electrochemical tests show that
the FePS₃ and NiPS₃ nanosheets have much poorer electrocatalytic activities compared to the exfoliated Ni₁₋ₓFeₓPS₃ (x = 0.05, 0.1, 0.15) nanosheets that exhibited extremely high HER and OER activity and durability in the aqueous solution of 1 m KOH (Figure 18e–h). This is attributable to the increase of intrinsic conductivity and electrochemical active surface area. Interestingly, the results show that the Ni₀.₉Fe₀.₁PS₃ nanosheets, whose surface would be transformed into hydroxides as the real active species, serve as the OER electrocatalysts in alkaline media.

3.2. Electrochemical Storage

Despite being a very promising future green energy source, hydrogen suffers from the lack of efficient and safe storage systems. Layered compounds, in general, are thought to advance the technology of hydrogen storage owing to their ability to be reversibly intercalated with the corresponding ions. Promising performances were reported using MPX₃ compounds such as MnPS₃,[109] NiPS₃,[24] and FePS₃.[104] Hydrogen is assumed to be adsorbed on the surface, in the micropores, and in the interlayer spacing. The hydrogen sorption capacity over MnPS₃ at different temperatures and pressures can be observed from the work by Ismail et al. in Figure 19a.[109] MnPS₃ is found to exhibit an adsorption capacity of 0.7 wt% within 100 min and the same duration is required to desorb it completely. The capacity reaches to 2.9 wt% at an elevated pressure of 30 bar in 30 min; however, in this case, a longer duration is required for desorption. The hydrogen adsorption/desorption cycles do not affect their crystal structure, but the overall performance is altered by the crystallinity of the material. The effect of crystallinity of the FePS₃ powders in hydrogen sorption at 193 °C is illustrated in Figure 19b.[104] A linear progression can be observed up to 20 bar in the hydrogen sorption isotherm wherein the hydrogen sorption capacity for single crystalline and polycrystalline FePS₃ is recorded as 2.2 wt% and 1.7%, respectively (Figure 18b). A well-ordered single crystalline phase and wider interplanar space are usually associated with better performance for hydrogen sorption efficiency.[104] These findings emphasize the favorability of MPX₃ compounds for hydrogen storage and, hence, many other members can be explored following these promising performances.

MPX₃ compounds find substantial application in secondary Li/Na ion batteries due to their ability to create sufficient paths of lithium ion and exhibit high electronic conductivity with excellent ions mobility (Section 1.2.5). A particularly advantageous feature of this family in lithium batteries emanates from the broader van der Waals gap compared to TMDs, which make the unit cell parameter of the MPX₃ compounds remain unaffected after lithium intercalation.[29,110] Therefore, they provide enough capacity for ions while maintaining structure stable during the charge–discharge cycles. It has also been suggested that the very good Li/Na ion storage for battery application is following the electrochemical reaction involving nine lithium atoms per molecule of MPX₃ intercalation, as follows[22,87,111]

\[
\text{MPX}_3 + 9\text{Li}^+ + 9\text{e}^- \rightarrow 3\text{Li}_3 \text{X} + \text{Li}_2 \text{P} + \text{M}
\]  

(1)

The formation of lithium (the same works for sodium) phosphides and sulfides endows a better conductivity compared to the lithium/sodium oxides that are commonly formed from the metal oxide materials.[23,86] Thus, this family is expected to demonstrate a better rate and cycling performance with high specific capacity. The sufficient electron conduction and paths for lithium ions were corroborated via employing FePS₃ materials for lithium ion battery application.[112] In this set up, a
reversible charge–discharge processes under 0.13 mA cm\(^{-2}\) at room temperature was demonstrated. Furthermore, the work by Yan and co-workers\(^{[23]}\) is a typical experimental report demonstrating the Li/Na ions storage properties of FePS\(_3\), NiPS\(_3\), and CoPS\(_3\) nanosheets. The clean surface, high crystallinity, high surface area, and better contact with the electrolyte or current collector endow superior performance. They exhibit significantly better performance of Li-ion/Na-ion storage compared to their bulk (\(<300\) mA h g\(^{-1}\))\(^{[111,112]}\) or sulfide counterparts (\(<1000\) mA h g\(^{-1}\))\(^{[113]}\). The ultrathin nanosheets shorten the diffusion paths and accelerate the charge transfer process leading to a discharge and charge capacity of 1796 and 1100 mA h g\(^{-1}\) at a current density of 0.05 A g\(^{-1}\), respectively (Figure 19c), with an initial Coulombic efficiency (CE) of 61.2%. The CE reaches almost 100% after the third cycle due to the minimized loss of capacity from side reactions, such as electrolyte decomposition and solid-electrolyte interphase formation. Collectively, the fourth cycle specific capacities at current densities of 0.05 and 10 A g\(^{-1}\) can be gleaned from Figure 19d as 1026 and 383 mA h g\(^{-1}\) (NiPS\(_3\)), 1046 and 506 mA h g\(^{-1}\) (FePS\(_3\)), and 1086 and 465 mA h g\(^{-1}\) (CoPS\(_3\)), respectively.

On top of their intrinsic property, the improvement with respect to Li/Na storage performance is more pronounced by employing different strategies such as polymer intercalation, hybrid structure formation, etc. The effect of polymer intercalation in these materials has been investigated through intercalation with propylamine. In this case, the interlayer distance becomes further enlarged to allow easier ion accessibility and faster ion diffusion.\(^{[23]}\) Hybrid structure formation also plays its own role in enhancing the performance as exhibited in Li\(_2\)S–FePS\(_3\) composites where it appears to endow structural reversibility against the Li extraction/insertion reactions.\(^{[114]}\) Moreover, elemental doping along with the formation of 0D and 2D nanohybrids has recently been reported\(^{[115]}\) to elucidate the collective role of bimetallic MPX\(_3\) (Co\(_{0.5}\)Ni\(_{0.5}\)PS\(_3\)) and graphene in Li ion storage. The electrochemical performance is associated with the insertion of Li ions into the layered space of the (Co\(_{0.5}\)Ni\(_{0.5}\)PS\(_3\)) lattice, which is accompanied by gradual reduction of Co\(^{2+}\) and Ni\(^{2+}\) to elemental Co and Ni; and the formation of Li\(_2\)S. The graphene support offers a conductive scaffold which contributes to the improved stability and rate performance.

### 3.3. Other Applications

The continual effort to explore the fascinating properties of metal phosphorus trichalcogenides also applies to many other applications. These materials are acknowledged for their high carrier mobility.\(^{[22]}\) The recent experimental work by Lee et al.\(^{[116]}\) demonstrates the thickness dependent tunneling transport properties
of MnPS₃. Flakes of various thicknesses, including mono layer and tens of layers (AFM image, Figure 20a), were obtained via the CVT method followed by scotch-tape exfoliation. A Schottky junction tunneling behavior was observed across the indium tin oxides (ITO)/MnPS₃/Pt-Ir junction with a dielectric breakdown strength of 5.41 mV cm⁻¹. Figure 20b shows that the conductance depends on the number of layers, which exponentially decreases with the increase of the thickness (i.e., the number of layers), as illustrated in the inset of Figure 20b. Moreover, the availability of ample elemental choices in the MPX₃ family enables the adjustment of bandgaps in the range of 1.3–3.5 eV (from near infrared to the UV region). This wide range spectrum suggests their optoelectronic application in a broad wavelength horizon. Recently, high photodetectivity of 1.22 × 10¹² Jones and ultrafast rise times shorter than 5 ms have been observed[61] from ultrathin NiPS₃ (Figure 20c,d). The ease of integration with the Si substrate and the better performance comparable with a commercial GaN UV detector can initiate the investigation of many others in this family. It is, therefore, compelling to mention that the variation in metal components or in chalcogen components provides a conducive platform for the study of the incoming differences in spin-electron, electronic, or optoelectronic devices.

4. Future Perspectives

Layered MPX₃ compounds constitute members that spread over a wide range of the periodic table. The MII, MI, and MIII states are stably located in octahedral sulfur or selenium environments, which is a notable difference compared to TMDs, whose cationic components are in the form of the MIV state. The strong ionic bond between M cations and [P₂X₆]⁴⁻ endows MPX₃ materials with rich functionalities. These configuration features give rise to the unique chemical and physical properties as well as the key distinction from TMDs. Alteration in the size of metal atoms (MII), electronegativity, and electronic configuration can be used to study the structural, catalytic, and magnetic variation of the phases. As to the substituted phases of MIIIPX₃, they present different cationic ordering from the original which is more pronounced in magnetism and ferroelectricity due to the cationic radius size ratio.

In this review, we have discussed the relation between crystal structure and component variations, unique properties,
and progress in growth, characterization, and applications of MPX$_3$ crystals. The current growth status reveals the successful realization of ultrathin NiP$_3$ and MnP$_3$ nanosheets via the chemical vapor deposition method. It is reasonable to say that the growth of the MPX$_3$ monolayer, similar to the TMD monolayer, has yet to be thoroughly explored and predicted. More efforts should be devoted to the controllable growth of MPX$_3$. As mentioned, ionic bonding also contributes to the comparatively large bandgap range from 1.3 to 3.5 eV, which is unavailable for other 2D materials, indicating their potential application in optoelectronics and photo(electro)chemical catalysis. Another fascinating future direction would be designing heterostructures using MPX$_3$ as a component part and exploring the promising applications therein. At the same time, we envision that the magnetic 2D MPX$_3$ nanosheets play an indispensable role in spintronic devices. Their magnetism, especially the monolayer’s, needs to be comprehensively studied via experimental methods in the 2D limit. Meanwhile, this rich magnetism and spin ordering in the electronic structure can find a promising future in catalysis. With the application of external magnetic field, the carrier mobility may be accelerated thereby boosting the catalytic properties. The high ionic mobility and electronic transfer process are crucial for lithium and sodium batteries. Considering the general preparation approach, tunable interlayer spacing, and the ultrathin feature, such 2D MPX$_3$ crystals have great potential in energy conversion.

Acknowledgements

F.M.W. and T.A.S. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (Grant Nos. 61625524, 61474033, 61574050, 11674072, and 21703047), the Ministry of Science and Technology of China (Grant No. 2016YFA0200700), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA09040201), and the CAS Key Laboratory of Nanosystem and Hierarchical Fabrication. The authors also gratefully acknowledge the support of the Youth Innovation Promotion Association CAS. X.L. and F.X. are grateful for the support of the National Natural Science Foundation of China (Grant Nos. 6162540, 61474033, 61574050, 11674072, and 21703047), the Ministry of Science and Technology of China (Grant No. 2016YFA0200700), the CAS Key Laboratory of Nanosystem and Hierarchical Fabrication. The authors also gratefully acknowledge the support of the National Natural Science Foundation of China (Grant Nos. 21525523 and 21722507).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, current developments, metal phosphorus trichalcogenides, potential application, unique properties

Received: March 27, 2018
Revised: June 4, 2018
Published online: July 23, 2018

[1] K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, Nature 2012, 490, 192; Q. Bao, K. P. Loh, ACS Nano 2012, 6, 3677; Y. Kim, S. S. Cruz, K. Lee, B. O. Alawode, C. Choi, Y. Song, J. M. Johnson, C. Heidelberger, W. Kong, S. Choi, K. Qiao, I. Almanson, E. A. Fitzgerald, J. Kong, A. M. Kolpak, J. Hwang, J. Kim, Nature 2017, 544, 340; S. de Wijn, Nature 2016, 539, 502.
[2] D. Ovchinnikov, F. Gargiulo, A. Allain, D. Pasquier, D. Dumcenco, C. H. Ho, O. V. Yazyev, A. Kis, Nat. Commun. 2016, 7, 12391.
[3] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, J. N. Coleman, Science 2013, 340, 1226419; B.-Y. Xu, I. Belopolski, N. Aldoust, M. Neupane, G. Bian, C. Zhang, R. Sankar, G. Chang, Z. Yuan, C. C. Lee, S. M. Huang, H. Zheng, J. Ma, D. S. Sanchez, B. Wang, A. Bansil, F. Chou, P. P. Shibayev, H. Lin, S. Jia, M. Z. Hasan, Science 2013, 349, 613; Z. Ye, T. Cao, K. O. Brien, H. Zhu, X. Yin, Y. Wang, S. G. Louie, X. Zhang, Nature 2014, 513, 214; W. Xu, W. Liu, J. F. Schmidt, W. Zhao, X. Lu, T. Raab, C. Diederichs, W. Gao, D. V. Seleznyk, Q. Xiong, Nature 2016, 541, 62.
[4] F. Xia, H. Wang, Y. Jia, Nat. Commun. 2014, 5, 4458; B. Yuan, X. Liu, F. Afshinmanesh, W. Li, G. Xu, J. Sun, B. Lian, A. G. Curto, G. Ye, H. Ikitaka, Z. Shen, S. C. Zhang, X. Chen, M. Brongersma, H. Y. Hwang, Y. Cui, Nat. Nanotechnol. 2015, 10, 707.
[5] C. T. Wee, L. Huang, J. N. Rui, L. Wang, N. H. Dihan Md, J. D. Thorin, S. K. Karuppannann, A. N. Christian, C. Lee, K. W. Ang, Adv. Mater. 2017, 30, 1705039; B. Mucsemca, D. J. Gorenndjik, S. I. Blanter, G. A. Steele, H. S. J. van der Zant, A. Castellanos-Gomez, Nano Lett. 2014, 14, 3347; C. A. K. Wang, Y. Cui, Lithium, and Sodium Batteries.
[6] K. Watanabe, T. Taniguchi, H. Kanda, Nat. Mater. 2004, 3, 404; B. G. Cassabois, P. Valvin, B. Gil, Nat. Photonics 2010, 6, 262; Y. Kubota, K. Watanabe, O. Tsuda, T. Taniguchi, Science 2007, 317, 932; M. Schnell, A. Garcia-Etxarri, A. J. Huber, K. Crozier, J. Aizpurua, R. Hillenbrand, Nat. Photonics 2009, 3, 287; M. Yankowitz, J. Xue, D. Cormode, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, P. Jariol-Herrero, P. Jacqoud, B. J. LeRoy, Nat. Phys. 2012, 8, 382; F. Wang, G. Chen, Z. Shi, C. C. Liu, L. Zhang, G. Xie, M. Cheng, D. Wang, R. Yang, D. Shi, K. Watanabe, T. Taniguchi, Y. Yao, Z. Zhang, G. Zhang, Nat. Mater. 2013, 12, 792; G. Liu, L. Ma, G. Shi, W. Zhou, G. Song, S. Lei, X. Yi, J. Zhang, J. Yu, K. P. Hackenberg, A. Babakhani, J. C. Idrobo, R. Vajtai, J. Lou, P. M. Ajayan, Nat. Nanotechnol. 2013, 8, 119; H. Dai, Z. Fei, Q. Fei, A. S. Rodin, M. Wagner, A. S. McLeod, M. K. Liu, W. Gannett, W. Regan, K. Watanabe, T. Taniguchi, M. Thiemons, G. Dominguez, A. H. C. Neto, A. Zettl, F. Keilmann, P. Jarillo-Herrero, M. F. Bogoll, D. N. Basov, Science 2014, 344, 1125.
[7] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. Castro Neto, Science 2016, 353, 461; G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seaback, S. K. Banerjee, L. Colombo, Nat. Nanotechnol. 2014, 9, 768; C. Zhong, P. Bampoulis, A. N. Rudenko, Q. Yao, A. van Houten, P. Boelsema, M. I. Katsnelson, H. J. W. Zandvilt, Phys. Rev. Lett. 2017, 116, 256804; D. A. Tonomikh, E. N. Voloshina, P. Werner, Blumtritt, B. Senkovski, G. Guntherodt, S. P. F. Parkin, W. R. Dedkov, Nat. Nanotechnol. 2016, 8, 23547; E. Y. Liu, N. O. Weiss, X. Duan, H. C. Cheng, Y. Huang, X. Duan, Nat. Rev. Mater. 2016, 1, 16042.
[8] P. Goli, J. Khan, D. Wickramaratne, R. K. Lake, A. A. Balandin, Nano Lett. 2012, 12, 5941; B. X. Li, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, K. F. Mak, Nat. Nanotechnol. 2015, 10, 765.
[9] X. Wang, A. M. Jones, K. L. Seyler, S. Tran, J. Jia, H. Zhao, H. Wang, L. Yang, X. Xu, F. Xia, Nat. Nanotechnol. 2015, 10, 517; M. A. McGuire, G. Clark, S. Kr, W. M. Chance, G. E. Jellison, V. R. Cooper, X. Xu, B. C. Sales, Phys. Rev. Mater. 2017, 1, 014001.
[10] H. Cai, B. Chen, G. Wang, E. Soignard, A. Khosravi, M. Manca, X. Marie, L. Y. Chang Shery, B. Urbaszek, S. Tongay, Adv. Mater. 2017, 29, 160551.
[116] S. Lee, K. Y. Choi, S. Lee, B. H. Park, J. G. Park, APL Mater. 2016, 4, 086108.
[117] E. Prouzet, G. Ouvrard, R. Brec, Mater. Res. Bull. 1986, 21, 195.
[118] Z. Wang, R. D. Willett, R. A. Laitinen, D. A. Cleary, Chem. Mater. 1995, 7, 856.
[119] R. Pfeiff, R. Kniep, J. Alloys Compd. 1992, 186, 111.
[120] P. Colombet, A. Leblanc, M. Danot, J. Rouxel, J. Solid State Chem. 1982, 47, 174.
[121] A. Pfitzner, S. Seidlmayer, Z. Anorg. Allg. Chem. 2009, 635, 704.
[122] S. Lee, P. Colombet, G. Ouvrard, R. Brec, Mater. Res. Bull. 1986, 21, 917.
[123] G. Ouvrard, R. Brec, Mater. Res. Bull. 1988, 23, 1199.
[124] R. Pfeiff, R. Kniep, Z. Naturforsch., B 1993, 48, 1270.
[125] I. P. Studenyak, V. V. Mitrovicj, S. Kovacs Gj, M. I. Gurzan, O. A. Mykajlo, M. Vysochanskii Yu, V. B. Caiipe, Phys. Status Solidi B 2003, 236, 678.
[126] C. Calareso, V. Grasso, L. Silipigni, J. Appl. Phys. 1997, 82, 6228.
[127] H. Mutka, C. Payen, P. Molinié, J. L. Soubeyroux, P. Colombet, A. D. Taylor, Phys. Rev. Lett. 1991, 67, 497.
[128] C. Payen, H. Mutka, J. L. Soubeyroux, P. Molinié, P. Colombet, J. Magn. Magn. Mater. 1992, 104–107, 797.
[129] Y. Huang, E. Sutter, N. N. Shi, J. Zheng, T. Yang, D. Englund, H. J. Gao, P. Sutter, ACS Nano 2015, 9, 10612.