Pressure-Induced Indirect-Direct Bandgap Crossover and Bandgap Engineering in Ductile Semiconductor Ag3PO4 with Negative Linear Compressibility

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Abstract

Silver orthophosphate (Ag3PO4) has aroused widespread interest since the discovery of visible-light-driven photocatalysis activity. However, its indirect bandgap nature at ambient becomes an obstacle to improve the photocatalysis efficiency and use in other application fields. In this study, the indirect-to-direct bandgap crossover was found during the pressure-induced phase transition from cubic to trigonal phase in Ag3PO4. The observed bandgap narrowing could be partially retained after pressure was released to ambient conditions, accelerating to efficiently utilize the solar spectrum. Moreover, Ag3PO4 was ductile like metals. Unexpectedly, this ion-conducting and ductile semiconductor photocatalyst further exhibited the negative linear compressibility (NLC) at pressure range of 7.5-25 GPa. This work, combining experimental and theoretical tools, provides an insight into the modulation mechanism of the electronic structure for silver-based semiconductors, and may broaden the applications of Ag3PO4.

Full Text

Preamble

Silver orthophosphate (Ag_3PO_4) has attracted widespread interest since the discovery of its visible-light-driven photocatalytic activity. However, its indirect bandgap nature at ambient conditions poses an obstacle to improving photocatalytic efficiency and limits its applications in other fields. In this study, we report an indirect-to-direct bandgap crossover during the pressure-induced phase transition from cubic to trigonal phase in Ag_3PO_4. The observed bandgap narrowing could be partially retained after pressure release to ambient conditions,

enabling more efficient utilization of the solar spectrum. Moreover, Ag_3PO_4 exhibited metallic-like ductility. Unexpectedly, this ion-conducting, ductile semiconductor photocatalyst further displayed negative linear compressibility (NLC) in the pressure range of 7.5–25 GPa. This work, combining experimental and theoretical approaches, provides insight into the electronic structure modulation mechanism of silver-based semiconductors and may broaden the applications of Ag_3PO_4.

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The direct and indirect bandgap characters of a semiconductor play a key role in photo-excited processes, including the separation, transfer, and recombination of photo-induced electrons and holes, which profoundly affect physicochemical properties and application performance. For an indirect bandgap semiconductor, the optical absorption coefficients and recombination rates are lower than in a direct semiconductor because absorption involves not only incident photons but also phonons. Interestingly, indirect/direct bandgap crossover could balance absorption and recombination and may lead to exotic phenomena such as valley-based properties. Recently, the crossover from indirect to direct bandgap has been widely observed in monolayered materials due to quantum confinement effects. Applying tensile strain or increasing temperature can also induce crossover in multilayered materials through decoupling interplay and lattice expansion. Pressure is an effective approach to tune the crystal structure, lattice parameters, and electronic structure of materials. Unfortunately, materials under pressure generally undergo direct-to-indirect rather than indirect-to-direct bandgap transitions due to compressive effects.

Silver ion conductors represent a versatile class of materials with rich mechanical, optical, and transport properties. Owing to the weak interplay of Ag atoms with their environment, these materials are usually ductile under stress and possess excellent ionic conductivity, such as the soft semiconductor α-Ag_2S and super-ionic conductor α-AgI. Recently, the discovery of visible-light-driven photocatalytic activity for water splitting in the ion-conducting Ag_3PO_4 semiconductor has attracted significant interest in developing silver-based photocatalysts. Under illumination with visible light (wavelength < 500 nm), this novel photocatalyst can achieve an extremely high quantum efficiency of ~90% toward oxygen evolution. However, the indirect bandgap nature of Ag_3PO_4 at ambient conditions may impede improvement of absorption properties, thereby lowering photocatalytic efficiency. Furthermore, Ag_3PO_4 should possess good ductility like α-Ag_2S and other exotic properties for new applications.

In this work, combining high-pressure experiments and density functional theory (DFT) calculations, we found that the indirect-to-direct bandgap crossover in Ag_3PO_4 under pressure couples with a phase transition from cubic to trigonal. Experimentally, the bandgap of Ag_3PO_4 narrowed from 2.37 eV to 1.82 eV via compression, and the shrunken bandgap could be partially retained after releasing pressure to ambient conditions. Additionally, this material exhibits good ductility and negative linear compressibility. Through DFT calculations, we confirmed the high-pressure phase atomic structure, the indirect-to-direct bandgap crossover, and the bandgap narrowing. Our results shed light on materials with direct/indirect bandgap engineering under pressure and may promote potential applications in new fields.

Results

High-purity Ag_3PO_4 powder (Figure S1) was employed to study ductility, atomic structure evolution, and electronic structure changes through pressure treatments (Figure 1a [Figure 1: see original paper]). Upon pressurization, the yellow powder could be easily formed into a sheet between the diamond culets, demonstrating excellent ductility (Figure S2). We then explored pressure effects on the optical properties of this sheet-formed material using in situ UV-vis absorption spectroscopy. Figures 1b and 1c show the absorption spectra of a typical Ag_3PO_4 slice under compression and decompression, respectively. As pressure increased from ambient to 50 GPa, the absorption edge red-shifted from 500 nm to around 650 nm. Meanwhile, the slope of the absorption edge clearly decreased when pressure exceeded 8.2 GPa, revealing degeneration of the indirect and direct bandgap characteristics. In the pressure range from 18.9 GPa to 50 GPa, the slope showed a subtly increasing trend (Figure S3), which may imply a direct-to-indirect bandgap transition. Upon decompression, the changes in both the position of the absorption edge and the slope were reversible.

Figure 1. Optical properties of ductile Ag_3PO_4 semiconductor. (a) Scheme of crystal structure and indirect-to-direct transitions for ductile Ag_3PO_4 semiconductor by pressure treatment. (b and c) UV-vis absorption spectra of Ag_3PO_4 under compression and decompression, respectively. (d) Optical bandgap as a function of pressure. The indirect bandgap is denoted by red (spherical) and black (square) data points, and the direct bandgap is denoted by blue (star) data points.

The optical bandgap of Ag_3PO_4 as a function of pressure (Figure 1d) was derived from the absorption spectra via the Tauc method (Figure S4). The region with direct bandgap is marked by a gray background between 7.5 GPa and 15 GPa. Below the critical pressure of 7.5 GPa, the indirect bandgap was 2.37 eV, consistent with previous reports, and remained stiff, corresponding to the cubic phase. In the gray region, the direct bandgap of Ag_3PO_4 with Trigonal-I phase jumped to ~2.5 eV and then decreased with further pressure increase. After the direct-to-indirect transition, the indirect bandgap of the sample monotonically narrowed to 1.82 eV with increasing pressure. Meanwhile, the sample color changed from yellow to orange during compression, as shown in the inserted photographs of the Ag_3PO_4 slice (Figure 1d). Upon decompression, the bandgap hysteretically broadened from 1.82 eV to 2.26 eV, while the color returned to yellow. Unexpectedly, the bandgap of the quenched sample at ambient conditions decreased by 5% compared with the starting material, which may lead to enhanced photocatalytic activity.

Structural evolution should dominate the variations in electronic structure, leading to the indirect/direct bandgap transitions and bandgap tuning under pressure. In this work, Raman spectroscopy and angle-dispersive synchrotron X-ray diffraction (AD-XRD) experiments combined with theoretical calculations were conducted under pressure to obtain local and global structural information. At ambient conditions, Ag_3PO_4 possesses a body-centered cubic structure (P-43n, No. 218) with a lattice parameter of ~6.01 Å. In this structure, the regular $[PO_4]$ tetrahedra constituting the body-centered cubic lattice are isolated by highly distorted $[AgO_4]$ tetrahedra, and each oxygen atom coordinates to one phosphorus atom and three silver atoms. Owing to the greater electronegativity of P relative to Ag, the P-O bonds are stronger than the covalence-like Ag-O bonds, resulting in a prominent Raman peak at 908 cm^{-1} in the ambient Raman spectra (Figure S5a, b), identified as the symmetric stretching vibration of $[PO_4]$ tetrahedra. In high-pressure Raman experiments, the vibration trended to higher frequency with increasing pressure, except for a turning range near 7.5 GPa showing a red shift of 2 cm^{-1} (Figure S5a, b, d, e), indicating a phase transition in Ag_3PO_4. Meanwhile, the prominent Raman peaks gradually broadened after a sharp jump around the phase transition point (Figure S5c, f), suggesting slight lattice distortion under elevated pressure. During decompression to ambient pressure, the broadened Raman peaks could not be fully recovered, while the frequency of the $[PO_4]$ phonon mode rapidly reverted to the original position except for hysteresis during the high-pressure phase.

Figure 2 [Figure 2: see original paper]. Pressure-induced structural evolution. (a) Synchrotron X-ray diffraction patterns of Ag_3PO_4 under both compression and decompression (λ = 0.6199 Å). (b) Rietveld refinements of the experimental (black fork) XRD data at 1.0 GPa, 9.7 GPa, and 26.5 GPa. The blue lines denote the difference between the experiments (black) and refinements (red), and the green vertical lines stand for the refined peak positions. (c, d) Pressure-dependent lattice parameters and molar volume of Ag_3PO_4. The relationship between molar volume and pressure was fitted by the 3rd-order Birch-Murnaghan (BM3) equation of state (EOS). (e) Variation of compressibility for the Trigonal I-II unit-cell axis as a function of pressure.

Knowledge of pressure-induced structural evolution can be gained from synchrotron X-ray diffraction (XRD) spectra. Figure 2a shows the XRD patterns of Ag_3PO_4 under compression up to 50 GPa and decompression to ambient pressure. All Bragg peaks shifted toward higher angles when pressure was applied up to 5.2 GPa due to unit cell contraction, suggesting that the cubic structure of the low-pressure phase could survive above 5.2 GPa. Three trigonal phases (R3c, No. 161) appeared in the pressure range of 9.7–50.7 GPa. Particularly, the cubic and Trigonal-I phases coexisted around 7.2 GPa. A peak around 13.5° (marked by the star in Figure 2a) gradually merged with the nearby peak and disappeared under a pressure of 14.8 GPa, indicating another phase (Trigonal-II) transition occurred. Subsequently, the peaks in the range of 12°–14° continued to merge into one peak when pressure increased to 26.5 GPa, revealing the emergence of the Trigonal-III phase. Figure 2b shows typical Rietveld refinements of the XRD patterns at 1.0 GPa, 9.7 GPa, and 26.5 GPa, respectively (Table S1 and S2). The good refinements confirmed that Ag_3PO_4 underwent phase transitions from cubic to trigonal structures under high pressure. To our best knowledge, the pressure-induced phase transition from cubic to trigonal is observed for the first time in A_3BX_4-type compounds.

The crystal structure refinement parameters of all diffraction patterns are summarized in Figures 2c and d. The lattice parameters and molar volume of cubic Ag_3PO_4 decreased with increasing pressure. Unusually, the c-axis of the Trigonal-I and II (or Tri. I and Tri. II) phases exhibits negative linear compressibility of -3.02 to -2.87 TPa^{-1} (Figures 2c and e). Hence, Ag_3PO_4 has potential applications in highly sensitive pressure sensors, optical fibers with high shock resistance, and artificial muscles. The anisotropy of the compressive behavior should be ascribed to the relatively compact stacking along the <001> orientation and the distortion of the [AgO] polyhedron. After the transition from Trigonal-II to Trigonal-III phases around 26 GPa, the lattice parameter c became steady, while a continued to decrease at a slower rate. From the volume-pressure relationship shown in Figure 2d, the percentage decrease of molar volumes from cubic to Trigonal-I phase around 7.5 GPa was calculated to be 3%. In addition, a 3rd-order Birch-Murnaghan (BM3) equation of state (EOS) was employed to fit the experimental data for each structure. The EOS parameters were determined to be $B_0 = 101.29$ GPa and $V_0 = 217.47$ Å^3 for cubic Ag_3PO_4, $B_0 = 121.04$ GPa and $V_0 = 210.77$ Å^3 for Trigonal I-II structures, and $B_0 = 228.96$ GPa and $V_0 = 191.80$ Å^3 for Trigonal-III structure. For cubic Ag_3PO_4, the bulk modulus is very small, suggesting that Ag_3PO_4 is very soft like some metals and the ductile semiconductor α-Ag_2S with a bulk modulus of 59.7 GPa. Therefore, the semiconductor Ag_3PO_4 could be applied in flexible devices such as resistive random access memory.

After decompression to ambient pressure, the cubic structure of Ag_3PO_4 was recovered with hysteresis evident from the shifted Bragg peaks, which agrees with Raman observations. This means the pressure-induced phase transition of Ag_3PO_4 is partially reversible. Comparatively, the quenched sample possesses the same lattice parameter of 6.01 Å as the pristine sample but with broadened peaks (Figure S6). Considering the rapid recovery of the $[PO_4]$ tetrahedra from high- to low-pressure phases (see Raman results), the hysteresis and broadening should be attributed to the slow movement of silver atoms to their original positions in the cubic unit cell, which is related to the bandgap hysteresis during compression.

Figure 3 [Figure 3: see original paper]. Mechanism and details of phase transitions. (a) Calculated enthalpy of the phase transition at 7.5 GPa. Insets show the pressure-induced structural change of 2$×2×$2 unit cells viewed from the [111]Cubic // [001]Trigonal direction. (b, c, and d) Theoretical bond lengths of Ag-O, Ag-Ag, and P-O as a function of pressure, respectively.

To better understand the phase transition, theoretical calculations of Ag_3PO_4 were conducted using the Stochastic Surface Walking (SSW) method, which has been successful in TiO_2 and FeOOH systems. Pathway sampling was carried out initially using the VASP package starting from cubic Ag_3PO_4 (2 Ag_3PO_4 units per cell) to generate a database of pathways connecting Ag_3PO_4 with other phases. In total, 120 pathways were collected from 500 SSW-crystal steps of pathway sampling. While the majority of pathways (80) converted cubic Ag_3PO_4 to Trigonal-I phase, other pathways leading to phases such as monoclinic were also identified. First-principles DFT calculations based on the variable-cell double-ended surface walking method were then utilized to verify the energetics of every low-energy pathway, from which the lowest-energy reaction pathway was obtained. The lowest-energy pathway leaving the cubic Ag_3PO_4 phase connects cubic Ag_3PO_4 and Trigonal-I phase as a one-step transition, with other transition pathways being energetically much higher. The reaction profile is shown in Figure 3a, starting from a cubic Ag_3PO_4 lattice to a Trigonal-I phase lattice. We found the phase transition is remarkably simple, involving only rotation of the [PO_4] polyhedrons. To our surprise, the phase transition barrier from cubic to Trigonal-I phase is almost zero, as calculated by the NEB method. This was indeed observed in our XRD experiment, where the phase transition occurs at 7.5 GPa. Furthermore, the calculated XRD patterns and volume-pressure relationship are consistent with experimental results (Figures S7 and S8).

The phase transition of Ag_3PO_4 from cubic to trigonal phases is schematically shown in the insets of Figure 3a, viewed from the [111]Cubic // [001]Trigonal orientation. Apparently, applied pressure induced changes in the [AgO_4] polyhedrons, resulting in reversed rotation of approximately 10° for alternating [PO_4] tetrahedrons along the [111]Cubic // [001]Trigonal direction. To obtain more details, the calculated bond lengths of Ag-O, Ag-Ag, and P-O in Ag_3PO_4 under pressure are summarized in Figures 3b-d. All bond lengths split due to atomic rearrangement after the cubic-trigonal transition, revealing symmetry breakage of the [AgO] polyhedron. As pressure increased, bonds in the trigonal phase generally shrank. Notably, one of the P-O bonds in both cubic and trigonal phases narrowed linearly with increasing pressure, reflected in the Raman vibration (Figure 3d and S5). Along the [001]Trigonal direction, the regular [PO_4] tetrahedra were slightly squashed by 1-2% and the [AgO] polyhedrons underwent significant distortion, resulting in compact stacking of Ag_3PO_4 trigonal structures.

To gain insight into the substantial correlation between crystal structure and optical properties, the electronic band structures of Ag_3PO_4 with different phases were calculated using DFT. It is well known that common exchange-correlation functionals such as LDA and GGA severely underestimate bandgaps. To overcome this, we used the PBE0 hybrid exchange-correlation functional to calculate band structures. As shown in Figure 4a [Figure 4: see original paper], the bandgap at ambient pressure is 2.42 eV, which is very consistent with the experimental value of 2.37 eV. The energy band configurations of cubic and trigonal phases are very different, implying distinctions in optical properties. In detail, the indirect bandgap of the cubic phase at 0 GPa degenerated to a direct bandgap at 8 GPa after the phase transition from cubic to Trigonal-I phase. As pressure increased beyond 17 GPa, the indirect bandgap reappeared in the Trigonal-II and III phases. Figure 4b summarizes the pressure-dependent indirect and direct bandgaps of Ag_3PO_4. The energy difference between direct and indirect bandgaps decreased from ~120 meV to 0 eV when the cubic phase transformed to Trigonal-I. Subsequently, the difference gradually increased to ~80 meV at 44 GPa for the Trigonal-III phase. The indirect/direct bandgap evolution trend agrees with experimental results.

Figure 4 [Figure 4: see original paper]. Electronic band structure and relation with silver coordination. (a) Calculated band structures for Ag_3PO_4 with cubic phase (0 GPa) and trigonal phases I (8 GPa), II (17 GPa), and III (44 GPa). (b) Theoretical direct/indirect bandgap of Ag_3PO_4 as a function of pressure. (c) Pressure-induced coordination change of silver in [AgO] polyhedrons.

The indirect-to-direct bandgap crossover typically occurs in transition metal dichalcogenides when transitioning from bulk to few-layer and especially monolayer forms, such as MoS_2, originating from quantum confinement effects. Applied tensile strain and temperature rise can also effectively drive bandgap crossover from indirect to direct via crystal lattice expansion. In contrast, pressure generally results in crystal cell shrinkage and coupling of neighboring atoms, leading to direct-to-indirect bandgap transitions, as observed in CdSe and $CsPbBr_3$ under pressure. In our case, the direct-to-indirect bandgap transition of trigonal Ag_3PO_4 under higher pressure verifies the pressure effect on electronic structure. However, it is anomalous that pressure-induced indirect-to-direct bandgap crossover occurs during the phase transition from cubic to Trigonal-I phase. Pressure should dominate the electronic band structure and optical properties. Therefore, the prolonged partial Ag-O and Ag-Ag bonds due to bond length splitting (Figures 3b and c) may primarily degenerate the indirect and direct bandgaps after the cubic-to-trigonal phase transition.

Based on structural prediction, the coordination number of Ag^+ and the scheme of the [AgO] group as a function of pressure were obtained and are shown in Figure 4c. The silver coordination of the Trigonal-I phase equals that of the cubic phase but varies the $[AgO_4]$ structure and breaks its centrosymmetry. When pressure rises to 44 GPa, the silver coordination increases from 4 to 7, accompanied by growing complexity of the [AgO] configuration. The transitions between indirect and direct bandgaps for Ag_3PO_4 display good correlation with the Ag^+ coordination number and [AgO] configuration.

In conclusion, the pressure modulations of crystal structure and optical properties in ductile Ag_3PO_4 semiconductor were systematically studied by in situ synchrotron X-ray diffraction and optical absorption spectroscopy combined with theoretical calculations. Under compression, the indirect bandgap Ag_3PO_4 semiconductor exhibited good ductility and underwent reversible phase transitions. The pressure-induced phase transitions from cubic to trigonal phases in Ag_3PO_4 are observed for the first time in A_3BX_4-type compounds. The bandgap of Ag_3PO_4 narrowed from 2.37 eV to 1.82 eV via compression, and the shrunken bandgap could be partially retained after releasing pressure to ambient conditions. Additionally, an indirect-to-direct bandgap crossover was found during the phase transition from cubic to the first trigonal structure, as predicted by theoretical calculations. At much higher pressure, the transition from direct to indirect bandgap was strongly correlated with bond weakening and increased Ag^+ coordination number. These results may provide clues for understanding the underlying mechanism that causes tuning of the electronic band structure and offer opportunities in designing better functional materials.

Methods

Diamond anvil cell sample loading. Silver orthophosphate powder (Ag_3PO_4, Alfa Aesar, 99%) was loaded into a Mao-Bell type symmetric diamond anvil cell (DAC, 300 m culets) with a ruby chip for pressure determination. T301 stainless steel or Rhenium foil (250 m thickness) was pre-indented to 40 m thickness and a hole was laser-drilled ($\lambda = 1064$ nm, Power < 0.3 W) at the indentation center to serve as the gasket and sample chamber. Silicone oil was employed as the pressure-transmitting medium (PTM). Pressures were measured using the in situ ruby fluorescence technique.

In situ high-pressure structural characterizations. In situ high-pressure angle-dispersive X-ray diffraction (AD-XRD) experiments were performed at the Shanghai Synchrotron Radiation Facility (SSRF, BL15U1), Advanced Light Source (ALS, BL12.2.2), and Stanford Synchrotron Radiation Lightsource (SSRL, BL10-2) with wavelengths of 0.6199, 0.49594, and 0.6199 Å. The resulting two-dimensional patterns were integrated using Fit2D software. Rietveld refinements were performed using the General Structure Analysis System (GSAS) with the EXPGUI user interface package. In situ high-pressure Raman spectroscopy experiments were performed on a Raman system in backscattering configuration with an excitation laser ($\lambda = 532$ nm, Renishaw 1000).

In situ high-pressure optical measurements. The powdered Ag_3PO_4 sample was pressurized (up to 3 GPa) by DAC without PTM to form a film with ~10 m thickness. Two pieces of film were peeled off the diamond culet and together with a ruby chip were loaded into the DAC sample chamber using silicone oil as PTM. High-pressure UV-vis spectroscopy measurements were carried out using a micro UV-vis spectroscopy system (DH-2000-BAL, Ocean Optics). During compression and decompression, the Ag_3PO_4 sample color change was photographed with an optical microscope (Leica M205C).

Stochastic Surface Walking (SSW) Global Structure Search. The potential energy surface (PES) of Ag_3PO_4 was explored using DFT-based SSW global structure search (SSW-DFT). The SSW method is an unbiased, automated approach to explore the multidimensional PES of complex systems by taking into account second derivative information. The method' s efficiency for exploring PES has been demonstrated for both aperiodic (molecules and clusters) and periodic (surfaces, crystals) systems. The PES of Ag_3PO_4 was explored in a 16-atom (2 Ag_3PO_4 units per cell) Ag_3PO_4 lattice using cubic structures of Ag_3PO_4 as seeds, which is the most stable phase at ambient conditions at 10 GPa. In the SSW search, we generally performed a series of parallel runs (4–10 depending on the system) starting from initial guess structures, collecting up to 300 minima in the first stage, from which the most stable configuration was obtained. We then verified the result against experimental data. If the most stable configuration from the first stage was inconsistent with experiment, another 300 minima were collected. This process was repeated until the configuration matched experimental observations. Through this random search, we found the most stable configuration, which agreed well with experiment.

SSW pathway sampling. The SSW algorithm has an automated climbing mechanism to drive an atomic configuration from a local energy-minimum state to a high-energy configuration along random directions, inheriting the idea of the bias-potential driven constrained-Broyden-dimer (BP-CBD) method for transition-state (TS) location. Three steps are involved in finding the lowest-energy pathway: (i) Pathway collection—starting from one phase, the SSW method explores all likely nearby phases. A structure selection module decides whether to accept/reject each new minimum. If a new phase different from the starting phase is identified, the initial state (IS) and final state (FS) of the current SSW step are recorded. The program then returns to the IS to continue exploration. If the new minimum is the same phase (e.g., same symmetry but a permutation isomer with varied lattice), the program accepts the new isomeric phase and continues exploration. This repeats until a certain number of IS/FS pairs are collected. (ii) Pathway screening—the variable-cell double-ended surface walking (DESW) method establishes pseudopathways connecting IS to FS for all pairs. The approximate barrier is obtained from the DESW pseudopathway, where the maximum energy point is generally a good estimate for the true TS. By sorting approximate barrier heights, candidates for the lowest-energy pathways are obtained. (iii) Lowest-energy pathway determination—candidate pathways are selected to precisely locate the true TS using the DESW TS-search method. By sorting the exact barrier (energy difference between TS and IS), the lowest-energy pathways are obtained. All lowest-energy pathways are further confirmed by extrapolating TS toward IS and FS, with TSs validated by phonon spectrum calculations showing one and only one imaginary mode. In this study, we explored structural transformation between cubic Ag_3PO_4 and high-pressure Ag_3PO_4 phases using the SSW method. Based on the sampled free energy landscape, pathways connecting initial and final structures on the PES were determined with atom-to-atom correspondence and exported using the nudged elastic band (NEB) method.

DFT calculation details. All calculations were performed using the plane-wave DFT program VASP, where electron-ion interactions of Ag, P, and O atoms are represented by the projector augmented wave (PAW) scheme and the exchange-correlation functional uses the GGA-PBE type. In SSW pathway sampling, 16-atom Ag_3PO_4 supercells (both and Py phases) at 10 GPa were used. To speed up PES exploration, we adopted: kinetic energy plane-wave cutoff of 400 eV; and Monkhorst-Pack k-point mesh of (4\$×4×4)*for*16 − *atomsupercells.Oncelow* − *energypathwayswerelocated*, *weswitchedtohigh* − *accuracycalculationsusingaplane*−*wavecutoffof*800*eVanddenserMonkhorst*− *Packk* − *pointmesh*(8×8×\$8) for 16-atom supercells. For all structures, both lattice and atomic positions were fully optimized until the maximal stress component was below 0.1 GPa and the maximal force component was below 0.01 eV/Å. Since GGA severely underestimates bandgaps, we calculated the density of states using the PBE0 hybrid exchange-correlation functional.

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