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Directing boron-phosphorus bonds in crystalline solid: oxidative polymerization of P=B=P monomers into 1D chains

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Supporting Information Placeholder

ABSTRACT: Over 20 years after the last inorganic ternary B-P compound was reported, Na_2BP_2, a new compound containing one-dimensional B-P polyanionic chains has been synthesized. Common high-temperature synthetic methods required for the direct reaction of boron and phosphorus negate the possible formation of metastable or low temperature phases. In this study, oxidative elimination was used to successfully condense 0D BP_2^{3-} anionic monomers found in Na_3BP_2 precursor into unique 1D BP_2^{2-} chains consisting of 5-member B_2P_3 rings connected by bridging P atoms in the crystal structure of Na_2BP_2. The synthesis was guided by *in-situ* X-ray powder diffraction studies, which revealed the metastable nature of the products of oxidative elimination reactions. Na_2BP_2 is predicted to be an electron balanced semiconductor which was confirmed by UV-vis spectroscopy with the experimentally determined bandgap of 1.1 eV.

The single covalent boron-phosphorus bond is relatively strong with a bond energy of 347 kJ/mol. A detailed analysis of the Cambridge Structural Database,[1a] demonstrated that there are over 1200 compounds with the B–P covalent bond among all compounds containing a C–H bond. These include polyatomic clusters, like B_4P_4 and B_2P_4 (Figure 1).[1] In turn, among inorganic compounds (without a C–H bond), very few compounds containing B-P bonds are reported. These include two stable binaries, BP (sphalerite-type 3D framework) and $B_{12}P_2$ (P-bridged B_{12} icosahedra),[2] and less than 10 ternary phases, which are either halide-terminated B-P clusters ($B_4F_6PF_3$ and $P_2B_4Cl_4$),[3] or A_3BP_2 (A = Na, K, Rb, Cs) compounds with isolated BP_2^{3-} anions isoelectronic to CO_2.[4] No chains, layers, or non-sphalerite three-dimensional frameworks composed of B and P were reported. We hypothesized that beyond the known metal boron phosphides synthesized by thermodynamically driven high-temperature routes, there are unexplored complex solids with diverse B-P anions. The main reasons these complex solids have not been discovered is the synthetic challenges of working with highly refractory boron and reactive phosphorus. A direct reaction of elements or flux-assisted synthesis typically resulted in the formation of inert metal phosphides and BP binaries. High temperatures required to activate those binaries may exceed the temperature stability regions for novel metal boron phosphide phases, which calls for innovative synthetic approaches. Only the high reactivity of alkali metals has been sufficient to overcome the inertness of binary byproducts, as in the synthesis of A_3BP_2.[4]

Our hypothesis is supported by the existence of ternary metal phosphides for heavier Group 13 elements, *AE*-*Tr*-P (*AE* = Ca, Sr, Ba, Eu, *Tr* = Al, Ga, In).[5] These compounds are accessible by flux-assisted synthesis or direct reaction of elements due to the low melting points of *Tr* ranging from 303 K to 933 K. For example, Cu_5InP_{16} can be made by a direct reaction of elements.[6] However, this is not feasible for boron, as its melting point is over 2273 K and requires either arc-welding or temperatures over 1273 K for an appreciable amount of boron to dissolve in metal fluxes.[7] Thus, the low-temperature synthesis of borides remains a challenge despite some recent progress in this field.[8] Despite scarcity, a B-P sphalerite framework compound is an important material for thermal management applications due to a unique combination of high hardness and ultra-high thermal conductivity.[9]

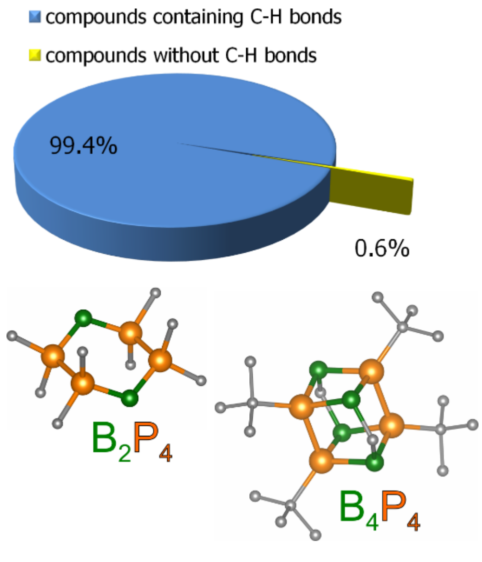

Figure 1. Top: Statistics for structurally characterized compounds containing at least one B–P covalent bond. Bottom: Examples of molecular B-P clusters.[1b,1c] B: green; P: orange; C: grey, H atoms are omitted for clarity.

Our synthetic approach to novel boron phosphides relies on thermodynamics to harness 0D BP_2 building blocks with covalent B-P bonds, and then condensing those building blocks into infinite 1D B-P polyanions via selective oxidation at mild conditions. Herein, we present the synthesis, crystal structure, and chemical bonding of a novel Na_2BP_2 boron-phosphide with 1D B-P chains.

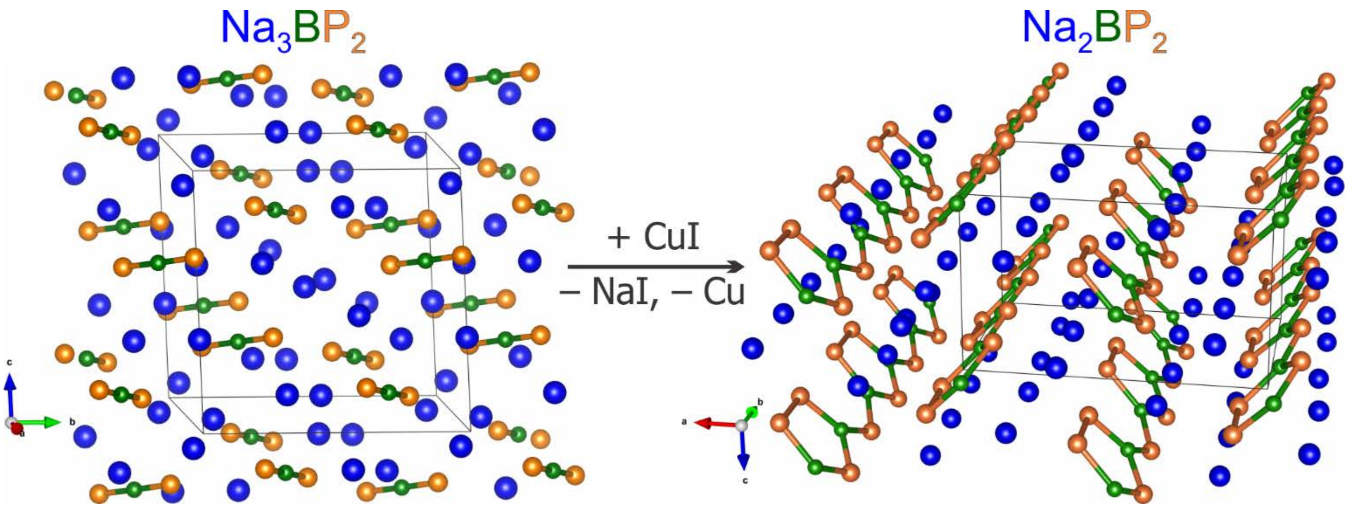

Figure 2. Oxidative elimination of ⅓ of Na cations from the crystal structure of Na_3BP_2 containing isolated P=B=P anions (left) resulted in the formation of Na_2BP_2 containing 1D BP_2 chains (right). Unit cells are shown with black lines. Na: blue; B: green; P: orange.

Oxidative elimination reactions are a powerful tool in synthetic solid-state chemistry. For example, binary alkali metal silicon clathrates cannot be produced by the direct reaction of elements or any flux-assisted reactions. Na-Si clathrates are synthesized by the depletion of cations from the Na-rich Na_4Si_4, whose structure consists of isolated Si_4^{4-} anions. The Si_4^{4-} anions condense into Si_{46} or Si_{136} 3D frameworks containing large cages hosting Na cations. This reaction may be driven by a combination of temperature and dynamic vacuum or by an oxidizing reactant.[10] Similar *chimie douce* methods resulted in the stabilization of novel allotropes of Si and Ge with guest-free clathrate frameworks.[11]

Increasing the level of complexity, we applied the oxidative elimination method to solids with complex anions built from two different elements, such as isolated BP_2^{3-} anions in Na_3BP_2 (Figure 2 left). Copper monohalides were selected as mild oxidation agents. Solid state reactions using Na_3BP_2 and CuCl precursors was the first course of action. To guide the reaction, *in-situ* powder X-ray diffraction (XRD) studies were performed (Figure S2) which revealed that a reaction had already begun to occur at 442 K as indicated by the formation of NaCl + Cu products. Around the temperature of 773 K, a set of new diffraction peaks was observed which could not be assigned to known phases. Decomposition of this new phase and formation of $NaCu_2P_2$ was observed at 967 K. Finally, a partial melt with the formation of Cu_3P was achieved at 1099 K. Cooling after melting only resulted in a mixture of NaCl and Cu_3P without traces of the new phase (Figure S2). Several additional *in-situ* experiments confirmed the stability region for the new phase as 645-805 K. In all experiments, decomposition of the new phase was irreversible, indicating the metastable nature.

Similar results were obtained in the lab reactions guided by temperatures determined in the synchrotron experiments. The formed compound appeared to be highly air-sensitive, and no suitable crystals for structural determination were found. To improve crystal quality, the oxidative elimination reaction was performed in a NaI:CsI eutectic flux, which has a melting point of 693 K. CuI instead of CuCl was used as an oxidation agent to reduce the number of elements present in the reaction mixture: $Na_3BP_2 + CuI \rightarrow Na_2BP_2 + Cu + NaI$ (Figure 2). The resulting products were glittery red and black clumps of powder. NaI/CsI, Cu, and another new phase (different than the product of the CuCl reaction) were detected by powder XRD. Single crystal X-ray diffraction on a small black crystal revealed the composition of the new phase to be $Na_2B_{0.94(4)}P_{2.00(5)}$, which will be referred to as Na_2BP_2. The calculated XRD pattern of Na_2BP_2 accounts for all unidentified diffraction peaks in the experimental powder XRD pattern of the products of the CsI/NaI flux reaction (Figure S1). The Na_2BP_2 phase is highly air-sensitive because the crystals degrade instantly when exposed to ambient atmosphere. Crystal handling was performed under a layer of Paratone oil, and even then, crystal degradation and the formation of bubbles was observed after several minutes.

In Na_3BP_2, the BP_2^{3-} anions are isoelectronic to CO_2.[4] The elimination of ⅓ of Na cations changes the charge of the anion to –2. This leads to the condensation of anions into one-dimensional chains, an ordered model of which is depicted in Figures 2 right and 3. In the determined crystal structure, there are several alternative positions of the ordered chains. The superposition of all the orientations of the ordered chains results in overall disordered chains with partial occupancies for P and B sites, as depicted in Figures S3 and S4. Complete ordering can be achieved in the *Pm* monoclinic space group with doubling of the *c* unit cell parameter (details can be found in the Supporting Information). The ordered model was obtained considering partial occupancies of B and P sites and under the assumption of mutual exclusion of B and P atoms forming too short, physically impossible distances, such as 1.18 Å and 1.67 Å. The shortest reported multiple B-P bond is 1.77 Å in K_3BP_2,[4d] compared with the 1.96 Å single B-P bond in cubic BP.[12] In the resulting chains, five-membered B_2P_3 rings are connected via bridging P atoms (Figure 3). The boron atoms have a trigonal-planar coordination while the bridging P atoms are engaged in two covalent B-P bonds. One P-P bond is formed by the P atoms in the ring. The chains are almost planar (Figure 3A). The B-P interatomic distances, 1.90 Å and 1.94 Å, are comparable with the sum of their covalent radii (1.95 Å) and the length of a single B-P bond (1.96 Å) found in the BP binary compound.[12] The P-P distance of 2.28 Å is slightly longer than the typical covalent P-P bond, but even longer P-P bonds have been reported in different metal phosphides.[13]

The ordered superstructural model was optimized using the Vienna Ab initio Simulation Package (VASP).[14] The model converges well with results shown in Fig. 2 right, 3C and 3D and S5. The optimized structure was analyzed with PLATON[15] and found to be best described in the orthorhombic space group $Pmc2_1$ (the resulting CIF is provided in the Supporting Information). This space group is not common for crystalline compounds with 109 records in the ICSD (frequency 0.05%),[16] nevertheless the pnictide compounds with 1D chains were shown to crystallize in the non-centrosymmetric space groups.[17] In the relaxed structure, P atoms inside the ring form shorter B-P bonds (1.90 Å) as compared to the B-P bonds connecting two rings (1.93 Å) (Figure 3D). A relaxation of Na sites was also detected, similar to Na1/Na2 disorder detected by single crystal X-ray diffraction (Figure S5).

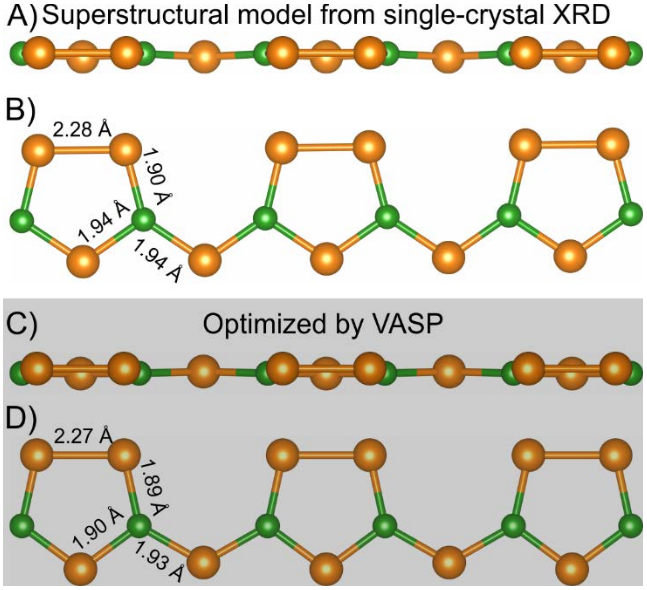

Figure 3. Ordered models of a BP_2^{2-} chain: A) and C) side view; B) and D) top view. A) and B) correspond to the superstructural model derived from single crystal data, while C) and D) correspond to the VASP optimized structure. Selected B-P and P-P interatomic distances are shown. B: green; P: orange.

To the best of our knowledge, B_2P_3 five-membered rings are unique and have not been reported. The closest analogues among molecular compounds are Al_2P_3 and B_2S_3 rings.[18] In the structure of the inorganic porphine, B_8S_{16}, four flat B_2S_3 rings are bridged together via additional S atoms connecting two B atoms from different rings.[18b] As a full phosphorus analogue, P_5^- planar aromatic rings are common soluble anionic fragment,[19] while P_5 distorted rings are common fragments for various P allotropes.[20]

The synthesized compound is expected to be electron balanced. Assuming the covalent nature of B-P and P-P interactions as 2*c*-2*e* bonds, three-bonded B atoms are neutral while two-bonded P atoms have a formal oxidation state of –1, leading to an overall formula of $(Na^+)_2(B^0)(P^{1-})_2$. Alternatively, boron may be considered as B^{3+}, bridging P atoms as P^{3-}, and dumbbell P atoms as P^{2-}, leading to an overall formula of $(Na^+)_2(B^{3+})(P^{3-})(P^{2-})$. Chemical bonding analysis using electron localization function (ELF) indicated that the former description is more appropriate (Figure 4). ELF attractors ①, ②, and ③ corresponds to covalent P-P and B-P bonds. Additionally, every P atom has unresolved electron lone pairs (attractors ④, ⑤, and ⑥), which is expected for two-bonded P atoms.[21] Electronic band structure calculations support the proposed electron-balanced model. Na_2BP_2 is predicted to be a semiconductor with a bandgap of 1.4 eV for the optimized ordered structure (Figure 5), which agrees with the black color of the crystals and the direct bandgap of 1.1 eV determined by UV-vis spectroscopy measurement (Figure S6). The contribution from P3*p* orbitals dominates in the states near the top of the valence band, while the conduction band is composed of similar contributions of Na, B, and P orbitals.

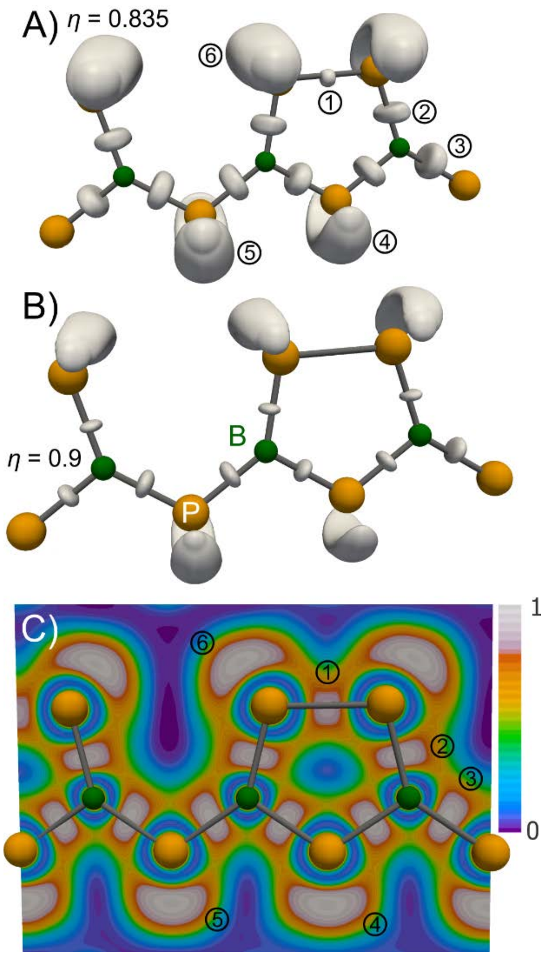

Figure 4. Chemical bonding in BP_2 chains according to electron localization function (ELF, η) analysis: A) and B) 3D isosurfaces of ELF with $\eta = 0.835$ and $\eta = 0.9$; C) Coloring of the ELF distributions for a slice of the crystal structure of Na_2BP_2. B: green; P: orange. Different types of attractors are marked with numbers in A) and C).

The newly synthesized Na_2BP_2 compound is the first example of a 1D B-P polyanion with planar B_2P_3 rings. One can assume that further oxidation of this compound may lead to the formation of bonds between the chains and their condensation into novel 2D or 3D B-P frameworks. Compounds with infinite B-P fragments may be useful precursors for creating novel low-dimensional materials analogous to other materials with strong covalent bonding within 1D and 2D pnictide-based fragments, such as SnIP or GeAs.[22] The synthesis of Na_2BP_2 demonstrates the power of the oxidative elimination method to access complex metastable and low-temperature stable phases. This method allows reactions to overcome the inertness of starting materials by using complex precursors with built-in covalent bonding between the components. Further exploration of this method for other boron-pnictides is currently underway.

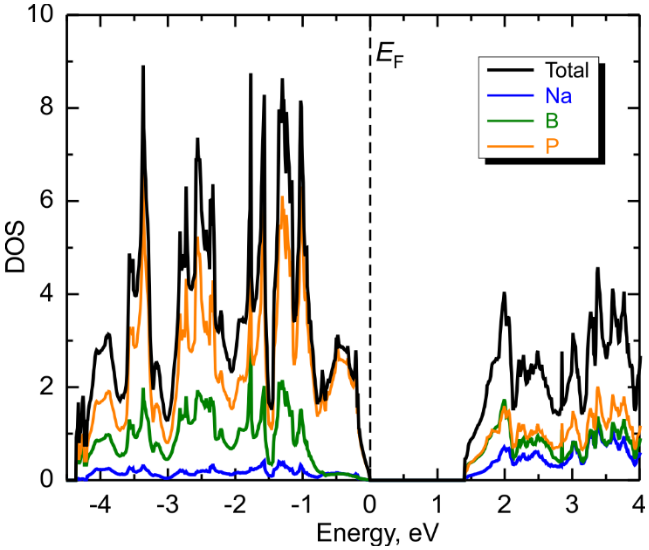

Figure 5. Electronic density of states for the ordered model of Na$_2$BP$_2$. Partial contributions of Na, B, and P are shown in blue, green, and orange colors, respectively. The Fermi level is shown as a dashed line at 0 eV.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Crystallographic information files for the experimentally-determined crystal structure and optimized ordered model of Na$_2$BP$_2$, experimental details, figures, and tables regarding synthesis, in-house and synchrotron *in-situ* powder X-ray diffraction, single-crystal X-ray diffraction, crystal structure parameters for the determined structure and superstructural ordered model, electronic structure and ELF calculations, and diffuse reflectance UV-vis spectroscopy.

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Author Contributions

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REFERENCES

(1) a) C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, The Cambridge Structural Database. *Acta Cryst.* **2016**, *B72*, 171-179; b) M. Driess, H. Pritzkow, W. Siebert, Novel Boron-Phosphorus Cages with C$_4$B$_4$P$_4$ and C$_2$B$_4$P$_4$ Frameworks *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 399-400; c) H. Schmidbaur, T. Wimmer, A. Grohmann, O. Steigelmann, G. Müller, Phosphane-borane chemistry. Open-chain and cyclic phosphane-boranes based on tetramethyldiphosphane. *Chem. Ber.* **1989**, *122*, 1607-1612; d) P. P. Power, Boron-Phosphorus Compounds and Multiple Bonding. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 449-460.

(2) P. Popper, T. A. Ingles, Boron Phosphide, a III–V Compound of Zinc-Blende Structure. *Nature*. **1957**, *179*, 1075.

(3) a) W. Haubold, W. Keller, G. Sawitzki, The First closo-Diphosphahexaborne, P$_2$B$_4$Cl$_4$. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 925-926; b) B. G. de Boer, A. Zalkin, D. H. Templeton, Crystal and molecular structure of phosphorus trifluoride- tris(difluoroboryl)borane, B$_4$F$_6$-PF$_3$. *Inorg. Chem.* **1969**, *8*, 836-841.

(4) a) H.-G. von Schnering, M. Somer, M. Hartweg, K. Peters, [BP$_2$]$^{3-}$ and [BAs$_2$]$^{3-}$, Zintl Anions with Propadiene Structure. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 65-67; b) M. Somer, T. Popp, K. Peters, H.-G. von Schnering, Crystal structure of caesium diphosphidoborate, Cs$_3$(BP$_2$). *Z. Kristallogr.* **1990**, *193*, 297-298; c) M. Somer, T. Popp, K. Peters, H.-G. von Schnering, Crystal structure of sodium diphosphidoborate, Na$_3$BP$_2$. *Z. Kristallogr.* **1990**, *193*, 281-282; d) M. Somer, M. Hartweg, K. Peters, H.-G. von Schnering, Crystal structure of potassium diphosphidoborate, K$_3$BP$_2$.*Z. Kristallogr.* **1990**, *191*, 311-312; e) M. Somer, W.C. Cabrera, E.M. Peters, K. Peters, H.G. von Schnering, Crystal structures of trirubidium diarsenidoborate, Rb$_3$BAs$_2$ and trirubidium diphosphidoborate, Rb$_3$BP$_2$. *Z. Kristallogr.* **1995**, *210*, 779-780.

(5) a) A.M. Goforth, H. Hope, C.L. Condron, S.M. Kauzlarich, N. Jensen, P. Klavins, S. MaQuilon, Z. Fisk. Magnetism and Negative Magnetoresistance of Two Magnetically Ordering, Rare-Earth-Containing Zintl phases with a New Structure Type: EuGa$_2$Pn$_2$ (Pn = P, As). *Chem. Mater.* **2009,** *21*, 4480-4489; b) H. He, C. Tyson, M. Saito, S. Bobev, Synthesis, Crystal and Electronic Structures of the New Zintl phases Ba$_3$Al$_3$Pn$_5$ (Pn = P, As) and Ba$_3$Ga$_3$P$_5$. *Inorg. Chem.* **2012**, *52*, 499-505; c) J. Mathieu, R. Achey, J.-H. Park, K.M. Purcell, S.W. Tozer, S.E. Latturner, Flux Growth and Electronic Properties of Ba$_2$In$_5$Pn$_5$ (Pn = P, As): Zintl Phases Exhibiting Metallic Behavior *Chem. Mater.* **2008**, *20*, 5675-5681.

(6) S. Lange, M. Bawohl, R. Weihrich, T. Nilges, Mineralization routes to polyphosphides: Cu$_2$P$_{20}$ and Cu$_5$InP$_{16}$. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 5654-5657.

(7) a) M. G. Kanatzidis, R. Pöttgen, W. Jeitschko, The metal flux: a preparative tool for the exploration of intermetallic compounds. *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 6996-7023; b) T. Mori, Thermoelectric and magnetic properties of rare earth borides: Boron cluster and layered compounds. *J. Solid State Chem.* **2019,** *275*, 70-82; c) G. Akopov, W.H. Mak, D. Koumoulis, H. Yin, B. Owens-Baird, M.T. Yeung, M.H. Muni, S. Lee, I. Roh, Z.C. Sobell, P.L. Diaconescu, R. Mohammadi, K. Kovnir, R.B. Kaner, Synthesis and Characterization of Single Phase Metal Dodecaboride Solid Solutions: Zr$_{1-x}$Y$_x$B$_{12}$ and Zr$_{1-x}$U$_x$B$_{12}$. *J. Amer. Chem. Soc.* **2019,** *141*, 9047-9062.

(8) a) P. R. Jothi, K. Yubuta, B. P. T. Fokwa. A Simple, General Synthetic Route toward Nanoscale Transition Metal Borides. *Adv. Mater.* **2018,** *30*, 1704181; b) V. Gvozdetskyi, M. P. Hanrahan, R. A. Ribeiro, T. H. Kim, L. Zhou, A. J. Rossini, P. C. Canfield, J. V. Zaikina, A Hydride Route to Alkali Metal Borides: A Case Study of Lithium Nickel Borides. *Chem. Eur. J.* **2019**, *25*, 4123; c) V. Gvozdetskyi, G. Bhaskar, M. Batuk, X. Zhao, R. Wang, S. L. Carnahan, M. P. Hanrahan, R. A. Ribeiro, P. C. Canfield, A. J. Rossini, C.-Z. Wang, K.-M. Ho, J. Hadermann, J. V. Zaikina. Computationally-driven discovery of the family of layered LiNiB polymorphs. *Angew. Chem. Int. Ed.* **2019,** *DOI: 10.1002/anie.201907499*.

(9) a) L. Lindsay, D. A. Broido, T. L. Reinecke, First-Principles Determination of Ultrahigh Thermal Conductivity of Boron Arsenide: A Competitor for Diamond? *Phys. Rev. Lett.* **2013,** *111*, 025901; b) J. S. Kang, H. Wu, Y. Hu, Thermal Properties and Phonon Spectral Characterization of Synthetic Boron Phosphide for High Thermal Conductivity Applications. *Nano Lett.* **2017,** *17*, 7507-7514.

(10) a) J. S. Kasper, P. Hagenmuler, M. Pouchard, C. Cros, Clathrate Structure of Silicon Na$_8$Si$_{46}$ and Na$_x$Si$_{136}$ ($x < 11$). *Science*, **1965**, *150*, 1713-1714; b) M. Beekman, M. Baitinger, H. Borrmann, W. Schnelle, K. Meier, G. S. Nolas, Y. Grin, Preparation and Crystal Growth of Na$_{24}$Si$_{136}$. *J. Amer. Chem. Soc.* **2009**, *131*, 9642-9643.

(11) a) A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, Y. Grin, A guest-free germanium clathrate. *Nature* **2006**, *443*, 320-323; b) A. Ammar, C. Cros, M. Pouchard, N. Jaussaud, J. M. Bassat, G. Villeneuve, M. Duttine, M. Menetrier, E. Reny, On the clathrate form of elemental silicon, Si$_{136}$: preparation and characterisation of Na$_x$Si$_{136}$ ($x \rightarrow 0$). *Solid State Sci.* **2004**, *6*, 393-400.

(12) S. Rundqvist, X-Ray Investigations of the Ternary System Fe-P-B. Some Features of the Systems Cr-P-B, Mn-P-B, Co-P-B and Ni-P-B. *Acta Chem. Scand.* **1962**, *16*, 1-19.

(13) a) R. Pöttgen, W. Hönle, H.-G. von Schnering, Phosphides: Solid-State Chemistry. in *Encyclop. Inorg. Chem.* Vol. 8, 2nd ed. (Ed: R. B. King), Wiley: Chichester, U.K., **2005**, pp 4255-4308; b) W. Hönle, H.-G. von Schnering, Chemistry and structural chemistry of phosphides and polyphosphides. 48. Bridging chasms with polyphosphides. *Chem. Rev.* **1988**, *88*, 243-273; c) J. Dolyniuk, J. V. Zaikina, D. C. Kaseman, S. Sen, K. Kovnir, Breaking the Tetra-Coordinated Framework Rule: New Clathrate Ba$_8$M$_{24}$P$_{28+\delta}$ (M = Cu/Zn). *Angew. Chem. Int. Ed.* **2017**, *56*, 2418-2422; d) X. Chen, L.-P. Zhu, S. Yamanaka, High-pressure synthesis and structural characterization of three new polyphosphides, α-SrP$_3$, BaP$_8$, and LaP$_5$. *J. Solid State Chem.* **2003,** *173*, 449-455; e) J. Wang, Y. He, N. E. Mordvinova, O. I. Lebedev, K. Kovnir, The smaller the better: hosting trivalent rare-earth guests in Cu-P clathrate cages. *Chem*, **2018,** *4*, 1465-1475.

(14) Kresse, G.; Furthmuller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996,** *6*, 15-50.

(15) Spek, A.L. Structure validation in chemical crystallography. *Acta Cryst. D*, **2009,** *D65*, 148-155.

(16) Inorganic Crystal Structure Database, ICSD, https://www.fiz-karlsruhe.de/en/produkte-und-dienstleistungen/inorganic-crystal-structure-database-icsd, accessed July-26-2019.

(17) Mark, J.; Wang, J.; Wu, K.; Lo, J.G.; Lee, S.; Kovnir, K. Ba$_2$Si$_3$P$_6$: 1D Nonlinear Optical Material with Thermal Barrier Chains. *J. Amer. Chem. Soc.* **2019,** *141*, 11976-11983.

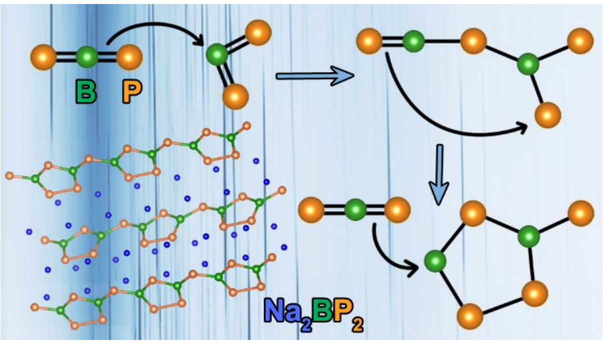
(18) a) Hoskin, A.J.; Stephan, D. W. The Main Group Macrocycle [{(PCH$_2$CH$_2$PAlMe$_2$)$_2$}$_4$]*4[AlMe$_3$]. *Angew. Chem. Int. Ed.* **2001,** *40*, 1865-1867; b) Krebs, B.; Hürter, H.-U. B$_8$S$_{16}$ – An "Inorganic Porphine" *Angew. Chem. Int. Ed.* **1980,** *19*, 481-482.

(19) a) Dragulescu-Andrasi, A.; Miller, L.Z.; Chen, B.; McQuade, D.T.; Shatruk, M. Facile Conversion of Red Phosphorus into Soluble Polyphosphide Anions by Reaction with Potassium Ethoxide. *Angew. Chem. Int. Ed.* **2016,** *55*, 3904-3908; b) Cossairt, B.M.; Piro, N.A.; Cummins, C.C. Early-Transition-Metal-Mediated Activation and Transformation of White Phosphorus. *Chem. Rev.* **2010,** *110*, 4164-4177; c) Fleischmann, M.; Jones, J.S.; Gabbaï, F.P.; Scheer, M. A comparative study of the coordination behavior of cyclo-P$_5$ and cyclo-As$_5$ ligand complexes towards the trinuclear Lewis acid complex (perfluoro-ortho-phenylene)mercury. *Chem. Sci.* **2015,** *6*, 132-139; d) Urnėžius, E.; Brennessel, W.W.; Cramer, C.J.; Ellis, J.E.; Schleyer, P.v.R. A Carbon-Free Sandwich Complex [(P$_5$)$_2$Ti]$^{2-}$. *Science*, **2002,** *295*, 832-834.

(20) a) Thurn, V.H.; Krebs, H. Über Struktur und Eigenschaften der Halbmetalle. XXll. Die Kristallstruktur des Hittorfschen Phosphors. *Acta. Cryst. B.* **1969,** *B25*, 125-135; b) Pfitzner, A.; Bräu, M.F.; Zweck, J.; Brunklaus, G.; Eckert, H. Phosphorus Nanorods – Two Allotropic Modifications of a Long-Known Element. *Angew. Chem. Int. Ed.* **2004,** *43*, 4228-4231; c) Ruck, M.; Hoppe, D.; Wahl, B.; Simon, P.; Wang, Y.; Seifert, G. Fibrous Red Phosphorus. *Angew. Chem. Int. Ed.* **2004,** *44*, 7616-7619; d) The Extended Stability Range of Phosphorus Allotropes. Bachhuber, F.; von Appen, J.; Dronskowski, R.; Schmidt, P.; Nilges, T.; Pfitzner, A.; Weihrich, R. *Angew. Chem. Int. Ed.* **2014,** *53*, 11629-11633.

(21) a) A. Savin, O. Jepsen, J. Flad, O. K. Andersen, H. Preuss, H. G. von Schnering, Electron Localization in Solid-State Structures of the Elements: the Diamond Structure. *Angew. Chem. Int. Ed. Engl.* **1992,** *31*, 187-188; b) A. Savin, R. Nesper, S. Wengert, T. F. Fässler, ELF: The Electron Localization Function. *Angew. Chem. Int. Ed. Engl.* **1997,** *36*, 1808-1832; c) Y. Grin, A. Savin, B. Silvi, The ELF Perspective of chemical bonding. in *The Chemical Bond: Fundamental Aspects of Chemical Bonding* (Eds.: G. Frenking, S. Shaik), Wiley-VCH, Weinheim, **2014,** p. 345-382; d) J. Fulmer, D. Kaseman, J. Dolyniuk, K. Lee, S. Sen, K. Kovnir, BaAu$_2$P$_4$: Layered Zintl Polyphosphide with Infinite (P$^-$) Chains. *Inorg. Chem.* **2013,** *52*, 7061-7067; e) J. Dolyniuk, J. Wang, K. Lee, K. Kovnir, Twisted Kelvin cells and truncated octahedral cages in the crystal structures of unconventional clathrates, AM$_2$P$_4$ (A = Sr, Ba; M = Cu, Ni). *Chem. Mater.* **2015,** *27*, 4476-4484.

(22) a) D. Pfister, K. Schäfer, C. Ott, B. Gerke, R. Pöttgen, O. Janka, M. Baumgartner, A. Efimova, A. Hohmann, P. Schmidt, S. Venkatachalam, L. van Wüllen, U. Schürmann, L. Kienle, V. Duppel, E. Parzinger, B. Miller, J. Becker, A. Holleitner, R. Weihrich, T. Nilges, Inorganic Double Helices in Semiconducting SnIP. *Adv. Mater.* **2016,** *28*, 9783-9791; b) C. Ott, F. Reiter, M. Baumgartner, M. Pielmeier, A. Vogel, P. Walke, S. Burger, M. Ehrenreich, G. Kieslich, D. Daisenberger, J. Armstrong, U. K. Thakur, P. Kumar, S. Chen, D. Donadio, L. S. Walter, R. T. Weitz, K. Shankar, T. Nilges, Flexible and Ultrasoft Inorganic 1D Semiconductor and Heterostructure Systems Based on SnIP. *Adv. Funct. Mater.* **2019,** 1900233; c) J. Guo, Y. Liu, Y. Ma, E. Zhu, S. Lee, Z. Lu, Z. Zhao, C. Xu, S.-J. Lee, H. Wu, K. Kovnir, Y. Huang, X. Duan, Few-layer GeAs field-effect transistors and infrared photodetectors. *Adv. Mater.* **2018**, *30*, 1705934.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