Electronic Supplementary Information

From BPS_4 to $AB_3P_2S_{10}$ (A = Na, K): Cations Inducing Dimension Reduction and Bandgap Enlargement

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CONTENTS

1. Synthesis of Title Compounds

High-purity chemicals such as the Na_2S powder (99%), K_2S powder (99.9%), B powder (99.9%), P_2S_5 powder (99.9%) and S powder (99.99%) were used as purchased from Shanghai Aladdin Biochemistry Technology Co., Ltd. To better ensure the reliability of the raw material ratio, vacuum glove box was chosen to complete the preparation process and avoid the effect of air oxidation.

$AB_3P_2S_{10}$ (A = Na, K) (ABPS). Raw mixture (A_2S: B: P_2S_5: S) with stoichiometric proportion of 1:6:2:9 was firstly loaded into the graphite crucible and then put it into inner wall-carbon plated silicon tube. Using the flame gun and air extractor, silica tube was carefully vacuum-sealed with the internal vacuum degree about 10^{-3} Pa. Muffle furnace was used to complete the crystallization reaction and the setting temperature process was shown as follows: firstly heated to 300 °C in 10 h and left at this temperature for 20 h to make the partial S participate into the reaction, further heated to 560 °C to ensure the mixture melt completely while kept at this temperature within 4 days, then slowly cooled down to 400 °C in 160 h, then slowly cooled down to 100 °C in 100 h, finally quickly down to the room temperature in one day. The air-stable colorless crystals were obtained after the above process. The synthesis of other alkali metals-contained compounds (Li, Rb, and Cs) in this system has been attempted by adjusting the different ratios of reagents or reaction temperatures, unfortunately, we were unable to obtain the crystals of $AB_3P_2S_{10}$ (A = Li, Rb, Cs).

BPS_4 (BPS). Raw mixture (B: P_2S_5: S) with 4:3:3 (not stoichiometric proportion of 1:1:4) was firstly loaded into the graphite crucible and then put it into inner wall-carbon plated silicon tube. Using the flame gun and air extractor, silica tube was carefully vacuum-sealed with the internal vacuum degree about 10^{-3} Pa. Muffle furnace was used to complete the crystallization reaction, the air-stable colorless blocky crystals (8×4×3 mm) were obtained after the setting temperature process was shown as follows:

30℃ (800 min) → 580℃ (9000 min) → 580℃ (5500 min) → 500℃ (6000 min) → 400℃ (1000 min) → 300℃ (300 min) → 80℃ (60 min) → 30℃.

Carefully ground microcrystal powders were used for powder X-ray diffraction (PXRD) measurement by an automated Bruker D2 X-ray diffractometer at room temperature. After test, experimental results are essentially in accordance with the calculated ones from the single-crystal data, respectively.

2. Structural Refinement and Crystal Data

A Bruker SMART APEX III 4K CCD diffractometer with Mo Ka radiation (λ = 0.71073 Å) was used to complete the crystal data collection at room temperature. Multi-scan method was used for absorption correction. The crystal structure was solved by the direct method and refined using the SHELXTL program package[1]. Note that all atom sites are completely occupied by each atom in ABPS. Crystal data and structure refinements of title compounds are given in Table S1. Table S2, and Table S3 summarize the atomic coordinates and isotropic displacement parameters of title compounds. Bond length and angles for ABPS were provided in Tables S4-S5.

3. Property Characterization

Powder X-ray diffraction measurement. An automated Bruker D2 X-ray diffractometer was used to carry out the powder X-ray diffraction (XRD) characterization for the ABPS and BPS, the 2θ range was from 5 to 70 ° with a step rate of 0.02 °/s.

UV–Vis–NIR Diffuse-reflectance Spectroscopy. Shimadzu SolidSpec-3700 DUV spectrophotometer was used to measure the diffuse-reflectance spectra within the wavelength range from 200 to 2600 nm. The absorption spectra were converted from the reflection spectra via the Kubelka-Munk function. Transmission measurement of BPS from 200 to 1600 nm was performed on a McPherson VUV as 2000 spectrophotometer by using an unpolished transparent 2.5×3.5 mm blocky crystal.

Infrared Spectroscopy. Ground micro-crystals mixed with KBr powder in the molar ratio of about 1:100, was dried and ground into fine powder, and then pressed into a transparent sheet on the tablet machine. The sheet was loaded in the sample chamber and were used to complete the IR spectroscopy measurement on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer within the range from 400 to 4000 cm^{-1}.

Raman Spectroscopy. Raman spectra on the crystals of title compounds were collected by a LABRAM HR Evolution spectrometer equipped with a CCD detector using 532 nm radiation from a diode laser in the region of 4000-40 cm^{-1}. For each sample, crystals were placed on a small glass slide and a 50 × objective lens was used to choose the area of the crystal specimens to be measured.

Energy dispersive X-ray spectroscopy. Elemental analysis was carried on clean single crystal surfaces with the aid of a field emission scanning electron microscope (SEM, SUPRA 55VP) equipped with an energy dispersive X-ray spectroscope (EDX, BRUKER x-flash-sdd-5010).

Computational Description

The band structures and optical properties of title compounds were calculated by density functional theory (DFT) based on first-principles calculations implemented in the CASTEP package[2]. The generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) and norm-conserving pseudo-potentials (NCP) were employed[3-5]. For BPS, its whole structure is 1D chains of edge-sharing (B/P)S_4 tetrahedra that are all oriented to the *c* axis. Considering the the B and P atoms share the same crystallographic site and the site occupancy was 0.5/0.5 for B/P, which cannot be directly calculated, so we established a crystal structure model for BPS_4, with the same stoichiometric ratio. During the calculation, the plane-wave cut-off energy was set as 700 eV for NBPS, 650 eV for KBPS and 650 eV for BPS. The k-points sampling of 4 × 4 × 3 for NBPS, 4 × 4 × 3 for KBPS, 3 × 2 × 3 for BPS was chosen to ensure the convergence for all computations. Na-$2s^2 2p^6 3s^1$, K-$3s^2 3p^6 4s^1$, B-$2s^2 2p^1$, P-$3s^2 3p^3$, and S-$3s^2 3p^4$ were treated as the valence electrons, respectively. The other calculated parameters used and convergent criteria were in line with the default values of the CASTEP code.

4. Tables

Table S1 Crystal Data and Structure Refinement for ABPS.

Empirical formula	$NaB_3P_2S_{10}$	$KB_3P_2S_{10}$
Formula weight	437.96	454.07
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/a$ (88)	$I4_1/a$ (88)
Unit cell dimensions (Å)	a=13.126(3) b=13.126(3) c=15.379(5)	a=13.0262(8) b=13.0262(8) c=16.5387(17)
Z/V (Å^3)	8/2649.6(15)	8/2806.3(4)
Density (g/cm^3)	2.196	2.149
Absorption coefficient (mm^{-1})	1.895	2.055
F (000)	1728	1792
Completeness to theta	99.8 %	99.6 %
Goodness-of-fit on F^2	1.071	1.060
Final R indices [$Fo^2 > 2\sigma(Fo^2)$][a]	R_1= 0.0341, wR_2= 0.0751	R_1=0.0465, wR_2=0.1230
R indices (all data)[a]	R_1= 0.0499, wR_2= 0.0867	R_1=0.0710, wR_2=0.1391
Largest diff. peak and hole (eÅ^{-3})	0.564 and -0.409	0.553 and -0.736

[a] $R_1 = F_0 - F_c/F_0$ and $wR_2 = [w(F_0^2 - F_c^2)^2/wF_o^4]^{1/2}$ for $F_0^2 > 2\sigma(F_0^2)$

Table S2 Atomic coordinates, equivalent isotropic displacement parameters and bond valences for NBPS.

Atom	x	y	z	Ueq	Occupancy	Bond valence
Na (1)	0.500000	0.500000	0.500000	0.0971(14)	1	0.74
B (1)	0.500000	0.250000	0.7327(3)	0.0160(9)	1	3.04
B (2)	0.6442(2)	0.3337(2)	0.8759(2)	0.0161(7)	1	3.05
P (1)	0.56428(6)	0.48271(6)	0.73196(5)	0.01641(19)	1	5.00
S (1)	0.46894(6)	0.14192(6)	0.65338(5)	0.01956(19)	1	2.03
S (2)	0.62030(5)	0.21828(5)	0.79946(4)	0.01405(17)	1	2.20
S (3)	0.76472(6)	0.31183(6)	0.94217(5)	0.01864(19)	1	1.95
S (4)	0.68705(6)	0.44887(6)	0.80986(5)	0.01832(19)	1	1.98
S (5)	0.59646(6)	0.60009(6)	0.65848(5)	0.0244(2)	1	1.79

Table S3 Atomic coordinates, equivalent isotropic displacement parameters and bond valences for KBPS.

Atom	x	y	z	Ueq	Occupancy	Bond valence
K (1)	0.250000	0.750000	0.250000	0.1046(11)	1	1.05
B (1)	0.5875(3)	0.3933(3)	0.3753(3)	0.0227(9)	1	3.06
B (2)	0.500000	0.250000	0.2427(4)	0.0254(13)	1	3.07
P (1)	0.44242(9)	0.48542(8)	0.24122(6)	0.0269(3)	1	5.08
S (1)	0.41551(9)	0.60346(9)	0.17211(7)	0.0366(3)	1	1.98
S (2)	0.56863(8)	0.51499(8)	0.31310(7)	0.0291(3)	1	1.95
S (3)	0.70446(8)	0.43293(8)	0.43721(6)	0.0283(3)	1	1.98
S (4)	0.62214(7)	0.27923(7)	0.30511(6)	0.0222(3)	1	2.21
S (5)	0.52774(9)	0.14106(8)	0.16918(7)	0.0308(3)	1	2.08

Table S4 Selected bond Lengths [Å] and angles [°] for NBPS.

Na1-S5	3.0445(11)	S5#7-Na1-S5#8	68.03(3)
Na1#3-S1	3.0332(10)	S5#7-Na1-S5#6	111.97(3)
Na1#4-S5	3.1488(11)	S5#6-Na1-S5#8	180.0
B1-S1	1.915(3)	S5#7-Na1-S5	180.0
B1-S2	1.929(3)	S5-Na1-S5#8	111.97(3)
B2-S2	1.942(3)	S2-B1-S2#3	115.7(2)
B2#1-S2	1.931(3)	S1-B1-S2#3	108.95(4)
B2-S3	1.904(3)	S1#3-B1-S2	108.95(4)
B2-S4	1.906(3)	S1#3-B1-S2#3	110.70(4)
P1-S4	2.0566(11)	S1-B1-S2	110.70(4)
P1-S1#3	2.0801(11)	S1#3-B1-S1	100.9(2)
P1-S3#2	2.0684(11)	S2#2-B2-S2	115.48(17)
P1-S1#3	1.9568(11)	S4-B2-S2	110.13(16)
S1#5-Na1-S1#3	180.0	S4-B2-S2#2	110.13(16)
S1#3-Na1-S5#6	97.44(3)	S3-B2-S2	109.93(16)
S1#3-Na1-S5	65.58(3)	S3-B2-S2#2	110.74(16)
S1#5-Na1-S5#6	82.56(3)	S3-B2-S4	99.19(15)
S1#5-Na1-S5#7	65.58(3)	S4-P1-S3#2	110.01(5)
S1#5-Na1-S5#8	97.44(3)	S4-P1-S1#3	109.44(5)
S1#3-Na1-S5#8	82.56(3)	S3#2-P1-S1#3	108.65(5)
S1#3-Na1-S5#7	114.42(3)	S5-P1-S4	109.72(5)
S1#5-Na1-S5	114.42(3)	S5-P1-S3#2	109.79(5)
S5-Na1-S5#6	68.03(3)	S5-P1-S1#3	109.21(5)

Symmetry transformations used to generate equivalent atoms:
#1 1/4+Y, 3/4-X, 7/4-Z; #2 3/4-Y, -1/4+X, 7/4-Z; #3 1-X,1/2-Y, +Z;
#4 1/4+Y, 5/4-X, 1/4+Z; #5 +X, 1/2+Y, 1-Z; #6 -1/4+Y, 5/4-X, 5/4-Z;
#7 1-X, 1-Y, 1-Z; #8 5/4-Y, -1/4+X, -1/4+Z

Table S5 Selected bond Lengths [Å] and angles [°] for KBPS.

K1-S1	3.1546(12)	S1#10-K1-S1	180.0
K1#4-S1	3.3361(12)	S1#10-K1-S1#9	115.14(4)
K1#3-S5	3.3669(11)	S1-K1-S1#9	64.86(4)
B1-S2	1.905(5)	S1#9-K1-S1#8	180.00(4)
B1-S3	1.907(4)	S1-K1-S1#8	115.14(4)
B1-S4	1.939(4)	S4#4-B1-S4	115.5(2)
B1#1-S4	1.927(4)	S3-B1-S4	110.1(2)
B2-S4	1.935(3)	S3-B1-S4#4	110.4(2)
B2-S5	1.903(4)	S2-B1-S4	110.2(2)
P1-S1	1.9477(14)	S2-B1-S4#4	109.8(2)
P1-S2	2.0651(16)	S2-B1-S3	99.7(2)
P1#1-S3	2.0567(15)	S4#2-B2-S4	115.5(3)
P1#2-S5	2.0700(15)	S5-B2-S4	109.36(5)
S5#6-K1-S5#7	180.0	S5#2-B2-S4#2	109.36(5)
S1#8-K1-S5#6	121.60(3)	S5#2-B2-S4	110.51(5)
S1#9-K1-S5#7	121.60(3)	S5-B2-S4#2	110.51(5)
S1#10-K1-S5#7	95.66(3)	S5#2-B2-S5	100.6(3)
S1#10-K1-S5#6	84.34(3)	S3#4-P1-S2	109.71(6)
S1#8-K1-S5#7	58.40(3)	S3#4-P1-S5#2	108.92(6)
S1-K1-S5#6	95.66(3)	S2-P1-S5#2	108.92(6)
S1#9-K1-S5#6	58.40(3)	S1-P1-S3#4	110.47(7)
S1-K1-S5#7	84.34(3)	S1-P1-S2	109.50(7)
S1#10-K1-S1#8	64.86(4)	S1-P1-S5#2	108.93(7)

Symmetry transformations used to generate equivalent atoms:
#1 1/4+Y, 3/4-X, 3/4-Z; #2 1-X, 1/2-Y, +Z; #3 5/4-Y, -1/4+X, -1/4+Z;
#4 3/4-Y, -1/4+X, 3/4-Z; #5 -1/4+Y, 3/4-X, -1/4+Z; #6 1/4-Y, 1/4+X, 1/4-Z;
#7 1/4+Y, 5/4-X, 1/4+Z; #8 3/4-Y, 1/4+X, 1/4+Z; #9 -1/4+Y, 5/4-X, 1/4-Z;
#10 1/2-X, 3/2-Y, 1/2-Z

5. Figures

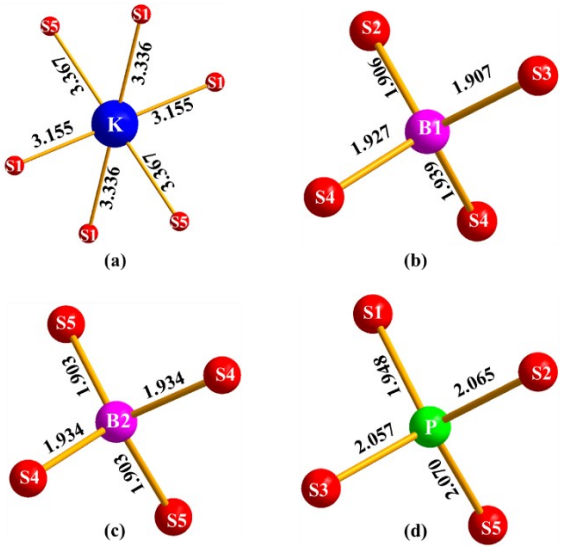

Fig. S1. Coordination environment of K (a), B1 (b), B2 (c) and P (d).

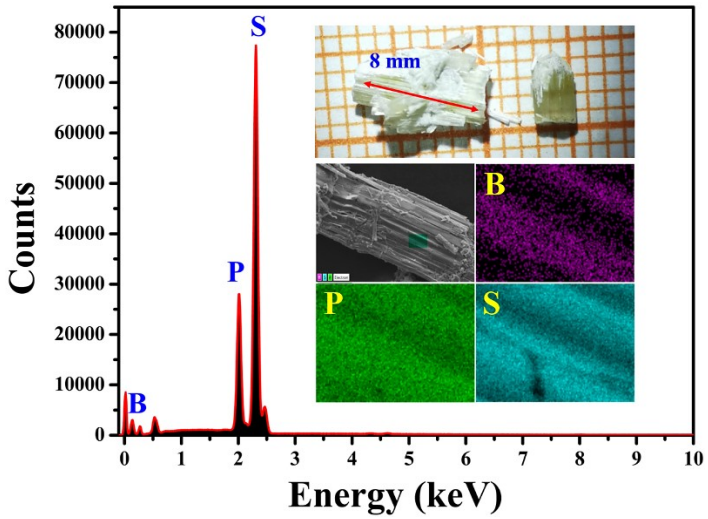

Fig. S2. EDS curves of BPS, the millimeter crystals of BPS (insert the top picture).

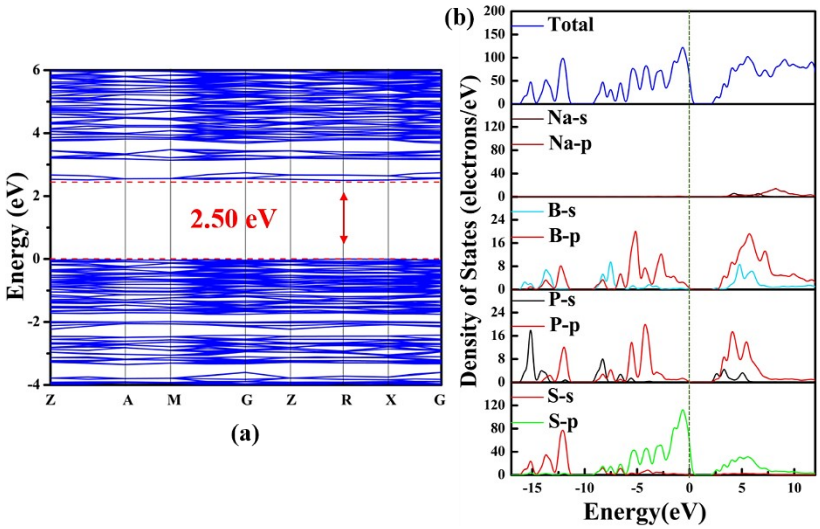

Fig. S3. (a) The calculated band structure of NBPS based on GGA function; (b) The partial density of states (PDOS) of NBPS.

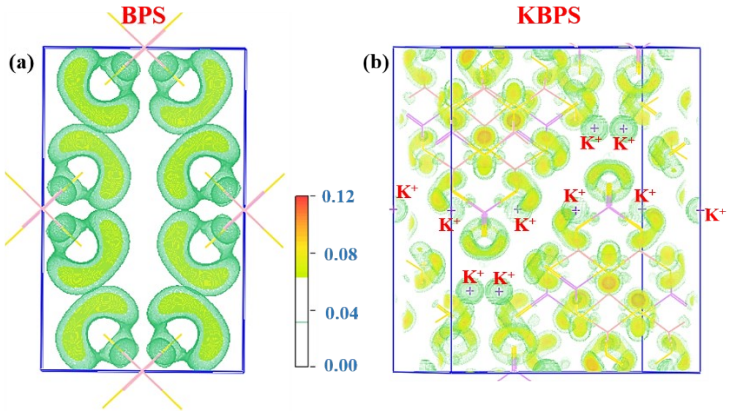

Fig. S4. (a) The electron localization function (ELF) of BPS; (b) The electron localization function (ELF) of KBPS.

6. References

1 G. M. Sheldrick, *SHELXTL, version 6.14*, Bruker Analytical X-ray Instruments, Inc. Madison, WI, 2008.

2 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005, **220**, 567.

3 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.

4 C. Aversa and J. E. Sipe, *Phys. Rev. B*, 1995, **52**, 14636.

5 J. Lin, M. H. Lee, Z. P. Liu, C. Chen and C. J. Pickard, *Phys. Rev. B*, 1999, **60**, 13380.