

Supporting Information

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Uncovering a Vital Band Gap Mechanism of Pnictides

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Supporting Information
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Uncovering a Vital Band Gap Mechanism of Pnictides

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Abstract: Pnictides are superior IR NLO material candidates, but the exploration of NLO pnictides is still tardy due to lack of rational material design strategies. An in-depth understanding structure-performance relationship is urgent for designing novel and eminent pnictide NLO materials. Herein, we unraveled a vital band gap mechanism of pnictides, namely P atom with low coordination numbers (2 CN) will cause the decrease of band gap due to the delocalization of non-bonding electron pairs. Accordingly, a general design paradigm for NLO pnictides, ionicity–covalency–metallicity regulation was proposed for designing wide-band gap NLO pnictides with maintained SHG effect. Driven by this idea, millimeter-level crystals of MgSiP₂ were synthesized with a wide band gap (2.34 eV), a strong NLO performance (3.5 x AgGaS₂) and a wide IR transparency range (0.53-10.3 μm). This work provides an essential guidance for the future design and synthesis of NLO pnictides, and also opens a new perspective at Zintl chemistry important for other material fields.

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Table S1. Crystallographic Data and Refinement Details for MgSiP₂.

Formula	MgSiP ₂
Formula weight	114.34
Temperature/K	293
Radiation	Ga K α ($\lambda = 1.34139$)
Crystal system	tetragonal
Space group	I-42d
a/Å	5.7156(5)
c/Å	10.074(2)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	329.11(10)
Z	4
ρ calc (g/cm ³)	2.308
μ (mm ⁻¹)	9.737
F (000)	224
Index ranges	-5 \leq h \leq 3, -7 \leq k \leq 6, -11 \leq l \leq 12
Reflections collected	395
Independent reflections	175 [R _{int} = 0.0141]
Data/restraints/parameters	175/0/11
Goodness-of-fit on F ²	1.212
Final R indexes [$>=2\sigma$ (I)]	R ₁ = 0.0328, wR ₂ = 0.0862
Final R indexes [all data]	R ₁ = 0.0330, wR ₂ = 0.0866
Largest diff. peak/hole / e Å ⁻³	0.596/-0.659
Flack parameter	0.1(5)

Table S2. The relationship between the coordination number of P atom and the band gap of phosphides.

Compounds	Coordination number of P atom (CN)	Band gap (eV)	Reference
Zn ₃ P ₃	4	2.85	1
Cd ₂ P ₂ Cl ₂	4	>2.5	2
Cd ₃ P ₃	4	2.44	1
GaP	4	2.4	3
MgSiP ₂	4	2.33	4
Cd ₄ P ₂ Cl ₃	4	2.36	5
CdSiP ₂	4	2.2	6
α -ZnP ₂	4	2.25	7
α -CdP ₂	4	2.0	8
IrSi ₃ P ₃	4	1.93	9
RuSi ₄ P ₄	4	1.83	9
NaGe ₃ P ₃	3	2.06	10
SiP (monolayer)	3	2.59	11
Ba ₂ Si ₃ P ₆	2 and 3	1.88	12
KSi ₂ P ₃	2 and 3	1.72	13
BaSi ₇ P ₁₀	2 and 3	1.1	14
SrSi ₇ P ₁₀	2 and 3	1.1	14
Ba ₂ SiP ₄	2	1.45	15

Sr_2SiP_4	2	1.41	15
BaGe_2P_2	2	1.36	16
LaSiP_3	1, 2 and 3	1.3	17
$\beta\text{-Ca}_2\text{CdP}_2$	1, 2 and 3	1.55	18

Table S3. Calculated values of g_{ijk} and C .

Compounds	Groups	g_{ijk}	C
	[ZnP ₄]	$g_{123} = 0.99950$	0.99949
ZnGeP ₂	[GeP ₄]	$g_{123} = 0.99947$	
	[AgS ₄]	$g_{123} = 0.98764$	0.98513
AgGaS ₂	[GaS ₄]	$g_{123} = 0.98263$	
	[MgP ₄]	$g_{123} = 0.98653$	0.98521
MgSiP ₂	[SiP ₄]	$g_{123} = 0.98389$	

Table S4. Comparison of MgSiP₂ with famous and recently reported NLO chalcogenides.

Compounds	E_g (eV)	d_i (pm/V)	Reference
MgSiP ₂	2.34	31.2	this work
AgGaS ₂	2.75	14	19
AgGaSe ₂	1.83	30	19
BaGa ₄ Se ₇	2.64	20.6	20
LiInSe ₂	2.83	12.5	21
BaGa ₂ GeSe ₆	2.31	23.6	19
AgGaGeS ₄	2.78	15	22
AgGaGe ₅ Se ₁₂	2.2	29	23
CdSe	1.65	36	24
m-Ga ₂ Se ₃	1.86	23.2	25
Sr ₆ Cd ₂ Sb ₆ O ₇ S ₁₀	1.89	27.8	26
SnI ₄ (S ₉) ₂	2.17	6.3	27
Na ₂ CdSn ₂ Se ₆	2.15	20.3	28
Ba ₆ In ₆ Zn ₄ Se ₁₉	2.2	16.3	29
Hg ₂ GeSe ₄	1.17	24.56	30

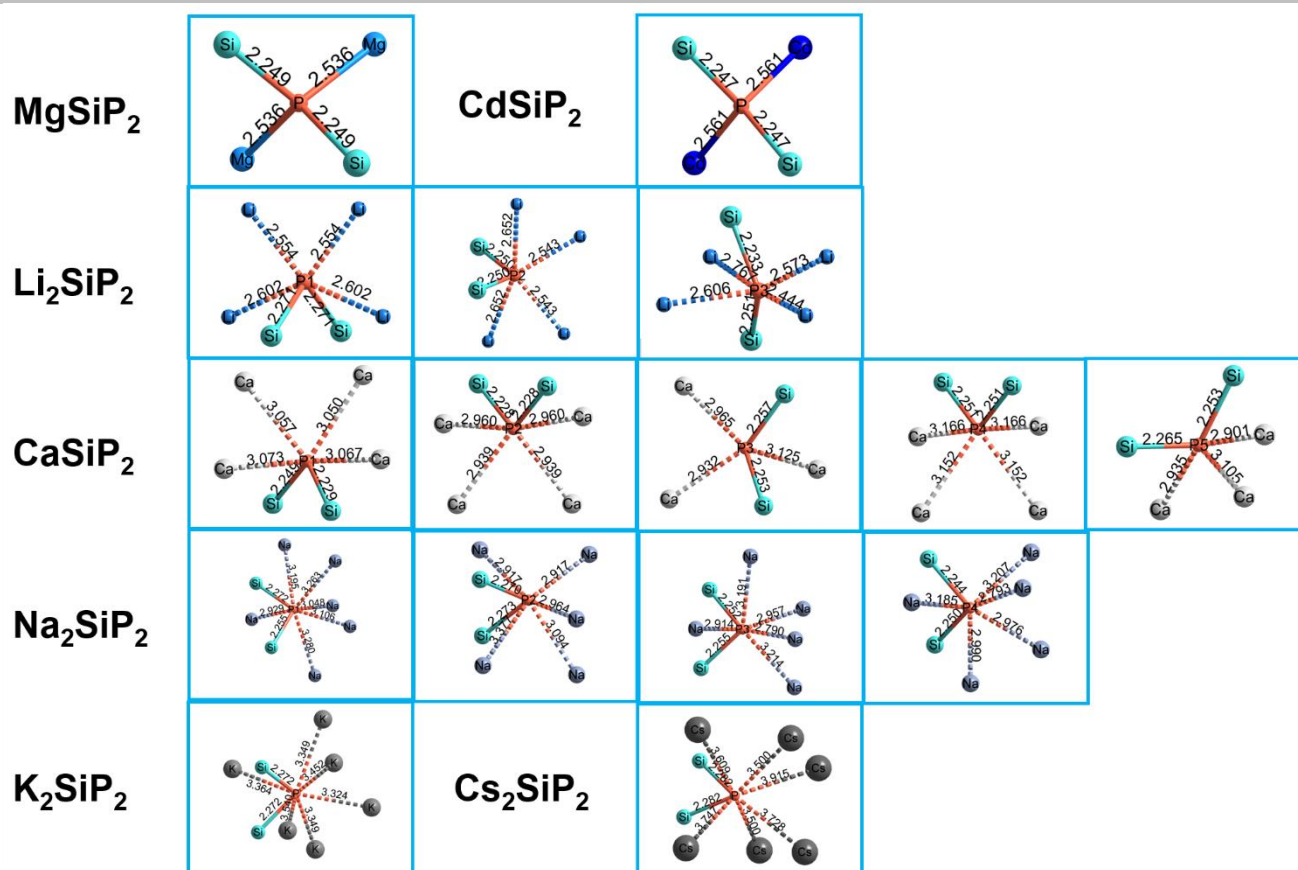


Figure S1. Coordination environment of P atoms.

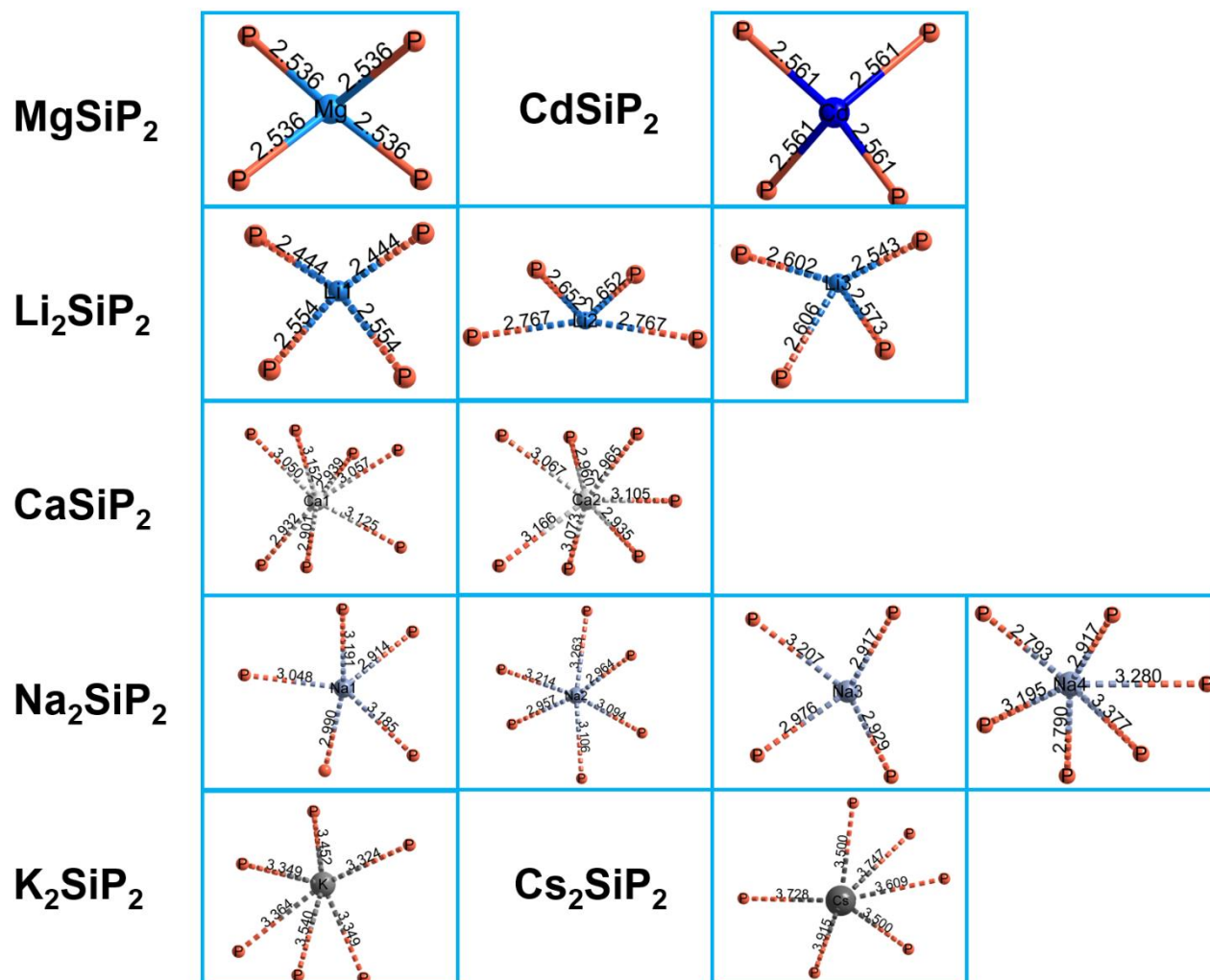


Figure S2. Coordination environment of A site atoms.

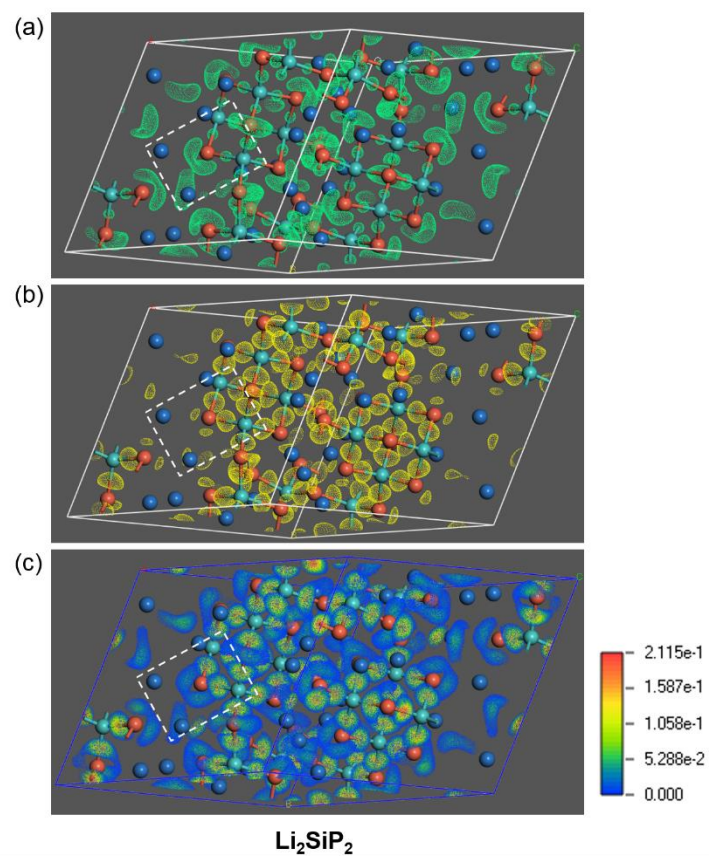


Figure S3. 3D ELF isosurfaces at $\eta = 0.5$ (a), EDD isosurfaces at $\eta = 1/2 \times \text{maximum}$ (b) and EDD distributions (c) of Li_2SiP_2 . White dashed boxes represent two nearest Si and Li atoms of P atom.

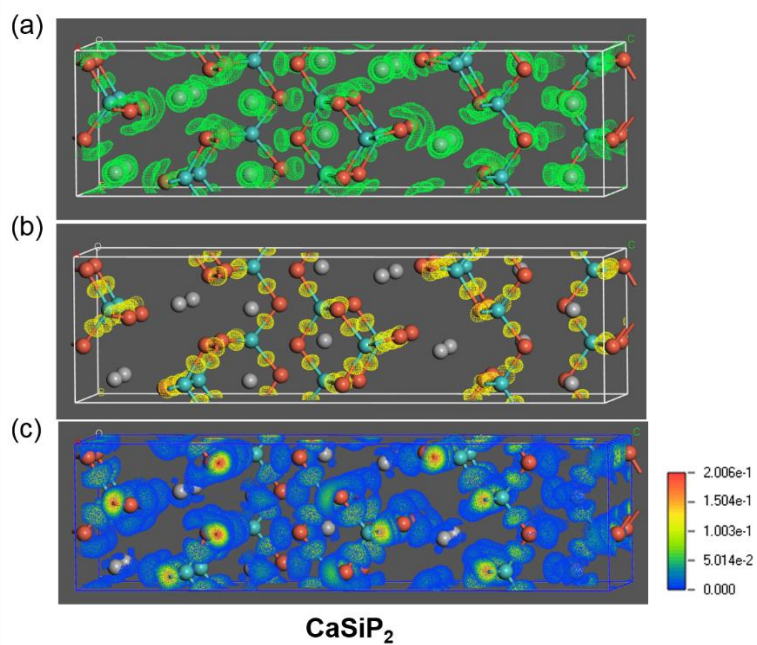


Figure S4. 3D ELF isosurfaces at $\eta = 0.5$ (a), EDD isosurfaces at $\eta = 1/2 \times \text{maximum}$ (b) and EDD distributions (c) of CaSiP_2 .

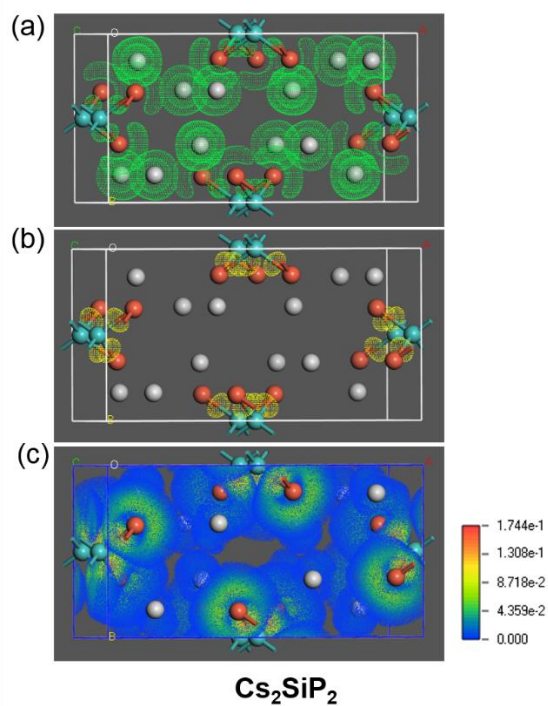


Figure S5. 3D ELF isosurfaces at $\eta = 0.5$ (a), EDD isosurfaces at $\eta = 1/2 \times \text{maximum}$ (b) and EDD distributions (c) of Cs_2SiP_2 .

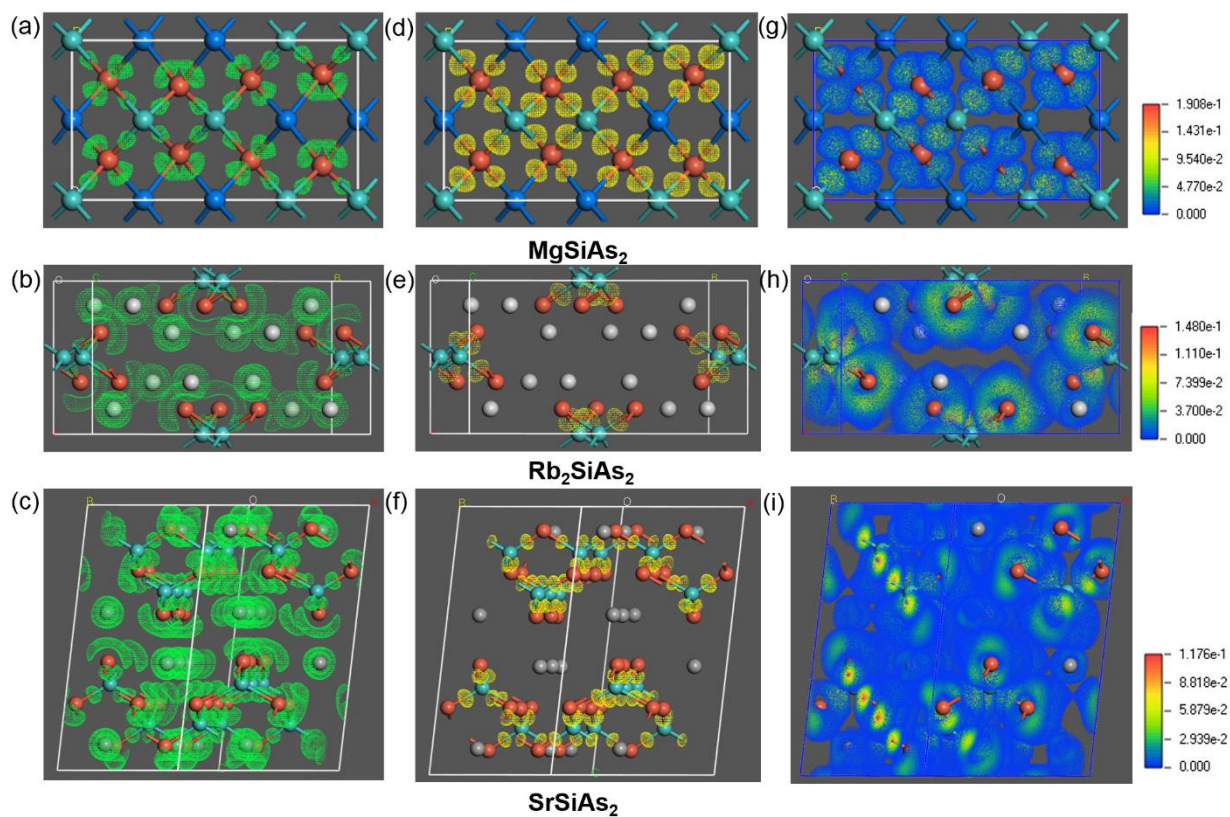


Figure S6. 3D ELF isosurfaces at $\eta = 0.5$ (left column), EDD isosurfaces at $\eta = 1/2 \times \text{maximum}$ (middle column) and EDD distributions (right column) of MgSiAs_2 (a, d and g), Rb_2SiAs_2 (b, e and h), SrSiAs_2 (c, f and i)

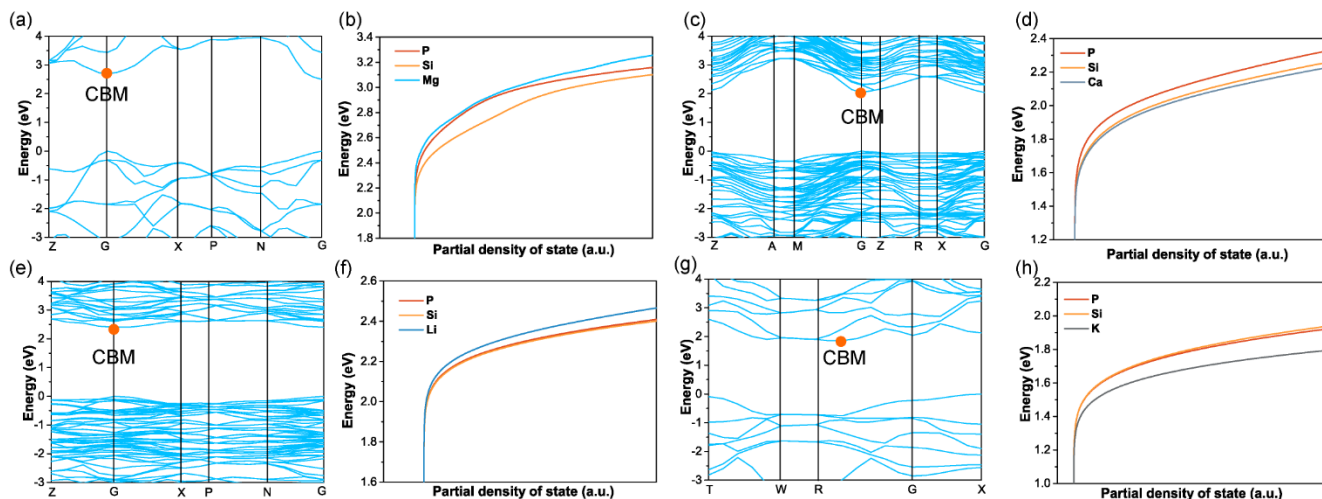


Figure S7. CBM structure comparison of MgSiP_2 (a, b) and CaSiP_2 (c, d), Li_2SiP_2 (e, f) and K_2SiP_2 (g, h).

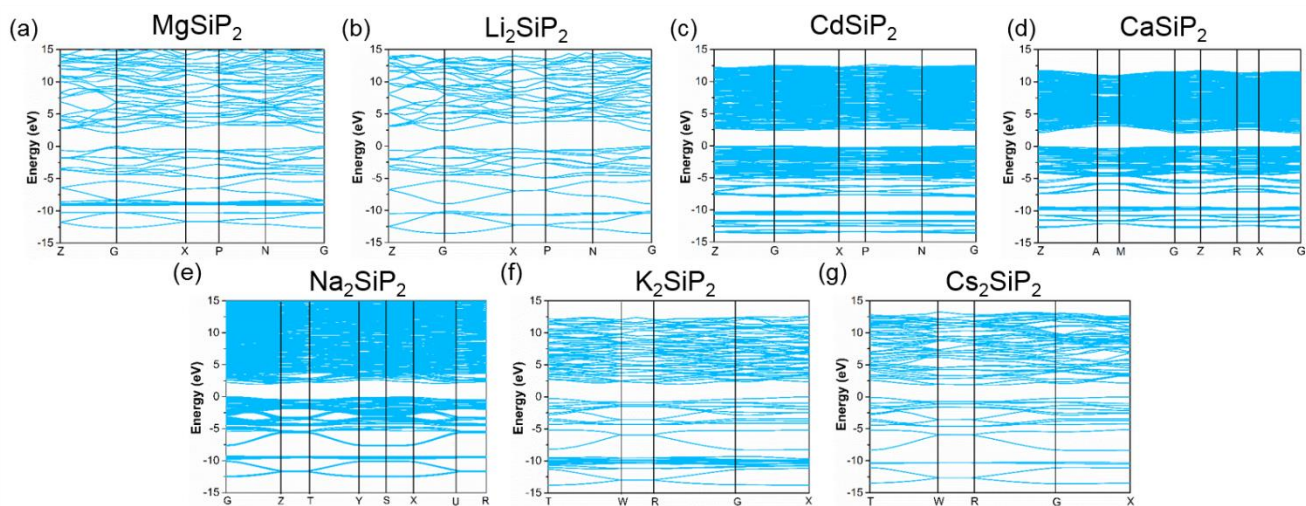


Figure S8. Band structure of MgSiP_2 (a), Li_2SiP_2 (b), CdSiP_2 (c), CaSiP_2 (d), Na_2SiP_2 (e), K_2SiP_2 (f) and Cs_2SiP_2 (g).

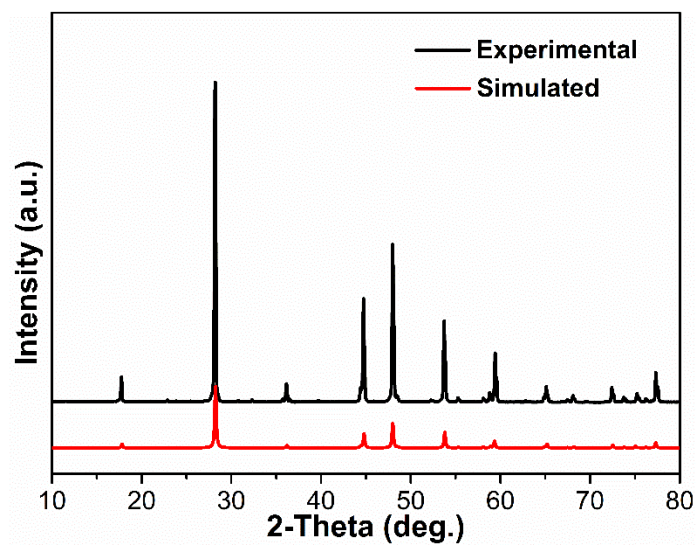
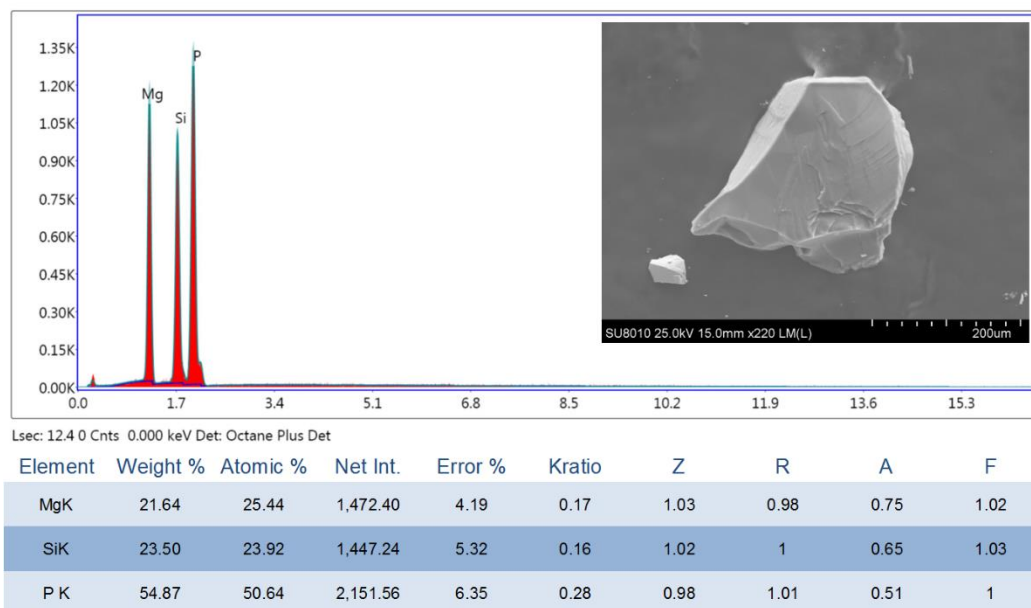
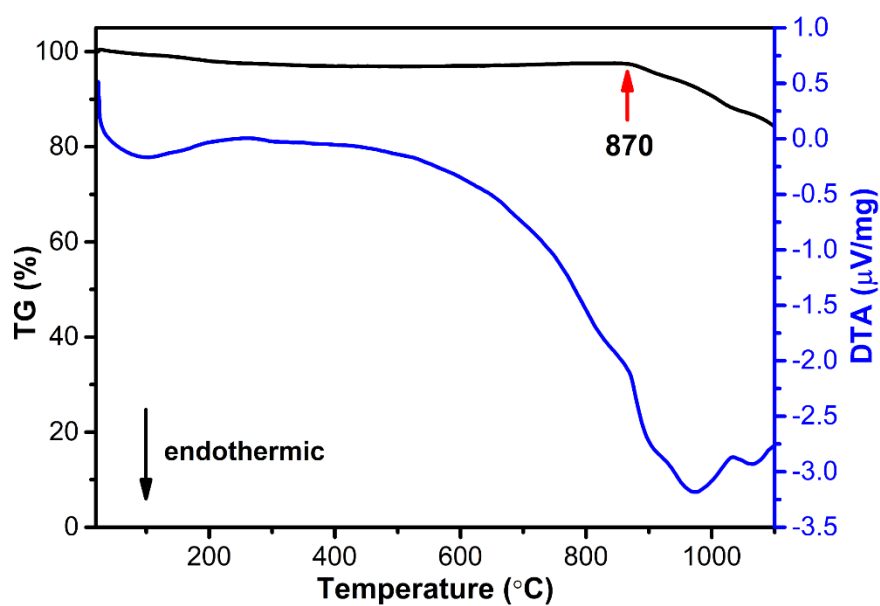


Figure S9. Powder XRD patterns of the experimental and simulated for MgSiP₂.Figure S10. Energy-dispersive X-ray Spectroscopy analysis of MgSiP₂.Figure S11. TG-DTA curves of MgSiP₂.

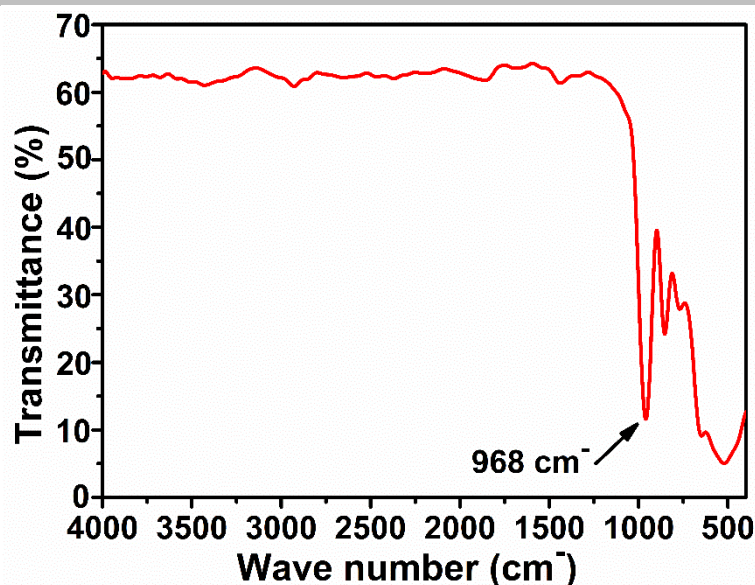


Figure S12. IR transmittance spectrum of MgSiP₂.

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