Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Greatly enhanced optical anisotropy in thiophosphates inspired by rational coupling tetrahedra and ethane-like $[P_2S_6]^{4-}$ groups

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1. Tables

Table S1. The summary of raw materials and the ratio, sintering temperature, crystal color, yield, and the stability of the six new synthesized thiophosphates.

Compounds	Raw materials and the ratio	Temperature (℃)	Crystal color	Yield	Stability
$Na_4MgP_2S_8$	$Na_2S/MgS/P_2S_5$ = 2:1:1	750	colorless	>95%	unstable
$Na_3SbP_2S_8$	$Na_2S/Sb_2S_3/P_2S_5$ = 3:1:2	700	yellow	>95%	stable
$KGaP_2S_6$	$K/Ga_2S_3/P_2S_5/P$ = 10:5:9:2	750	colorless	>95%	stable
$Na_3CuP_2S_6$	$Na/Cu/P_2S_5/S$ = 3:1:1:1	750	red	-	unstable
$K_3CuP_2S_6$	$K/Cu/P_2S_5/S$ = 3:1:1:1	750	yellow	>95%	unstable
$Na_2ZnP_2S_6$	Na/ZnS/P/S = 2:1:2:5	600	colorless	>95%	stable

Table S2. The summary of space group, P-S group, link modes of MS_n and P-S groups, experimental band gap ($E_{g(exp.)}$), calculated band gap ($E_{g(cal.)}$) and birefringence (Δn) in A-M-P-S system.

A-M-P-S system	Space group	P-S group	Link modes of MS_n and P-S groups	$E_{g(exp.)}$ (eV)	$E_{g(Cal.)}$ (eV)	Δn
$Na_4MgP_2S_8$	$P2/n$	$(PS_4)^{3-}$	0D $[Mg_2P_4S_{16}]^{8-}$ cluster	3.48	3.097	0.037
$K_4MgP_2S_8$[1]	$P2/c$	$(PS_4)^{3-}$	0D $[Mg_2P_4S_{16}]^{8-}$ cluster	3.60	2.870	0.034
$Na_3SbP_2S_8$	$P2_1/c$	$(PS_4)^{3-}$	0D $[SbP_2S_8]^{3-}$ cluster	2.26	2.076	0.107
$KGaP_2S_6$	$C2/c$	$(P_2S_6)^{4-}$	1D $[GaP_2S_6]_n$ chain	3.40	2.670	0.068
$NaAlP_2S_6$[2]	$Fdd2$	$(P_2S_6)^{4-}$	3D network	-	3.574	0.076
$Na_3CuP_2S_6$	$P2_1/c$	$(P_2S_6)^{4-}$	1D $[CuP_2S_6]_n$ chain	-	2.337	0.151
$K_3CuP_2S_6$	$P2_1/c$	$(P_2S_6)^{4-}$	1D $[CuP_2S_6]_n$ chain	2.27	2.188	0.124
$K_2ZnP_2S_6$[3]	$C2/c$	$(P_2S_6)^{4-}$	1D $[ZnP_2S_6]_n$ chain	-	3.033	0.150
$Na_2ZnP_2S_6$	$P2_1/n$	$(P_2S_6)^{4-}$	2D layer	3.26	2.940	0.136
$KSbP_2S_6$[4,5]	$P2_1$	$(P_2S_6)^{4-}$	2D layer	2.9(1)[5]	2.192	0.186

Table S3. The distorted degrees (Δd) of MS_4 in A-M-P-S system.

A-M-P-S system	MS_4	Δd
$Na_3SbP_2S_8$	SbS_4	4.805
$KGaP_2S_6$	GaS_4	0.062
$Na_3CuP_2S_6$	CuS_4	0.278
$K_3CuP_2S_6$	CuS_4	1.239
$K_2ZnP_2S_6$	ZnS_4	0.054
$Na_2ZnP_2S_6$	ZnS_4	0.163

2. Figures

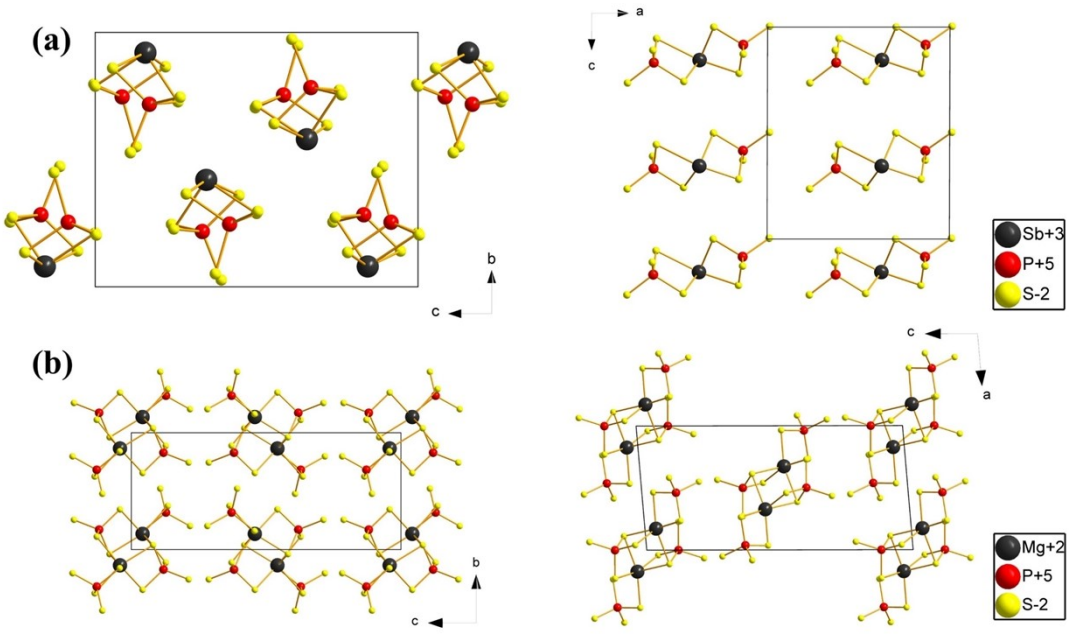

Fig. S1. Crystal structures of $Na_3SbP_2S_8$ (a) and $Na_4MgP_2S_8$ (b).

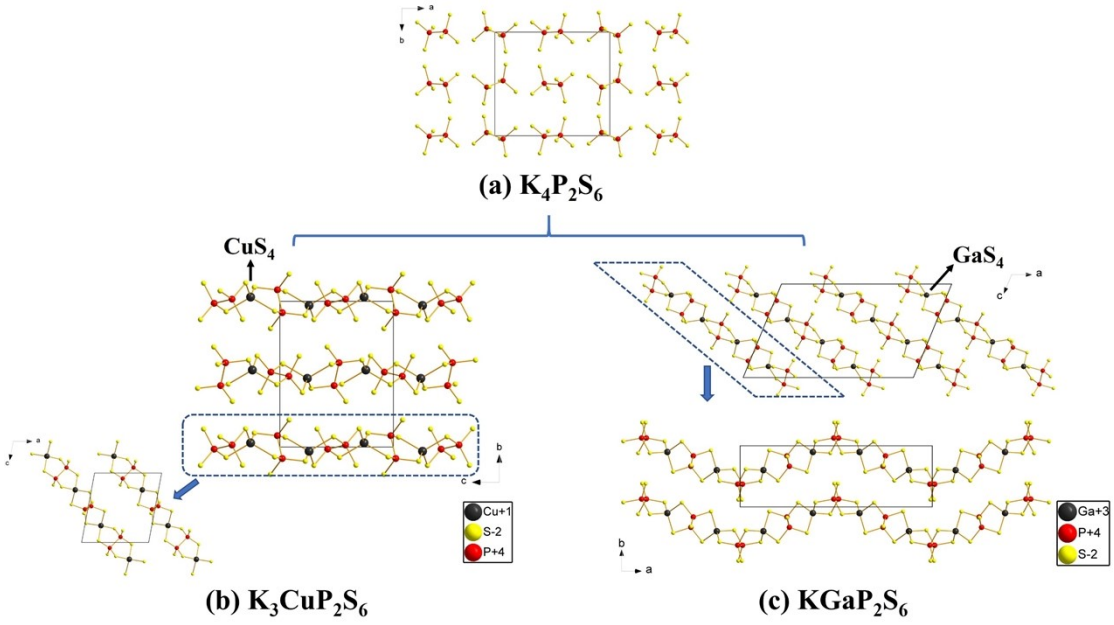

Fig. S2. The comparison about $[P_2S_6]^{4-}$ arrangement in $K_4P_2S_6$ (a), $K_3CuP_2S_6$ (b) and $KGaP_2S_6$ (c).

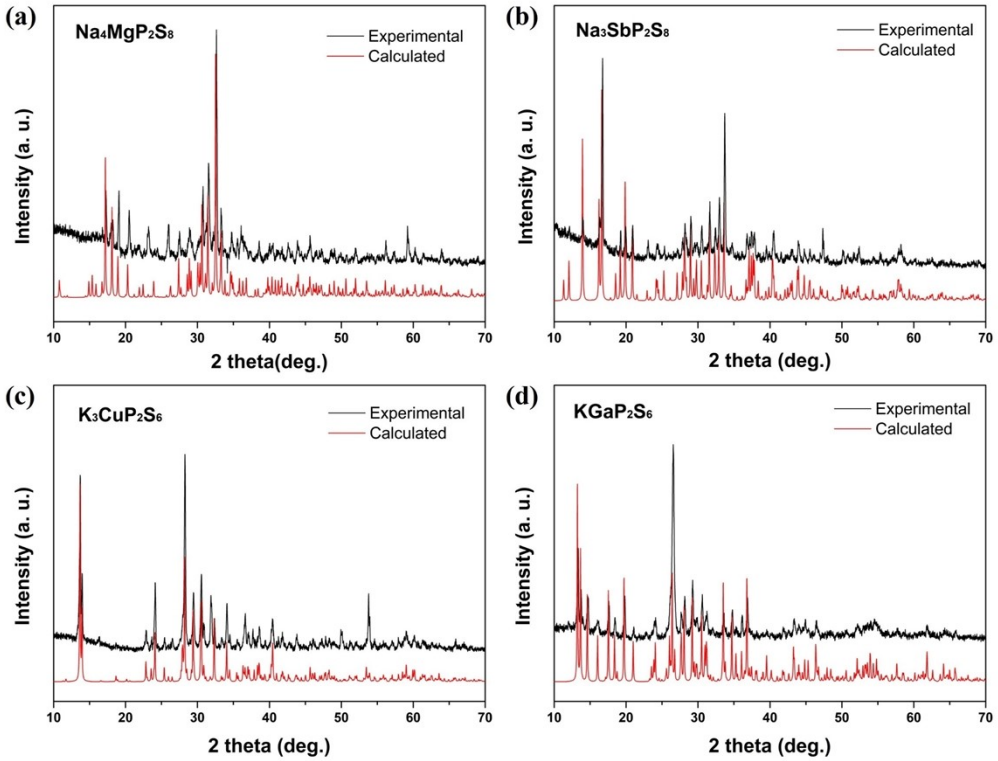

Fig. S3. Powder XRD patterns for (a)$Na_4MgP_2S_8$; (b) $Na_3SbP_2S_8$; (c) $K_3CuP_2S_6$ and (d) $KGaP_2S_6$.

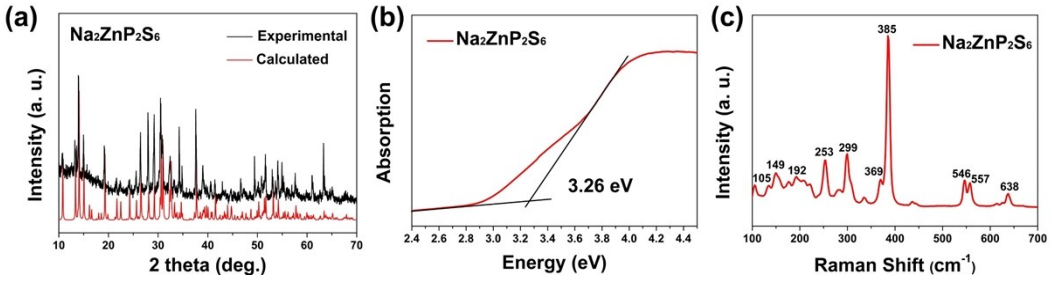

Fig. S4. Powder XRD patterns (a), band gap (b) and Raman spectrum (c) of $Na_2ZnP_2S_6$.

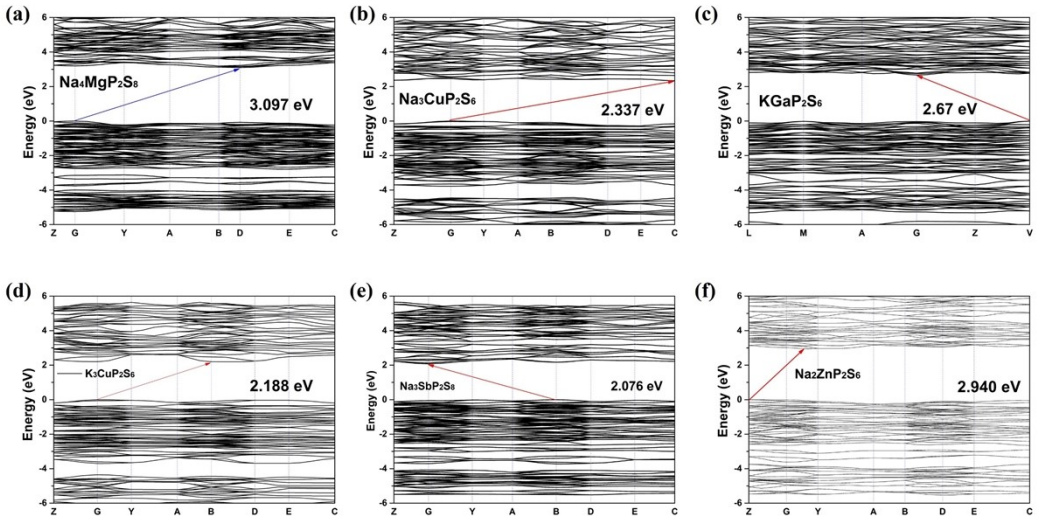

Fig. S5 Band structures of (a) $Na_4MgP_2S_8$; (b)$Na_3CuP_2S_6$; (c) $KGaP_2S_6$; (d) $K_3CuP_2S_6$; (e) $Na_3SbP_2S_8$ and (f) $Na_2ZnP_2S_6$.

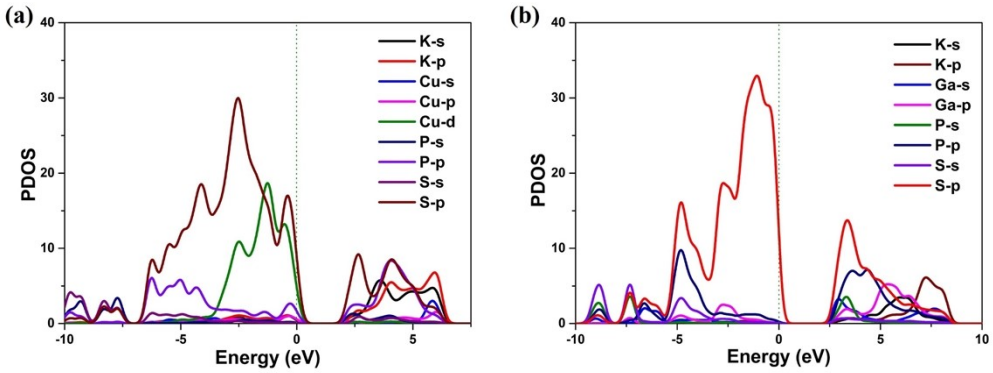

Fig. S6. PDOS diagrams of (a) $K_3CuP_2S_6$ and (b) $KGaP_2S_6$.

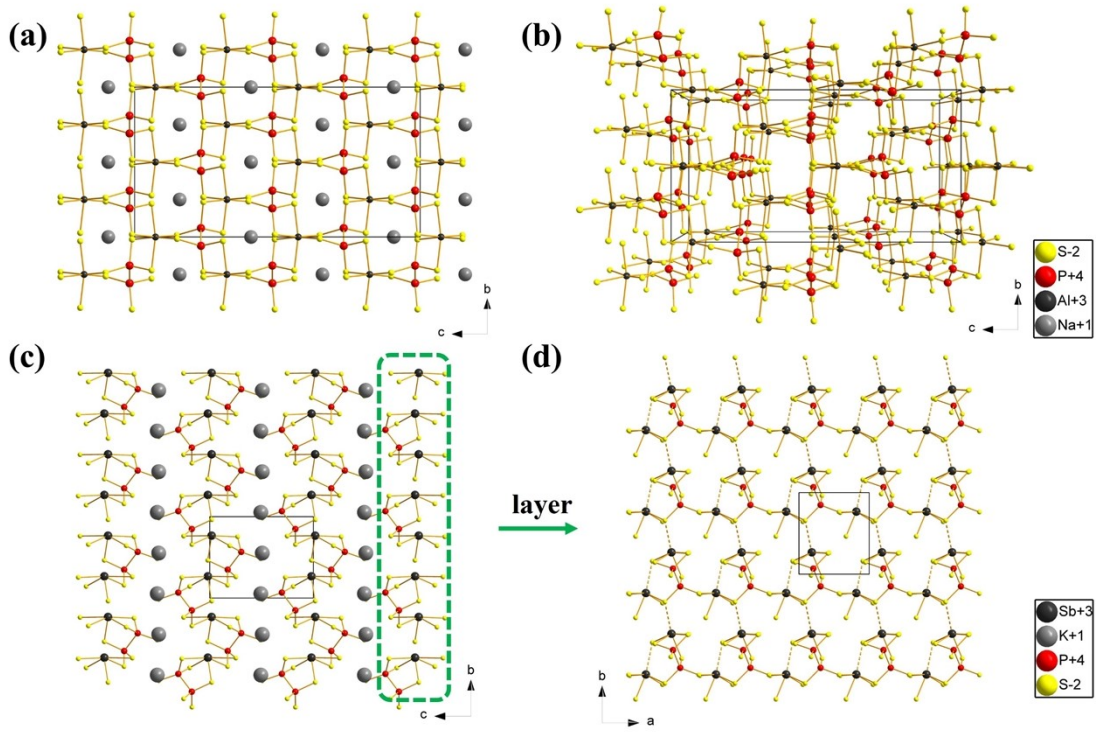

Fig. S7. Whole structure (a) and 3D network (b) of $NaAlP_2S_6$; whole structure (c) and 2D layer (d) of $KSbP_2S_6$.

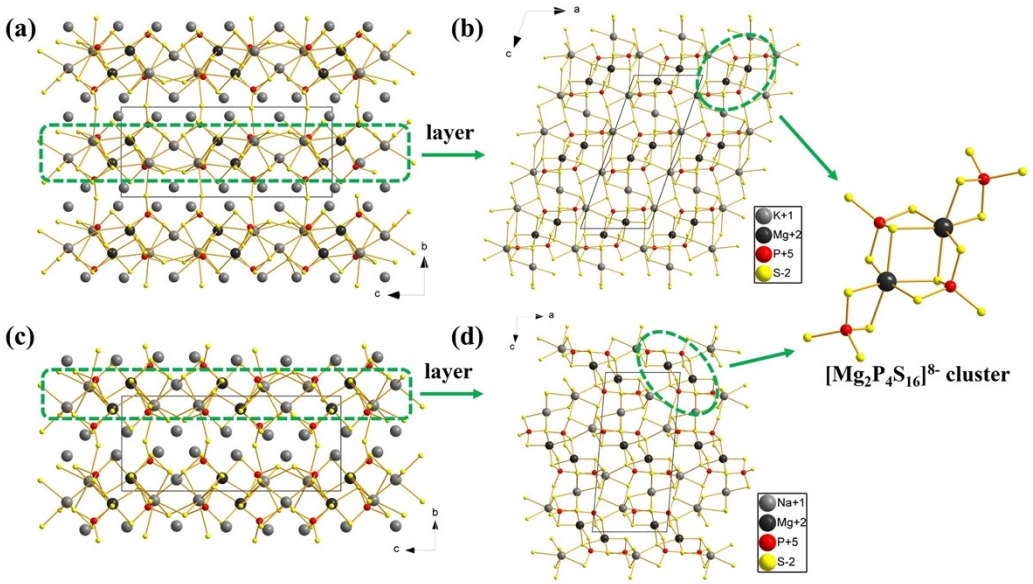

Fig. S8. Crystal structures of $A_4MgP_2S_8$: whole structure (a) and 2D layer (b) of $K_4MgP_2S_8$; whole structure (c) and 2D layer (d) of $Na_4MgP_2S_8$.

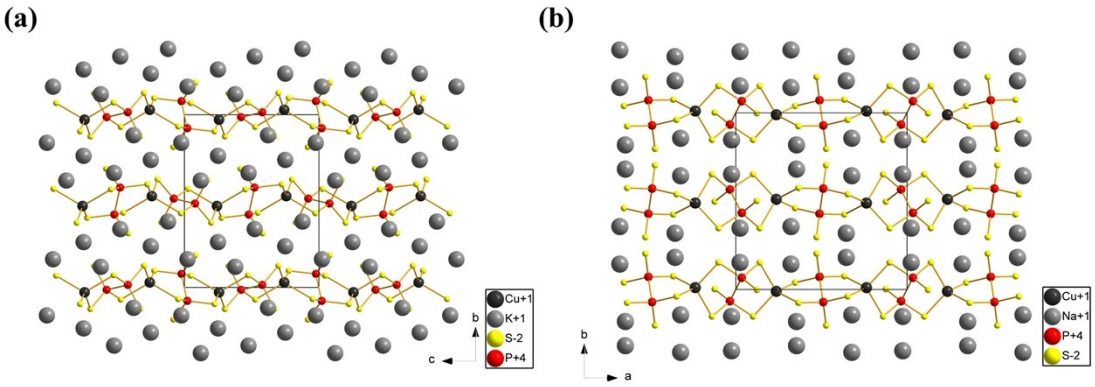

Fig. S9. Crystal structures of $K_3CuP_2S_6$ (a) and $Na_3CuP_2S_6$ (b).

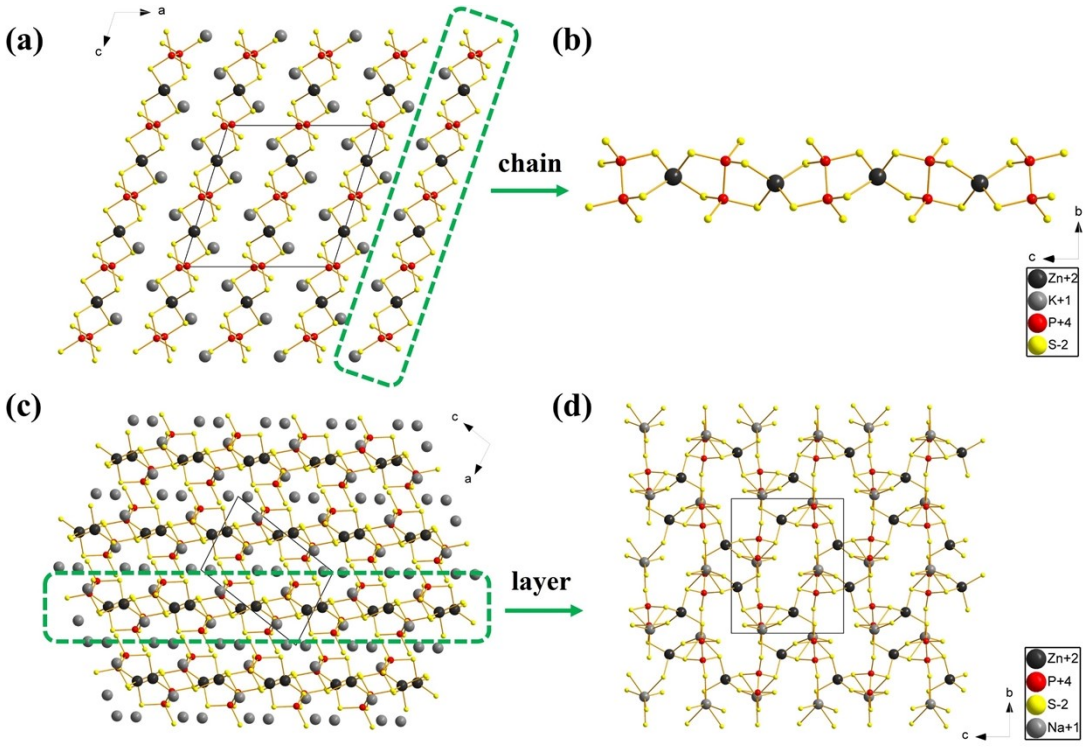

Fig. S10. Crystal structures of $A_2ZnP_2S_6$: whole structure (a) and 1D chain (b) of $K_2ZnP_2S_6$; whole structure (c) and 2D layer (d) of $Na_2ZnP_2S_6$.

3. References

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