Electronic Supplementary Information

Wide band gap thiophosphates $ASrPS_4$ (A=Li, Na, K, Rb, Cs): cation size effect induced successive structure transformation

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters for $ASrPS_4$ (A=Li, Na, K, Rb, Cs).

Atom	x	y	z	Ueq	Occupancy
$LiSrPS_4$					
Li(1)	0.250000	0.9668(9)	0.500000	0.040(2)	1
Sr(1)	0.000000	0.750000	0.625000	0.0196(2)	1
Sr(2)	0.500000	0.750000	0.625000	0.0183(2)	1
P(1)	0.250000	0.71546(9)	0.500000	0.0143(2)	1
S(1)	0.10315(6)	0.61568(7)	0.49747(4)	0.0191(2)	1
S(2)	0.24719(7)	0.81655(6)	0.58371(4)	0.0211(2)	1
$NaSrPS_4$					
Na(1)	0.5934(3)	0.7825(3)	0.7429(4)	0.0447(7)	1
Sr(1)	0.14540(6)	0.89567(4)	0.26861(7)	0.02039(18)	1
P(1)	0.23952(15)	0.54354(12)	0.2954(2)	0.0178(3)	1
S(1)	0.34959(15)	0.68125(13)	0.4712(2)	0.0229(3)	1
S(2)	0.04491(15)	0.62849(12)	0.16092(19)	0.0195(3)	1
S(3)	0.18406(16)	0.39595(12)	0.4582(2)	0.0229(3)	1
S(4)	0.36384(16)	0.48212(13)	0.1039(2)	0.0242(3)	1
$KSrPS_4$					
K(1)	0.7877(2)	0.250000	1.0225(8)	0.0414(11)	1
Sr(1)	0.52226(8)	0.250000	0.2100(2)	0.0211(4)	1
P(1)	0.5983(2)	0.250000	0.7222(6)	0.0159(7)	1
S(1)	0.6670(2)	0.250000	0.4689(6)	0.0240(8)	1
S(2)	0.4793(2)	0.250000	0.6577(6)	0.0230(8)	1
S(3)	0.62181(14)	0.4957(4)	0.8977(4)	0.0222(6)	1
$RbSrPS_4$					
Rb(1)	0.70958(3)	1.250000	0.49457(9)	0.04372(15)	1
Sr(1)	0.52061(2)	0.750000	0.20859(6)	0.02230(11)	1
P(1)	0.59667(6)	0.750000	0.72308(15)	0.01719(19)	1
S(1)	0.66281(6)	0.750000	0.46728(16)	0.0242(2)	1
S(2)	0.61909(4)	0.50528(9)	0.89890(11)	0.02319(15)	1
S(3)	0.48101(6)	0.750000	0.65956(16)	0.0260(2)	1
$CsSrPS_4$					
Cs(1)	0.70669(3)	0.750000	0.45337(13)	0.0470(2)	1
Sr(1)	0.51730(4)	0.250000	0.20509(11)	0.02371(19)	1
P(1)	0.59489(10)	0.250000	0.7239(3)	0.0183(4)	1
S(1)	0.65593(11)	0.250000	0.4603(3)	0.0242(4)	1
S(2)	0.48352(11)	0.250000	0.6650(3)	0.0290(4)	1
S(3)	0.61640(8)	0.49263(19)	0.9007(2)	0.0252(3)	1

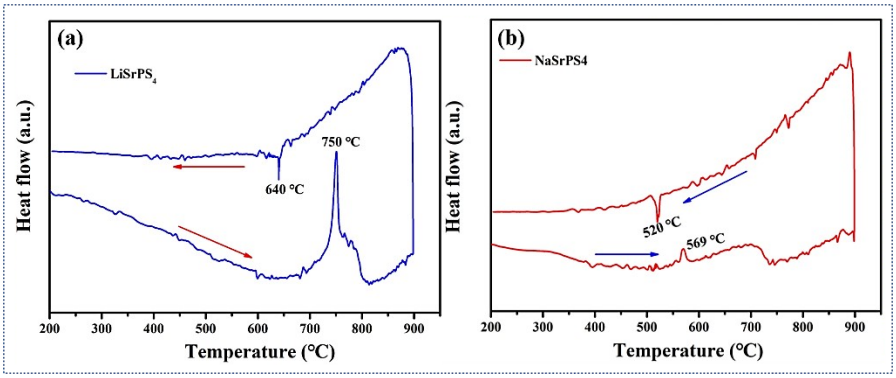

Figure S1. Differential scanning calorimetry (DSC) curves of $LiSrPS_4$ (a) and $NaSrPS_4$ (b).

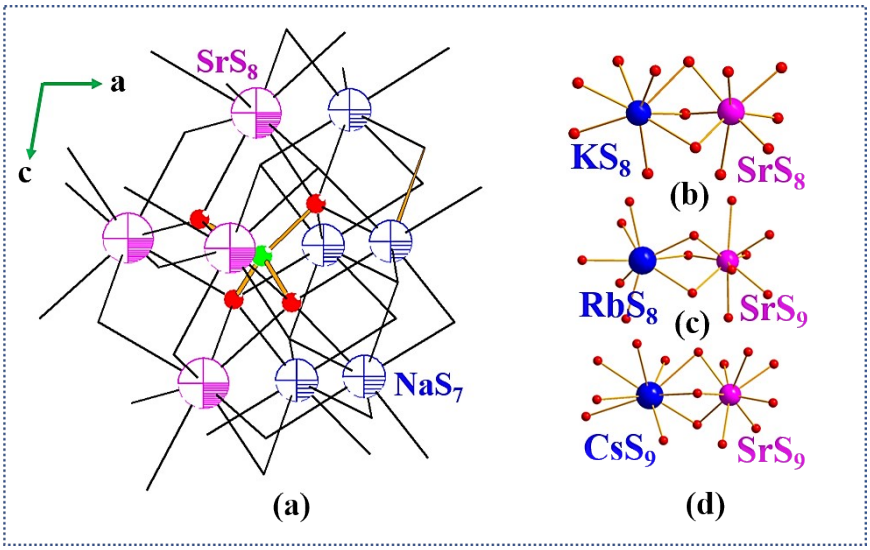

Figure S2. (a) The connection of $[PS_4]$ tetrahedra with $[SrS_8]$ and $[NaS_7]$ by sharing S atoms to form the 3D structure. (b) The connection of $[KS_8]$ and $[SrS_8]$ in $KSrPS_4$. (c) The connection of $[RbS_8]$ and $[SrS_9]$ in $RbSrPS_4$. (d) The connection of $[CsS_9]$ and $[SrS_9]$ in $CsSrPS_4$.

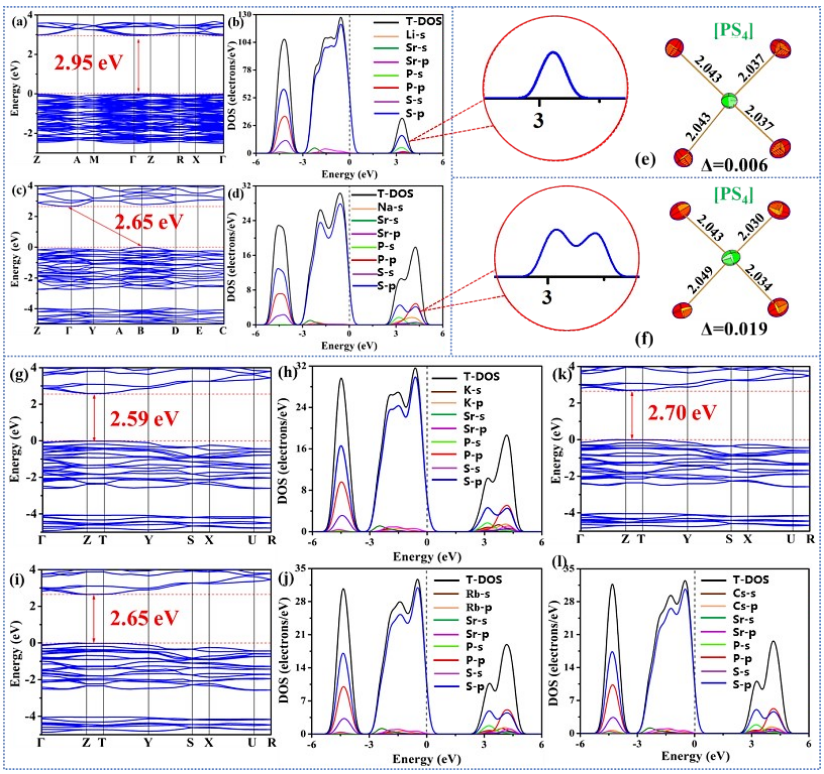

Figure S3. The theoretical band gap and the partial density of states (PDOS) of $ASrPS_4$ (A=Li, Na, K, Rb, Cs), (e) and (f) are isolated $[PS_4]$ units with bond distance of P-S.