Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information:

Alkali Halide Flux Synthesis, Crystal Structure, and Photoelectric Response of Quaternary Thiosilicates $K_3Ga_3Si_7S_{20}$ and $K_2ZnSi_3S_8$

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1. Synthesis Procedures

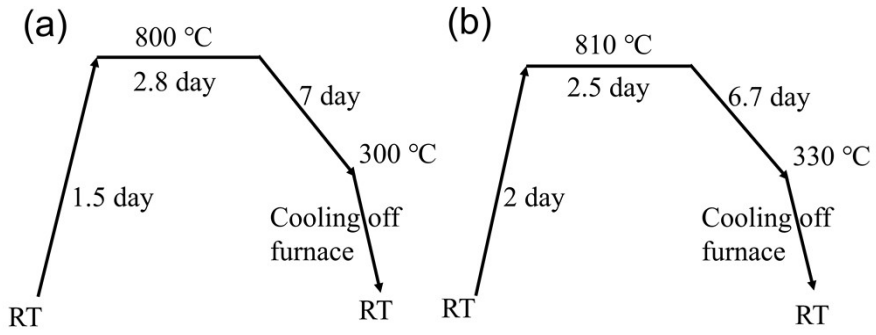

Figure S1 Synthetic temperature control roadmaps for **1** (a) and **2** (b).

2. Supporting Figures

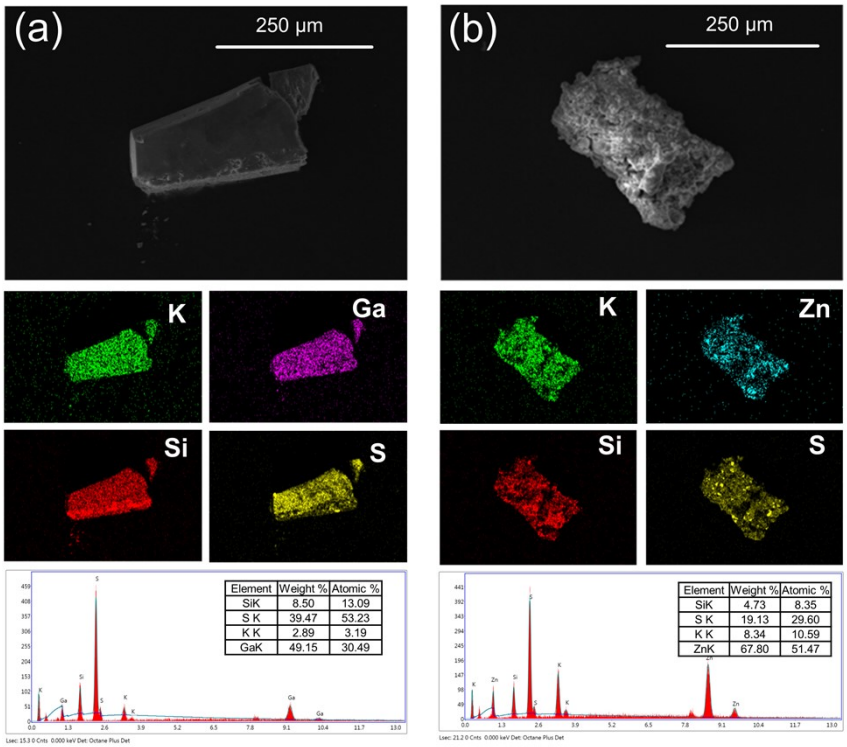

Figure S2 SEM images of **1** (a) and **2** (b) and their elemental distribution maps and the EDS results of **1** and **2**.

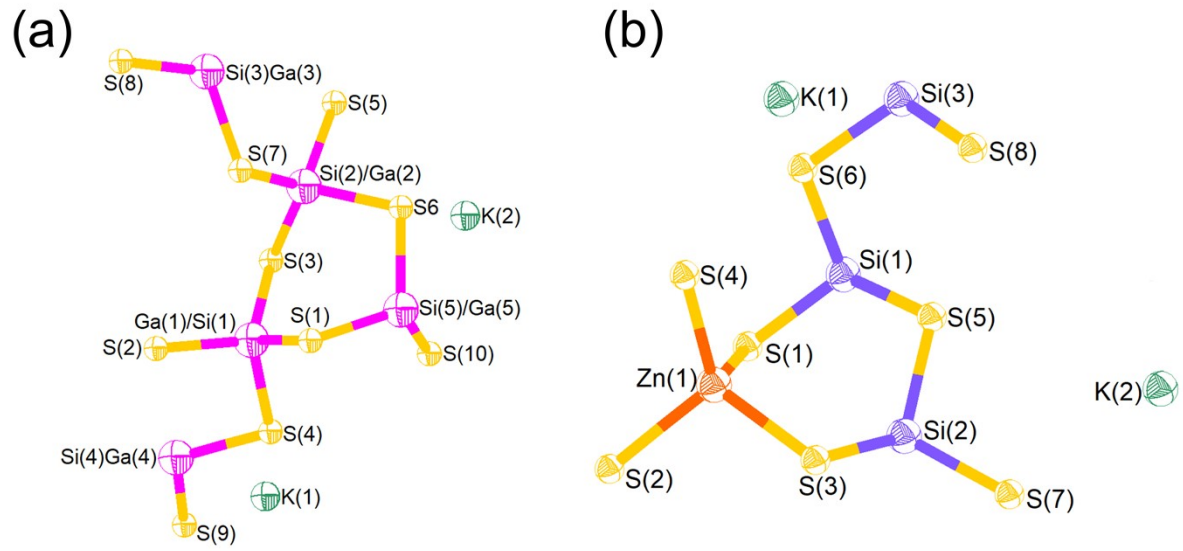

Figure S3 *ORTEP* drawings (50% ellipsoid probability) of the asymmetric units of **1** (a) at 296 K and **2** (b) at 297 K.

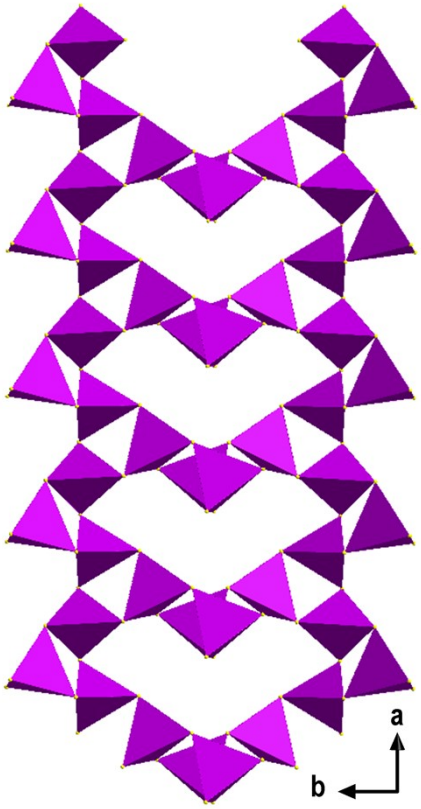

Figure S4 A 1-D band in **1** viewed along the *c*-axis.

3. X-ray Crystallography

Table S1 Crystallographic data and structural refinement details for **1** and **2**.

Empirical formula	$K_3Ga_3Si_7S_{20}$	$K_2ZnSi_3S_8$
F_w	1164.29	484.32
a (Å)	6.6732	6.9955
b (Å)	36.810	7.4508
c (Å)	6.6191	14.2302
α (°)	90.0	87.204
β (°)	90.946	81.546
γ (°)	90.0	69.495
Space group	$P2_1/c$	$P\bar{1}$
V (Å^3)	1625.7	687.16
Z	2	2
θ range (°)	3.480 to 29.657	3.588 to 29.588
ρ_{calcd} (g/cm^3)	2.379	2.341
μ (Mo$K\alpha$) / (mm^{-1})	4.401	3.826
Crystal size (mm^3)	0.200 × 0.200 × 0.150	0.150 × 0.150 × 0.100
λ (Mo$K\alpha$) (Å)	0.71073	0.71073
Temperature (K)	296	297
Total/independent reflections	11559 / 3901	6921 / 3252
Reflections with $I > 2\sigma(I)$	$R_1 = 0.0549$, $wR_2 = 0.0955$	$R_1 = 0.0572$, $wR_2 = 0.1154$
$R_1{}^a/wR_2{}^b$	$R_1 = 0.0967$, $wR_2 = 0.1117$	$R_1 = 0.0818$, $wR_2 = 0.1289$
Goodness of fit	1.044	1.122
Index ranges	$-8 \le h \le 9$, $-47 \le k \le 46$, $-7 \le l \le 8$	$-8 \le h \le 8$, $-10 \le k \le 9$, $-19 \le l \le 17$
F (000)	1136	476

$^aR_1 = \Sigma||Fo| - |/\Sigma|Fo|$. $^bwR_2 = [w(|Fo|^2\text{-}Fc|^2)^2 / \Sigma w(|Fo|^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **1** and **2**.

Compound **1**			
M(1)-S(3)	2.2041(18)	*M*(5)-S(2)#5	2.121(2)
M(1)-S(1)	2.2260(17)	*M*(5)-S(1)	2.125(2)
M(1)-S(2)	2.228(2)	*M*(5)-S(10)	2.145(2)
M(1)-S(4)	2.2420(17)	*M*(5)-S(6)	2.1569(19)
M(2)-S(3)	2.1436(19)	S(1)-K(1)	3.3667(16)
M(2)-S(7)	2.155(2)	S(2)-K(2)#7	3.663(3)
M(2)-S(5)	2.1553(19)	S(3)-K(2)#3	3.606(3)
M(2)-S(6)	2.195(2)	S(4)-K(1)	3.5042(19)
M(3)-S(5)#1	2.1563(19)	S(5)-K(2)	3.762(3)
M(3)-S(8)	2.165(2)	S(6)-K(2)#6	3.322(3)
M(3)-S(8)#2	2.1664(19)	S(6)-K(2)	3.359(3)
M(3)-S(7)	2.1812(18)	S(7)-K(2)#6	3.704(3)
M(4)-S(4)	2.132(2)	S(7)-K(2)#7	3.758(3)
M(4)-S(10)#3	2.145(2)	S(8)-K(2)#7	3.285(3)
M(4)-S(9)	2.152(2)	S(9)-K(1)#8	3.6138(19)
M(4)-S(9)#4	2.167(2)	S(10)-K(2)	3.364(3)
S(3)-*M*(1)-S(1)	115.15(7)	S(5)#1-*M*(3)-S(8)	115.91(8)
S(3)-*M*(1)-S(2)	120.64(7)	S(5)#1-*M*(3)-S(8)#2	117.04(8)
S(1)-*M*(1)-S(2)	96.31(7)	S(8)-*M*(3)-S(8)#2	100.39(8)
S(3)-*M*(1)-S(4)	106.70(7)	S(5)#1-*M*(3)-S(7)	106.13(8)
S(1)-*M*(1)-S(4)	108.69(7)	S(8)-*M*(3)-S(7)	106.05(8)
S(2)-*M*(1)-S(4)	108.68(7)	S(8)#2-*M*(3)-S(7)	110.88(8)
S(3)-*M*(2)-S(7)	113.11(9)	S(4)-*M*(4)-S(10)#3	113.36(8)
S(3)-*M*(2)-S(5)	110.02(8)	S(4)-*M*(4)-S(9)	108.87(9)
S(7)-*M*(2)-S(5)	117.14(8)	S(10)#3-*M*(4)-S(9)	108.31(8)
S(3)-*M*(2)-S(6)	112.01(8)	S(4)-*M*(4)-S(9)#4	113.57(9)
S(7)-*M*(2)-S(6)	108.40(8)	S(10)#3-*M*(4)-S(9)#4	113.48(9)
S(5)-*M*(2)-S(6)	94.75(8)	S(9)-*M*(4)-S(9)#4	97.92(8)

(*M* = 0.3 Ga + 0.7 S.)

Compound **2**			
Zn(1)-S(1)	2.3141(19)	S(2)-K(2)#1	3.319(2)
Zn(1)-S(4)	2.332(2)	S(2)-K(1)#2	3.336(3)
Zn(1)-S(2)	2.3364(17)	S(2)-K(2)#6	3.431(2)
Zn(1)-S(3)	2.3540(19)	S(3)-K(2)#2	3.145(2)
Zn(1)-K(2)#1	3.8702(18)	S(3)-K(2)#1	3.358(3)
Zn(1)-K(1)#2	4.011(2)	S(3)-K(1)#7	3.733(3)
Si(1)-S(1)	2.078(2)	S(4)-K(1)#8	3.445(3)
Si(1)-S(2)#3	2.090(2)	S(4)-K(1)#7	3.536(3)
Si(1)-S(6)	2.154(2)	S(5)-K(1)#7	3.740(3)
Si(1)-S(5)	2.171(3)	S(6)-K(1)	3.691(3)

Si(2)-S(3)	2.065(2)	S(7)-K(2)	3.379(2)
Si(2)-S(5)	2.114(2)	S(7)-K(2)#9	3.389(3)
Si(2)-S(7)#1	2.156(3)	S(7)-K(2)#2	3.705(2)
Si(2)-S(7)	2.163(2)	S(8)-K(1)#10	3.581(3)
Si(3)-S(4)#3	2.063(3)	S(8)-K(1)#7	3.593(3)
Si(3)-S(6)	2.130(2)	K(1)-K(1)#11	4.817(4)
Si(3)-S(8)#4	2.146(2)	K(2)-K(2)#12	4.018(3)
Si(3)-S(8)	2.158(3)	K(2)-K(2)#13	4.330(4)
Si(3)-Si(3)#4	2.822(4)	K(2)-K(2)#9	4.972(3)
S(1)-K(2)#5	3.179(3)		
S(1)-Zn(1)-S(4)	108.52(7)	S(3)-Si(2)-S(5)	114.27(11)
S(1)-Zn(1)-S(2)	102.94(7)	S(3)-Si(2)-S(7)#1	115.89(10)
S(4)-Zn(1)-S(2)	114.97(7)	S(5)-Si(2)-S(7)#1	112.19(11)
S(1)-Zn(1)-S(3)	109.27(7)	S(3)-Si(2)-S(7)	110.07(11)
S(4)-Zn(1)-S(3)	113.55(8)	S(5)-Si(2)-S(7)	106.41(9)
S(2)-Zn(1)-S(3)	106.99(7)	S(7)#1-Si(2)-S(7)	96.02(9)
S(1)-Si(1)-S(2)#3	108.01(11)	S(4)#3-Si(3)-S(6)	116.14(12)
S(1)-Si(1)-S(6)	107.15(9)	S(4)#3-Si(3)-S(8)#4	110.37(10)
S(2)#3-Si(1)-S(6)	111.09(10)	S(6)-Si(3)-S(8)#4	104.23(10)
S(1)-Si(1)-S(5)	114.92(10)	S(4)#3-Si(3)-S(8)	113.16(11)
S(2)#3-Si(1)-S(5)	110.53(10)	S(6)-Si(3)-S(8)	112.89(10)
S(6)-Si(1)-S(5)	105.11(10)	S(8)#4-Si(3)-S(8)	98.06(10)

Symmetry transformations used to generate equivalent atoms for **1**: #1 *x*,-*y*+1/2,*z*-1/2; #2 *x*,-*y*+1/2,*z*+1/2; #3 *x*+1,*y*,*z*; #4 -*x*+2,-*y*,-*z*+1; #5 *x*-1,*y*,*z*; #6 *x*,*y*,*z*-1; #7 *x*+1,*y*,*z*-1; #8 *x*,*y*,*z*+1; #9 -*x*+1,-*y*,-*z*; #10 -*x*+1,-*y*,-*z*+1; #11 *x*-1,y,*z*+1.

Symmetry transformations used to generate equivalent atoms for **2**: #1 -*x*+1,-*y*+2,-*z*+1; #2 *x*-1,*y*,*z*; #3 *x*+1,*y*,*z*; #4 -*x*+2,-*y*+2,-*z*; #5 *x*,*y*-1,*z*; #6 *x*-1,*y*-1,*z*; #7 *x*-1,*y*+1,*z*; #8 -*x*+2,-*y*+1,-*z*; #9 -*x*+1,-*y*+3,-*z*+1; #10 *x*,*y*+1,*z*; #11 -*x*+3,-*y*,-*z*; #12 -*x*+2,-*y*+3,-*z*+1; #13 -*x*+2,-*y*+2,-*z*+1; #14 *x*+1,*y*-1,*z*; #15 *x*+1,*y*+1,*z*.

Table S3 Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), SOFs and atomic sites for **1** and **2**. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Compounds	Atom	*x*	*y*	*z*	*U*(eq)	SOF	site
Compound **1**	Ga1	0.59169(12)	0.09369(2)	0.24859(13)	0.0232(3)	0.658(4)	4e
	Ga2	0.39997(18)	0.17859(3)	0.25484(19)	0.0223(4)	0.234(4)	4e
	Ga3	0.61040(17)	0.24121(3)	-0.05578(17)	0.0230(4)	0.326(4)	4e
	Ga4	0.9167(2)	0.03527(3)	0.4805(2)	0.0240(5)	0.153(4)	4e
	Ga5	0.0922(2)	0.10365(3)	0.2026(2)	0.0242(5)	0.129(4)	4e
	Si1	0.59169(12)	0.09369(2)	0.24859(13)	0.0232(3)	0.342(4)	4e
	Si2	0.39997(18)	0.17859(3)	0.25484(19)	0.0223(4)	0.766(4)	4e
	Si3	0.61040(17)	0.24121(3)	-0.05578(17)	0.0230(4)	0.674(4)	4e
	Si4	0.9167(2)	0.03527(3)	0.4805(2)	0.0240(5)	0.847(4)	4e
	Si5	0.0922(2)	0.10365(3)	0.2026(2)	0.0242(5)	0.871(4)	4e
	S1	0.3390(2)	0.08643(4)	0.0277(3)	0.0304(4)	1	4e
	S2	0.8369(2)	0.08851(4)	0.0261(3)	0.0321(4)	1	4e
	S3	0.5708(2)	0.14210(4)	0.4425(3)	0.0327(4)	1	4e
	S4	0.6022(2)	0.04548(4)	0.4551(3)	0.0366(4)	1	4e
	S5	0.3367(3)	0.22774(4)	0.4183(3)	0.0323(4)	1	4e
	S6	0.0842(2)	0.16203(4)	0.2253(3)	0.0315(4)	1	4e
	S7	0.5197(3)	0.18439(4)	-0.0435(3)	0.0341(4)	1	4e
	S8	0.8128(3)	0.24557(5)	-0.3067(3)	0.0345(4)	1	4e
	S9	0.9742(3)	0.00235(4)	0.7438(3)	0.0342(4)	1	4e
	S10	0.0935(3)	0.08377(4)	0.5070(3)	0.0321(4)	1	4e
	K1	0.5	0	0	0.1081(14)	1	2b
	K2	0.0200(4)	0.16486(6)	0.7269(3)	0.0819(8)	1	4e
Compound **2**	Zn1	0.34302(11)	0.70167(12)	0.25836(5)	0.0196(2)	1	2i
	Si1	0.8582(3)	0.6620(3)	0.25616(12)	0.0149(4)	1	2i
	Si2	0.4842(3)	0.9748(3)	0.40176(12)	0.0162(4)	1	2i
	Si3	1.0826(3)	0.8432(3)	0.05951(12)	0.0190(4)	1	2i
	S1	0.6609(2)	0.5102(3)	0.29753(12)	0.0203(4)	1	2i
	S2	0.1325(2)	0.5236(3)	0.31241(12)	0.0205(4)	1	2i
	S3	0.2204(3)	0.9846(3)	0.34967(13)	0.0245(4)	1	2i
	S4	0.3771(3)	0.7560(3)	0.09496(13)	0.0293(4)	1	2i
	S5	0.7341(3)	0.9628(3)	0.29570(12)	0.0238(4)	1	2i
	S6	0.9113(3)	0.6597(3)	0.10313(11)	0.0210(4)	1	2i
	S7	0.4231(3)	1.2281(2)	0.48575(11)	0.0200(4)	1	2i
	S8	0.9084(3)	1.1408(3)	0.09196(12)	0.0234(4)	1	2i
	K1	1.3642(4)	0.2273(4)	0.12895(16)	0.0567(6)	1	2i
	K2	0.8737(3)	1.3055(3)	0.47565(12)	0.0303(4)	1	2i

4. Thermal stability

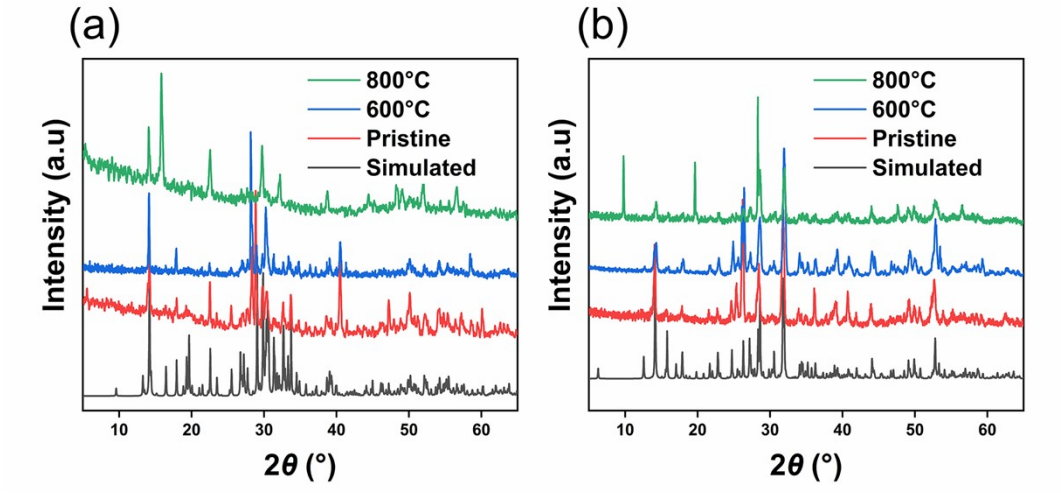

Figure S5 PXRD patterns for **1** (a) and **2** (b) including those for the pristine and the samples after TG tests up to 600 or 800 ℃. The simulated PXRD patterns for **1** and **2** are presented at the bottom of each figure for comparison, respectively.

5. Band gap

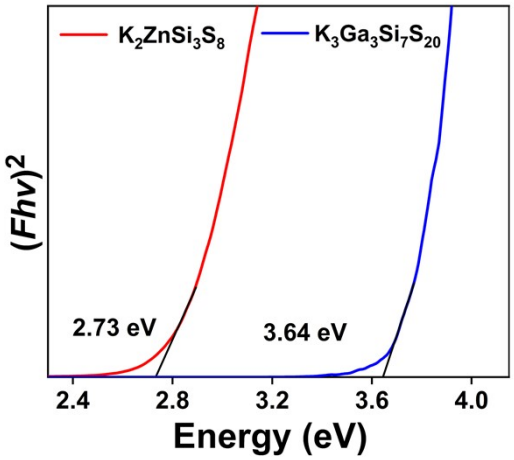

Figure S6 Tauc plots for **1** and **2**.

6. Density functional theory (DFT) calculation

The first-principles calculations were performed using the Vienna Ab-initio Simulation Package (VASP).[1, 2] The Perdew−Burke−Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was used to describe the exchange correlation functional, and the projector augmented wave (PAW) method was used in the present work. Here the cutoff energy of plane wave was chosen at 450 eV. The relaxation of geometry optimization and static self-consistent-field calculation were performed until the total energy change was within

10^{-5} eV/atom and the Hellmann−Feynman force on all atomic sites was < 0.01 eV/ Å.

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
2. G. Kresse and J. Furthmuller, *Phys. Rev. B*, 1996, **54**, 11169-11186.