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$[ASr_4Cl][Ge_3S_{10}]$ (A=Na, K) and $[KBa_4Cl][Ge_3S_{10}]$: New salt-inclusion infrared nonlinear optical crystals with zero-dimensional $[Ge_3S_9]$ clusters

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Table S1. Crystal data and structure refinement for $[NaSr_4Cl][Ge_3S_{10}]$, $[KSr_4Cl][Ge_3S_{10}]$, and $[KBa_4Cl][Ge_3S_{10}]$.

Empirical formula	$NaSr_4ClGe_3S_{10}$	$KSr_4ClGe_3S_{10}$	$KBa_4ClGe_3S_{10}$
Formula weight	947.29	963.40	1162.28
Temperature (K)		273(2)	
Crystal system		Hexagonal	
Space group		$P6_3$	
a (Å)	9.578(4)	9.713(9)	9.922(6)
c (Å)	11.830(6)	11.937(16)	12.205(13)
Volume(Å^3)	939.8(8)	975.5(2)	1040.7(17)
Z		2	
D_c (g cm^{-3})	3.347	3.280	3.709
μ (mm^{-1})	17.246	16.810	13.027
F(000)	872	888	1032
Completeness to theta	99.7%	100%	99.8%
GOF on F^2	1.077	1.063	1.063
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0468, 0.1166	0.0446, 0.1075	0.0479, 0.1268
R_1, wR_2 (all data)	0.0612, 0.1249	0.0700, 0.1195	0.0592, 0.1340
Flack x parameter	0.207 (0.022)	0.247 (0.016)	0.186 (0.030)
Largest diff. peak and hole (eÅ^{-3})	0.886 and -1.544	0.796 and -1.339	1.854 and -1.436

[a] $R_1 = S||F_o| - |F_c||/S|F_o|$ and $wR_2 = [Sw(F_o^2 - F_c^2)^2 / Sw\,F_o^4]^{1/2}$ for $F_o^2 > 2s(F_o^2)$

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$), bond valence sums (BVSs) for $[NaSr_4Cl][Ge_3S_{10}]$, $[KSr_4Cl][Ge_3S_{10}]$, and $[KBa_4Cl][Ge_3S_{10}]$.

$NaSr_4ClGe_3S_{10}$

Atom	x/a	y/b	z/c	U(eq)	BVS
Na1	0	0	0.3943(18)	0.049(4)	0.93
Sr1	0.33333	0.6667	0.3295(3)	0.0165(7)	2.37
Sr2	0.0869(3)	0.3401(3)	0.6507(3)	0.0476(7)	1.87
Ge1	0.4479(2)	0.3356(2)	0.49056(15)	0.0160(5)	4.21
S1	0.33333	0.6667	0.5869(8)	0.024(2)	2.09
S2	0.4435(7)	0.1128(6)	0.4278(5)	0.0253(12)	1.82
S3	0.2510(6)	0.3237(6)	0.3907(5)	0.0220(11)	2.09
S4	0.4240(7)	0.3484(8)	0.6710(5)	0.0334(14)	2.01
Cl1	0	0	0.6400(9)	0.029(2)	1.20

$KSr_4ClGe_3S_{10}$

Atom	x/a	y/b	z/c	U(eq)	BVS
K1	0	0	0.6018(6)	0.0403(16)	1.07
Sr1	0.666667	0.333333	0.67099(19)	0.0195(5)	2.44
Sr2	0.3449(2)	0.2558(2)	0.3447(2)	0.0504(6)	1.70
Ge1	0.34283(17)	0.88912(16)	0.50620(11)	0.0203(4)	4.20
S1	0.3513(6)	0.9234(5)	0.3279(3)	0.0354(11)	1.79
S2	0.3390(5)	0.0754(5)	0.6044(4)	0.0383(11)	2.07
S3	0.1202(5)	0.6767(5)	0.5690(4)	0.0294(9)	2.01
S4	0.666667	0.333333	0.4123(7)	0.0333(16)	1.68
Cl1	0	0	0.3545(7)	0.0360(16)	1.14

$KBa_4ClGe_3S_{10}$

Atom	x/a	y/b	z/c	U(eq)	BVS
K1	0	0	0.3996(17)	0.063(4)	1.03
Ba1	0.3333	0.6667	0.3357(2)	0.0192(7)	2.36
Ba2	0.6599(2)	0.7439(2)	0.6556(2)	0.0436(6)	1.79
Ge1	0.4534(3)	0.3361(3)	0.49215(19)	0.0189(7)	4.15
S1	0.6692(8)	0.5474(8)	0.4292(5)	0.0233(16)	1.98
S2	0.3333	0.6667	0.5927(9)	0.025(3)	1.8
S3	0.2617(9)	0.3295(9)	0.4010(6)	0.0280(18)	1.93
S4	0.4268(8)	0.3404(9)	0.6666(6)	0.0304(18)	1.94
Cl1	0	0	0.6483(13)	0.031(3)	1.20

Table S3. Selected distances (Å) and angles (°) for $[NaSr_4Cl][Ge_3S_{10}]$, $[KSr_4Cl][Ge_3S_{10}]$, and $[KBa_4Cl][Ge_3S_{10}]$.

$NaSr_4ClGe_3S_{10}$

Atom–Atom	**Length [Å]**	S2#1-Sr2-S4#5	66.90(15)
Sr1-S4#12	3.045(6)	Cl1-Sr2-S3	78.2(2)
Sr1-S4#8	3.045(6)	S4-Sr2-S3	66.17(14)
Sr1-S3	3.057(5)	S4#5-Sr2-S3	117.88(15)
Sr1-S3#2	3.057(5)	Cl1-Sr2-S4#1	68.92(10)
Ge1-S4	2.157(6)	S4-Sr2-S4#1	143.26(17)
Ge1-S2	2.240(5)	S4#5-Sr2-S4#1	72.98(18)
Sr2-S1	2.922(4)	S1-Sr2-S3	71.34(19)
Sr2-S3#11	3.134(6)	S3#15-Sr2-S3	162.65(17)
Sr2-S2#1	3.232(7)	S2#1-Sr2-S3	63.50(14)
Sr2-S3	3.493(6)	S1-Sr2-S4#1	142.37(13)
S3-Na1	2.818(5)	S3#15-Sr2-S4#1	61.22(13)
Sr1-S4#10	3.045(6)	S2#1-Sr2-S4#1	65.14(13)
Sr1-S1	3.046(10)	S3-Sr2-S4#1	114.26(14)
Sr1-S3#3	3.057(5)	S3#4-Na1-Cl1#8	89.1(4)
Ge1-S3	2.179(5)	S3#4-Na1-S3	119.98(2)
Ge1-S2#4	2.245(6)	S3#4-Na1-Cl1	90.9(4)
Sr2-Cl1	2.935(3)	S3#1-Na1-Cl1#8	89.1(4)
Sr2-S4	3.199(6)	S3-Na1-Cl1#8	89.1(4)
Sr2-S4#3	3.331(7)	S2#1-Sr2-S4#5	66.90(15)
Sr2-S4#1	3.647(7)	S3#1-Na1-S3	119.98(2)
Na1-Cl1	2.910(2)	Cl1-Na1-Cl1#8	180
Atom–Atom–Atom	**Angle [°]**	S4#1-Sr2-S4#5	72.93(17)
S4-Ge1-S3	115.2(2)	S4-Ge1-S2	115.5(2)
S3-Ge1-S2	99.6(2)	S4-Ge1-S2#6	110.5(2)
S3-Ge1-S2#6	104.8(2)	S2-Ge1-S2#6	110.3(3)
S1-Sr2-Cl1	143.70(16)	S1-Sr2-S3#15	123.2(2)
Cl1-Sr2-S3#15	84.7(2)	S1-Sr2-S4	74.19(13)
Cl1-Sr2-S4	75.71(13)	S3#15-Sr2-S4	106.69(16)
S1-Sr2-S2#1	88.26(19)	Cl1-Sr2-S2#1	95.6(2)
S3#15-Sr2-S2#1	122.04(15)	S4-Sr2-S2#1	129.63(17)
S1-Sr2-S4#5	72.19(11)	Cl1-Sr2-S4#5	141.89(13)
S4-Ge1-S3	115.2(2)	S3#1-Na1-Cl1	90.9(4)
S4-Ge1-S2	115.5(2)	S3-Na1-Cl1	90.9(4)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1, x-y, z	#2 -x+y+1, -x+1, z	#3 -x+y+1, -x+2, z	#4 -x+y+2, -x+2, z
#5 -x+1, -y+1, z+1/2	#6 -x+2, -y+1, z+1/2	#7 -x+2, -y+2, z-1/2	#8 y, -x+y, z+1/2
#9 y, -x+y+1, z-1/2	#10 y, -x+y+1, z+1/2	#11 x-y, x-1, z+1/2	#12 x-y+1, x, z+1/2

$KSr_4ClGe_3S_{10}$

Atom–Atom	**Length [Å]**	S2#16-Sr2-S2	165.37(15)
Sr1-S2#2	3.011(4)	S2#3-Sr1-S2#6	113.30(9)
Sr1-S2	3.011(4)	S2#6-Sr1-S2	113.30(9)
Sr1-S1#11	3.053(4)	S2#6-Sr1-S1#15	82.95(13)
Sr1-S4	3.089(9)	S2#3-Sr1-S1#14	82.95(14)
Ge1-S1	2.150(4)	S2-Sr1-S1#14	156.37(14)
Ge1-S3	2.244(4)	S2#3-Sr1-S1#10	72.07(12)
Sr2-S4	2.938(3)	S2-Sr1-S1#10	82.95(14)
Sr2-S2#13	3.185(6)	S1#14-Sr1-S1#10	86.31(13)
Sr2-S3#1	3.304(5)	S2#6-Sr1-S4	74.70(11)
Sr2-S2	3.548(6)	S1#15-Sr1-S4	127.84(9)
K1-S2	2.995(4)	S1#10-Sr1-S4	127.83(9)
K1-S2#1	2.995(4)	S1-Ge1-S3	114.70(17)
Sr1-S2#2	3.011(4)	S2#3-Sr1-S1#15	156.36(14)
Sr1-S2#5	3.011(4)	S2-Sr1-S1#15	72.07(12)
Sr1-S1#12	3.053(4)	S2#6-Sr1-S1#14	72.07(12)
Sr1-S1#8	3.053(4)	S1#15-Sr1-S1#14	86.31(13)
Sr1-S2#5	3.011(4)	S2#6-Sr1-S1#10	156.37(14)
Ge1-S2	2.172(4)	S1#15-Sr1-S1#10	86.31(13)
Ge1-S3#4	2.251(4)	S2#3-Sr1-S4	74.70(11)
Sr2-Cl1	3.015(19)	S2-Sr1-S4	74.70(11)
Sr2-S1	3.267(5)	S1#14-Sr1-S4	127.83(9)
Sr2-S1#5	3.325(5)	S1-Ge1-S2	114.89(19)
K1-Cl1	2.952(12)	S2-Ge1-S3	100.12(18)
K1-S2#3	2.995(4)	S2-Ge1-S3#5	104.70(17)
K1-Cl1#6	3.016(12)	S4-Sr2-Cl1	143.32(13)
Atom–Atom–Atom	**Angle [°]**	S1#6-Sr2-S2	117.22(11)
S1-Ge1-S3#5	111.80(17)	Cl1-Sr2-S2#16	85.97(17)
S3-Ge1-S3#5	109.6(2)	Cl1-Sr2-S1	75.52(9)
S4-Sr2-S2#16	123.32(18)	S4-Sr2-S3#1	89.37(16)
S4-Sr2-S1	74.14(10)	S2#16-Sr2-S3#1	119.84(11)
S2#16-Sr2-S1	108.97(12)	S4-Sr2-S1#6	73.26(9)
Cl1-Sr2-S3#1	94.15(15)	S2#16-Sr2-S1#6	76.16(12)
S1-Sr2-S3#1	129.27(13)	S3#1-Sr2-S1#6	66.70(11)
Cl1-Sr2-S1#6	140.79(10)	Cl1-Sr2-S2	79.75(16)
S1-Sr2-S1#6	143.25(14)	S1-Sr2-S2	64.47(10)

Symmetry transformations used to generate equivalent atoms:

#1	-y, x-y, z	#2	-y, x-y-1, z	#3	-y+1, x-y, z	#4	-x+y, -x, z
#5	-x+y+1, -x, z	#6	-x+y+1, -x+1, z	#7	-x, -y, z+1/2	#8	-x, -y, z-1/2
#9	-x+1, -y, z-1/2	#10	-x+1, -y, z+1/2	#11	-x+1, -y+1, z-1/2	#12	-x+1, -y+1, z+1/2
#13	y, -x+y, z+1/2	#14	y+1, -x+y+1, z+1/2	#15	x-y, x, z+1/2	#16	x-y, x, z-1/2
#17	x-y+1, x, z+1/2						

Atom–Atom	Length [Å]	S(4)-Ge(1)-S(1)#1	114.4(3)
Ge(1)-S(4)	2.149(8)	S(3)-Ge(1)-S(1)#1	101.9(3)
Ge(1)-S(3)	2.176(7)	S(1)-Ge(1)-S(1)#1	108.3(4)
Ge(1)-S(1)	2.254(8)	S(3)-K(1)-Cl(1)	89.7(4)
Ge(1)-S(1)#1	2.257(7)	S(3)#8-K(1)-Cl(1)	89.7(4)
S(1)-Ba(2)#2	3.410(7)	S(3)#6-K(1)-Cl(1)	89.7(4)
S(2)-Ba(2)#3	3.032(4)	S(3)-K(1)-Cl(1)#5	90.3(4)
S(2)-Ba(2)	3.032(4)	S(3)#8-K(1)-Cl(1)#5	90.3(4)
S(2)-Ba(2)#4	3.032(4)	S(3)#6-K(1)-Cl(1)#5	90.3(4)
S(2)-Ba(1)	3.137(11)	Cl(1)-K(1)-Cl(1)#5	180.0
S(3)-K(1)	2.991(8)	S(2)-Ba(1)-S(3)#14	75.37(15)
S(3)-Ba(1)#2	3.155(8)	S(2)-Ba(1)-S(3)#8	75.37(15)
S(3)-Ba(2)#5	3.266(8)	S(3)#14-Ba(1)-S(3)#8	113.85(12)
S(3)-Ba(2)#6	3.601(8)	S(2)-Ba(1)-S(3)#15	75.37(15)
S(4)-Ba(1)#7	3.178(7)	S(3)#14-Ba(1)-S(3)#15	113.85(12)
S(4)-Ba(2)#6	3.403(7)	S(3)#8-Ba(1)-S(3)#15	113.85(12)
S(4)-Ba(2)#2	3.483(8)	S(2)-Ba(1)-S(4)#16	130.51(14)
S(4)-Ba(2)#8	3.673(8)	S(3)#14-Ba(1)-S(4)#16	85.1(2)
K(1)-Cl(1)	3.03(3)	S(3)#8-Ba(1)-S(4)#16	152.6(2)
K(1)-Cl(1)#5	3.07(3)	S(3)#15-Ba(1)-S(4)#16	71.90(19)
K(1)-Ba(2)#9	4.259(15)	S(2)-Ba(1)-S(4)#17	130.51(14)
K(1)-Ba(2)#10	4.259(15)	S(3)#14-Ba(1)-S(4)#17	71.90(19)
K(1)-Ba(2)#5	4.259(15)	S(3)#8-Ba(1)-S(4)#17	85.1(2)
K(1)-Ba(2)	4.363(15)	S(3)#15-Ba(1)-S(4)#17	152.6(2)
K(1)-Ba(2)#6	4.363(15)	S(4)#16-Ba(1)-S(4)#17	82.4(2)
K(1)-Ba(2)#8	4.363(15)	S(2)-Ba(1)-S(4)#5	130.51(14)
Ba(1)-Ba(2)#11	4.659(2)	S(3)#14-Ba(1)-S(4)#5	152.6(2)
Ba(1)-Ba(2)#10	4.659(2)	S(3)#8-Ba(1)-S(4)#5	71.90(19)
Ba(1)-Ba(2)#12	4.659(2)	S(3)#15-Ba(1)-S(4)#5	85.1(2)
Cl(1)-Ba(2)	3.046(2)	S(4)#16-Ba(1)-S(4)#5	82.4(2)
Cl(1)-Ba(2)#6	3.046(2)	S(4)#17-Ba(1)-S(4)#5	82.4(2)
Cl(1)-Ba(2)#8	3.046(2)	S(2)-Ba(2)-Cl(1)	143.27(17)
Atom–Atom–Atom	**Angle [°]**	S(3)-K(1)-S(3)#8	119.997(9)
S(4)-Ge(1)-S(3)	113.1(3)	S(3)-K(1)-S(3)#6	119.996(9)
S(4)-Ge(1)-S(1)	112.8(3)	S(3)#8-K(1)-S(3)#6	119.997(9)
S(3)-Ge(1)-S(1)	105.2(3)	S(4)-Ge(1)-S(1)#1	114.4(3)

S(2)-Ba(2)-S(3)#7	121.3(2)	Cl(1)-Ba(2)-S(1)#15	96.8(3)
Cl(1)-Ba(2)-S(3)#7	85.7(3)	S(3)#7-Ba(2)-S(1)#15	122.55(18)
S(2)-Ba(2)-S(4)#8	74.20(14)	S(4)#8-Ba(2)-S(1)#15	128.07(19)
Cl(1)-Ba(2)-S(4)#8	73.84(14)	S(2)-Ba(2)-S(4)#15	73.00(13)
S(3)#7-Ba(2)-S(4)#8	107.81(19)	Cl(1)-Ba(2)-S(4)#15	141.45(13)
S(2)-Ba(2)-S(1)#15	88.9(2)	S(3)#7-Ba(2)-S(4)#15	78.69(19)
S(4)#8-Ba(2)-S(4)#15	144.5(2)	S(4)#15-Ba(2)-S(3)#8	117.37(18)
S(1)#15-Ba(2)-S(4)#15	64.30(18)	S(2)-Ba(2)-S(4)#6	141.74(14)
S(2)-Ba(2)-S(3)#8	70.3(2)	Cl(1)-Ba(2)-S(4)#6	69.93(12)
Cl(1)-Ba(2)-S(3)#8	79.0(3)	S(3)#7-Ba(2)-S(4)#6	64.48(18)
S(3)#7-Ba(2)-S(3)#8	163.5(2)	S(4)#8-Ba(2)-S(4)#6	143.35(19)
S(4)#8-Ba(2)-S(3)#8	61.96(18)	S(1)#15-Ba(2)-S(4)#6	62.95(17)
S(1)#15-Ba(2)-S(3)#8	66.11(16)	S(4)#15-Ba(2)-S(4)#6	71.5(2)

Symmetry transformations used to generate equivalent atoms:

#1x-1, y-1, z+1 #2 x+1, y+1, z-1 #3 -y, x-y-1, z #4 -y+1, x-y-1, z

#5 -y+1, x-y, z-1 #6 -y+2, x-y, z #7 -x+y+1, -x, z #8 -x+y+2, -x+1, z-1

#9 -x+y+2, -x+1, z #10-x+y+2, -x+2, z-1 #11-x+2, -y, z-1/2 #12 -x+2, -y, z-1/2

#13 -x+2, -y+1, z-1/2 #14 -x+2, -y+1, z+1/2 #15y, -x+y, z+1/2 #16 y+1, -x+y+1, z-1/2

#17 y+1, -x+y+1, z+1/2 #18 y+2, -x+y+2, z-1/2 #19 x-y, x-1, z+1/2 #20 x-y, x, z-1/2

#21 x-y+1, x, z-1/2

Table S4. Dimensional distribution and arrangement pattern of $[M_xQ_y]$ units.

Compound	Anionic groups	Anionic group dimensions	(M + N)/Q[b]	Law of dimensions	Ref.
$[Rb_4Cl][Cd_{11}In_9S_{26}]$	$CdIn_3S_{10}$, Cd_3InS_{10}	3D	0.77	(M + N)/Q ≥ 0.5	1
$[K_4Cl][CdGa_9Q_{16}]$ (Q = S, Se)	Ga_4S_{10}, Ga_3CdS_{10}	3D	0.625		2
$Ba_3AGa_5Se_{10}Cl_2$ (A = Cs, Rb, K)	$GaSe_4$, Ga_4Se_{10}	3D	0.5		3
$Ba_4MGa_4Se_{10}Cl_2$ (M = Zn, Cd, Mn, Cu/Ga)	MSe_4, Ga_4Se_{10}	3D	0.5		4
$Li_2Cs_2Ga_3S_6Cl$	Ga_3S_9	3D	0.5		5
$Cs_2[Mn_2Ga_3S_7Cl]$	Ga_3S_9 MnS_6	2D	0.71		6
$ABa_2Ga_4S_8Cl$ (A = Rb, Cs)	Ga_4S_{10}	2D	0.5		7
$[ABr][Hg_3P_2S_8]$ (A = Rb, Cs; X = Cl, Br)	HgS_4, $HgPS_4$	2D	0.625		8, 10
$[A_3X][Ga_3PS_8]$ (A = K, Rb; X = Cl, Br)	$GaPS_4$ Ga_3PS_{10}	2D	0.5		9, 10
$NaGaS_2Cl$	Ga_4Se_{10}	2D	0.5		11
$Ba_7In_2Se_6F_8$	InS_4	1D	0.3		12
Ba_3GaS_4Cl	GaS_4	0D	0.25		
$K_2Ba_3Ge_3S_9Cl_2$	Ge_3S_9	0D	0.3	(M + N)/Q ≤ 0.33	13
$Ba_3SnS_3F_2$	SnS_4	0D	0.33		14
$NaSr_4ClGe_3S_{10}$	**Ge_3S_9**	**0D**	**0.3**		**This work**
$KSr_4ClGe_3S_{10}$	**Ge_3S_9**	**0D**	**0.3**		
$KBa_4ClGe_3S_{10}$	**Ge_3S_9**	**0D**	**0.3**		

[b] M = IIIA or IVA, N = IB or IIB or cations coordinated as $[M_xQ_y]$ anionic groups.

Table S5. Magnitude of Dipole Moments of $[NaSr_4Cl][Ge_3S_{10}]$, $[KSr_4Cl][Ge_3S_{10}]$, and $[KBa_4Cl][Ge_3S_{10}]$.

Crystals	Polyhedron	*x(a)*	*y(b)*	*z (c)*	Dipole moment (D)	Dipole moment ($\times 10^{-2}$ esu·cm^2/Å^3)
$NaSr_4ClGe_3S_{10}$	$Ge(1)S_4$	0.14	-1.48	-4.14	4.42	2.66
	$Ge(1)S_4$	-1.62	-0.14	-4.14	4.42	
	$Ge(1)S_4$	1.48	1.62	-4.14	4.42	
	Ge_3S_9	0	0	-12.43	12.43	
$KSr_4ClGe_3S_{10}$	$Ge(1)S_4$	0.47	-1.34	4.13	4.44	2.54
	$Ge(1)S_4$	1.34	1.83	4.13	4.44	
	$Ge(1)S_4$	-1.83	-0.47	4.13	4.44	
	Ge_3S_9	0	0	12.39	12.39	
$KBa_4ClGe_3S_{10}$	$Ge(1)S_4$	0.54	-1.36	-3.55	3.94	2.05
	$Ge(1)S_4$	1.36	1.90	-3.55	3.94	
	$Ge(1)S_4$	-1.90	-0.54	-3.55	3.94	
	Ge_3S_9	0	0	-10.65	10.65	

Fig. S1. Powder-XRD patterns of (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, and (c) $[KBa_4Cl][Ge_3S_{10}]$ from 650℃ to 850℃.

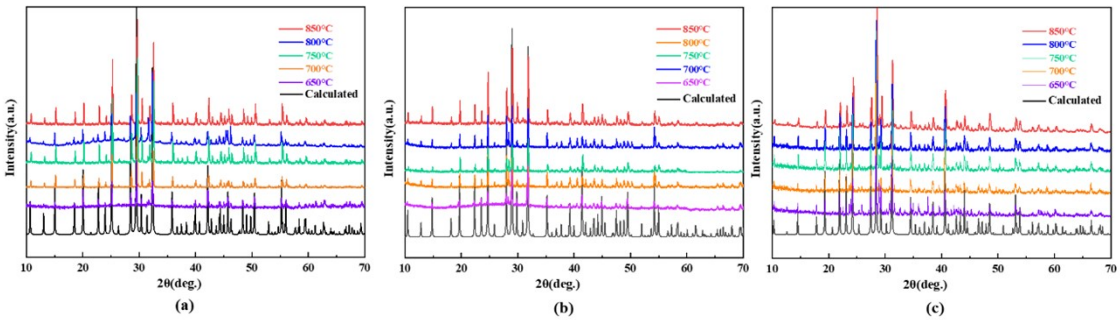
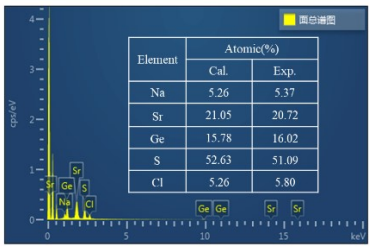
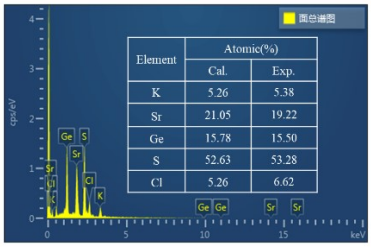


Fig. S2. EDS of (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, (c) and $[KBa_4Cl][Ge_3S_{10}]$.



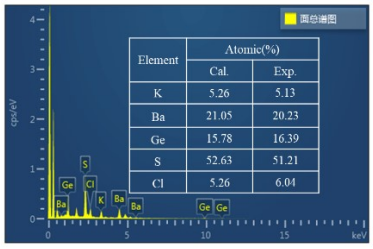
Element	Atomic(%)	
	Cal.	Exp.
Na	5.26	5.37
Sr	21.05	20.72
Ge	15.78	16.02
S	52.63	51.09
Cl	5.26	5.80

(a)



Element	Atomic(%)	
	Cal.	Exp.
K	5.26	5.38
Sr	21.05	19.22
Ge	15.78	15.50
S	52.63	53.28
Cl	5.26	6.62

(b)



Element	Atomic(%)	
	Cal.	Exp.
K	5.26	5.13
Ba	21.05	20.23
Ge	15.78	16.39
S	52.63	51.21
Cl	5.26	6.04

(c)

Fig. S3. IR spectra of (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, and (c) $[KBa_4Cl][Ge_3S_{10}]$. (IR samples were polycrystalline samples that synthesized by high temperature solid phase method in 1123 K)

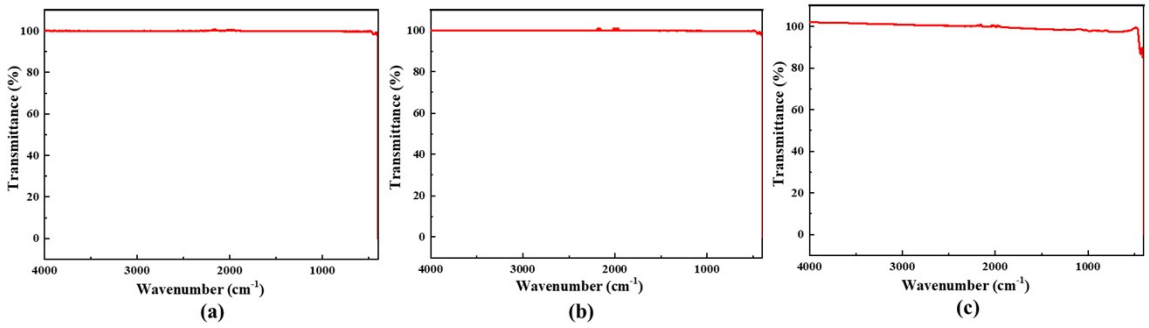


Fig. S4. Complete coordination environment of cations in $[NaSr_4Cl][Ge_3S_{10}]$.

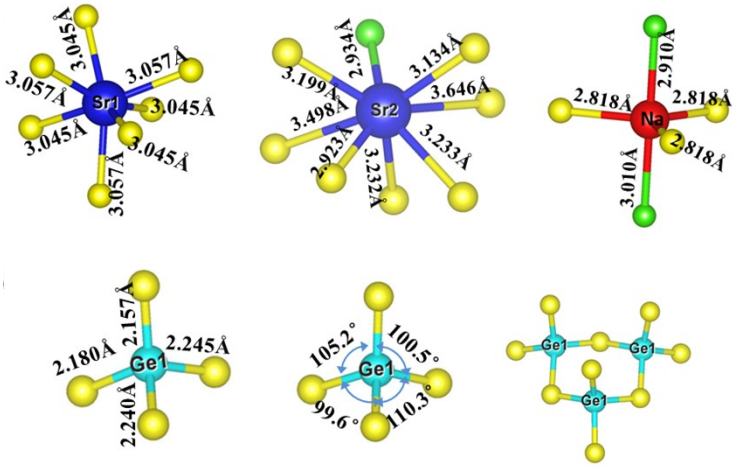


Fig. S5. Raman spectra of (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, and (c) $[KBa_4Cl][Ge_3S_{10}]$.

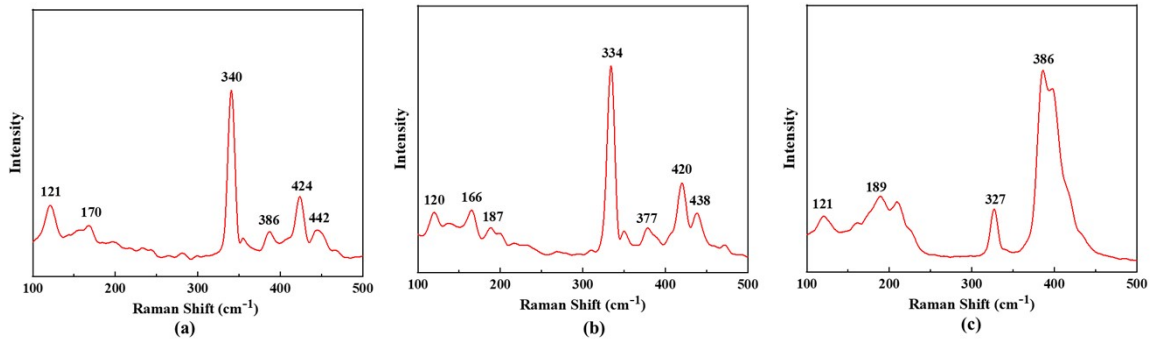


Fig. S6. Crystal for the birefringence determination and the interference colors observed in the cross-polarized light for (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, and (c) $[KBa_4Cl][Ge_3S_{10}]$; the crystal thicknesses for (d) $[NaSr_4Cl][Ge_3S_{10}]$, (e) $[KSr_4Cl][Ge_3S_{10}]$, and (f) $[KBa_4Cl][Ge_3S_{10}]$.

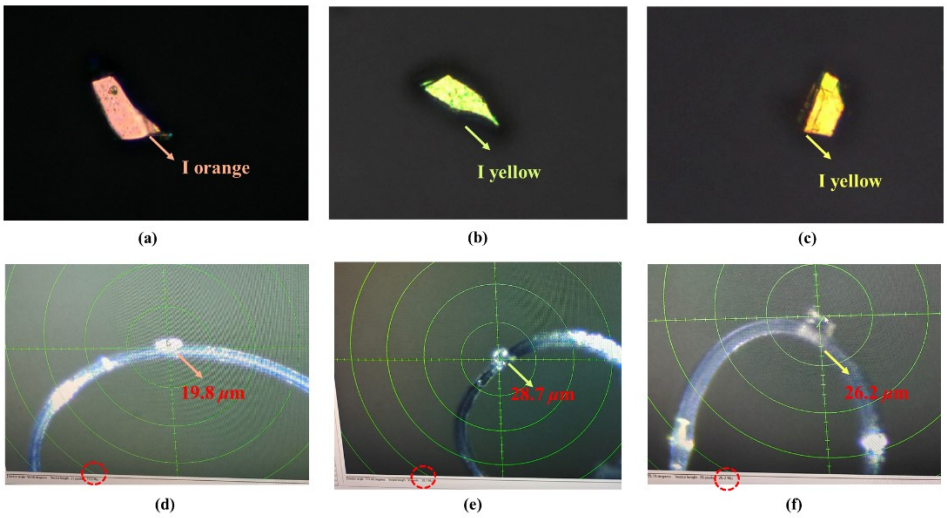


Fig. S7. Calculated birefringence (Δn) curves of (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, and (c) $[KBa_4Cl][Ge_3S_{10}]$.

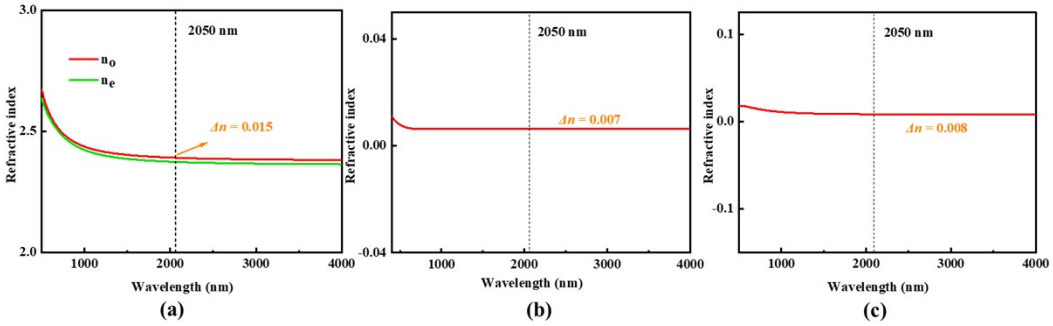


Fig. S8. Calculated band structure of (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, and (c) $[KBa_4Cl][Ge_3S_{10}]$.

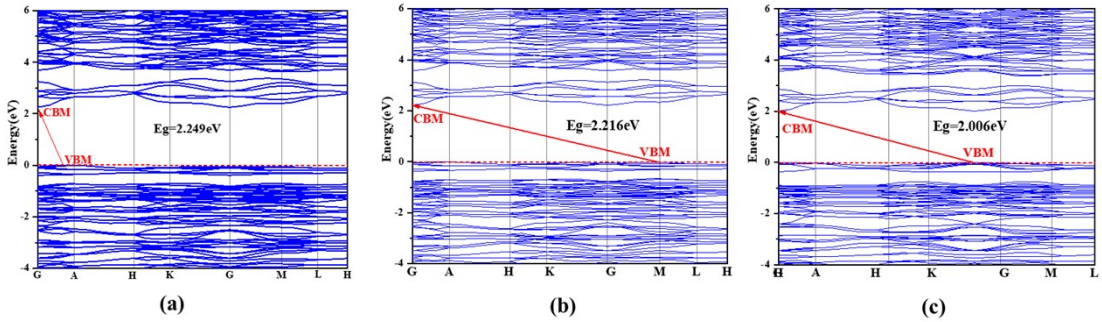
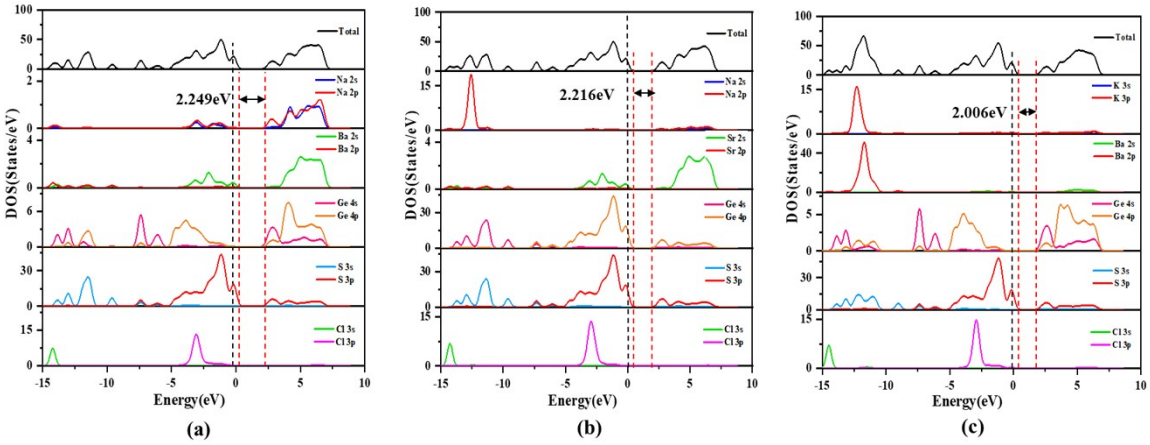


Fig. S9. Projected density of states of (a) $[NaSr_4Cl][Ge_3S_{10}]$, (b) $[KSr_4Cl][Ge_3S_{10}]$, and (c) $[KBa_4Cl][Ge_3S_{10}]$.



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