Supporting Information

Effect of cation-to-silicon ratio on structural transformation and optical performances in $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$

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CONTENTS

Experimental Section:

Reagents

All raw materials including NaCl (99%), SrS (99%), $SrCl_2$ (99%), Si (99%) and S (99%) were directly purchased from Aladdin Co., Ltd, and Fuchen (Tianjin) Chemical Reagent Co. Ltd. Without further purification.

Synthesis

All manipulations were carried out in an Ar-filled glove box. The single crystal of $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ were synthesized through the solid-state reaction method by mixing raw materials of SrS, NaCl, $SrCl_2$, Si, and S with molar ratio of 2:1:1:1:2 for $[NaSr_3Cl_3][SiS_4]$ and NaCl, SrS, Si, S for with molar ratio of 1:4:3:6 for $[NaSr_4SCl][Si_3S_9]$. After being ground to fine powder, the mixture was loaded into quartz tube and further evacuated to 1×10^{-3} Pa, and then sealed by flame. The sealed tube was placed in a muffle furnace and heated from room temperature to 900 °C for 15 hours. It was maintained at this temperature for 50 hours to ensure complete melting of the starting materials. Subsequently, the tube was cooled to 750 °C for 50 hours at a rate of 3 °C/h, and finally cooled to room temperature for 20 hours. Colorless block-shaped crystals of $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ were obtained in approximately 70% and 80% yield based on Si respectively.

Polycrystalline sample of $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ could be easily synthesized by heating stoichiometric mixtures sealed into an evacuated silica tube at 1123 K for 3 days. The purity of sample has been confirmed by the powder X-ray diffraction (PXRD).

Single Crystal X-ray Diffraction

Single crystal data was collected on a Bruker SMART APEX III 4 K CCD diffractometer using Mo-Kα (λ = 0.71073 Å) radiation at 293(2) K. The structures of two crystals were solved directly by the SHELXTL crystallographic software package and all atoms were refined by the full-matrix least squares technique. The final structures were examined for the presence of any missing symmetry elements using PLATON, and no additional higher symmetry elements were identified. The crystal data and structure refinement details, atomic coordination, displacement parameters, bond valence sums (BVSs), and selected bond lengths and angles are summarized in Tables S1-S4.[1-4]

Powder X-ray Diffraction

PXRD data measurements were carried out on a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation at room temperature. The 2θ range was 10–70° with a step size of 0.01° and a fixed counting time of 1 s/step. As shown in Fig. S1, the powder XRD patterns of $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ were in good agreement with the crystallographic information file (CIF) calculations, which indicate that the obtained phases are pure.

UV-vis-NIR diffuse-reflectance spectra

The UV-vis-NIR diffuse reflectance spectra of $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ were measured at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. The wavelengths of the spectra were in the range 240–2000 nm. Absorption (K/S) data were calculated from the following Kubelka–Munk function: $F(R) = (1-R)^2/2R = K/S$, where R represents the reflectance, K the absorption, and S the scattering factor.

Infrared spectroscopy

The infrared spectra of $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ were carried out on a Nicolet iS50 Fourier transform infrared (FT-IR) spectrometer to specify. The polycrystalline samples were mixed thoroughly with dried KBr (5 mg of the sample and 500 mg of KBr). The samples were measured in a range from 400 to 4000 cm^{-1}.

Birefringence measurement

The birefringence was measured using a Nikon Eclipse polarizing microscope E200MV POL with a halogen lamp. According to the formula $R = \Delta n \times d$, where R, Δn, and d represent optical path difference, birefringence, and thickness, respectively. The birefringence was calculated by measuring the optical path compared with the Michel-Levy chart and the thickness with a Bruker SMART APEX III. The transparent $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ crystal was selected for the measurement to ensure the results' precision.

Powder SHG Measurement

The SHG signals of $[NaSr_4SCl][Si_3S_9]$ and benchmark AGS were investigated under incident laser radiation of 2090 nm by the modified Kurtz-Perry method.[5] Samples of $[NaSr_4SCl][Si_3S_9]$ and AGS were sieved into several distinct particle size ranges (35−55, 55−75, 75−100, 100−135, 135−165 and 165−200 μm) for the PM measurements. The SHG signals were detected by a charge-coupled device. The AGS samples with similar particle size ranges were served as the standard samples.

Laser-induced Damage Threshold Measurement

The LIDTs of the $[NaSr_4SCl][Si_3S_9]$ and AGS powder at the particle size range of 75−100 μm were evaluated using a high-power laser irradiation of 1064 nm (pulse width τ_p = 10 ns) by the single-pulse method. The measurement processes were performed by gradually increasing the laser power until the damaged spot was observed under a microscope. The damage thresholds were derived from the equation $I_{(\text{threshold})} = E/(\pi r^2 \tau_p)$, where E is the laser energy of a single pulse, r is the spot radius, and τ_p is the pulse width.

Calculation

The electronic band structures, the partial density of states and optical properties for $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$ were carried out using the CASTEP package based on density functional theory (DFT).[6] Generalized gradient approximation (GGA) parametrized by Perdew-Burke-Ernzerhof (PBE) functional was chosen for the exchange-correlation energy, and the pseudopotential was set as norm-conserving pseudopotential (NCP).[7] The valence electrons were set as Na: $2s^22p^63s$, Sr: $4s^24p^65s^2$, Si: $3s^23p^2$, S: $3s^23p^4$ and Cl $3S^23p^5$. The plane wave energy cutoff value was set at 810.0 eV for both compounds. The corrssponding Monkhorst-Pack κ-point meshes were adopted 4 × 3 × 3 for $[NaSr_3Cl_3][SiS_4]$ 4 × 4 × 4 for $[NaSr_4SCl][Si_3S_9]$.[8] The numerical integration of the Brillouin zones was performed using Monkhorst-Pack k-point meshes spanning less than 0.03/Å^3. For calculating the optical properties, the same Monkhorst-pack grid and plane-wave cutoff energy were used and the dielectric function is defined as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, in which real part $\varepsilon_1(\omega)$, refractive index $n(\omega)$ were obtained by the Kramers-Kroning transform.[9] The SHG coefficients were calculated from the band wave functions using the so-called length-gauge formalism derived by Aversa and Sipe at a zero-frequency limit. The static second-order nonlinear susceptibilities $\chi_{\alpha\beta\gamma}^{(2)}$ can be reduced as:

$$\chi_{\alpha\beta\gamma}^{(2)} = \chi_{\alpha\beta\gamma}^{(2)}\,(VE) + \chi_{\alpha\beta\gamma}^{(2)}\,(VH)$$

In this sum-over-states type formalism, the total SHG coefficient $\chi(2)$ is divided into contributions from Virtual-Hole (VH), Virtual-Electron (VE) and Two-Band (TB) processes.

Table S1a. Crystal data and structure refinement for $[NaSr_3Cl_3][SiS_4]$.

Empirical formula	$[NaSr_3Cl_3][SiS_4]$
Formula weight	548.53
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/m$
Z	4
a (Å)	9.0129(8)
b (Å)	11.0360(10)
c (Å)	12.6681(10)
β (°)	108.085(2)
D_c (g cm^{-3})	3.042
μ (mm^{-1})	14.756
F(000)	1016
Radiation	Mo-K$_\alpha$ (λ = 0.71073)
2θ range(°)	2.377 to 25.100
Reflections collected	13028
Independent reflections / R_{int}	2244/0.0554
GOOF on F^2	0.971

Table S1a. Crystal data and structure refinement for $[NaSr_3Cl_3][SiS_4]$.

Empirical formula	$[NaSr_3Cl_3][SiS_4]$
R_1[a], wR_2 (I >2σ(I))[b]	0.0506, 0.0864
R_1 , wR_2 (all data)	0.1070, 0.1046
largest diff. peak and hole ($e \cdot Å^{-3}$)	1.197, -1.092

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b]$wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S1b. Crystal data and structure refinement for $[NaSr_4SCl][Si_3S_9]$.

Empirical formula	$[NaSr_4SCl][Si_3S_9]$
Formula weight	813.79
Temperature (K)	293(2)
Crystal system	Hexagonal
Space group	$P6_3$
Z	2
a (Å)	9.4413(3)
c (Å)	11.6355(7)
D_c (g cm^{-3})	3.009
μ (mm^{-1})	13.325
F(000)	764
Radiation	Mo-K_α (λ = 0.71073)
2θ range(°)	2.491 to 27.465
Reflections collected	11519
Independent reflections / R_{int}	1382/0.0658
GOOF on F^2	1.125
$R_1{}^a$, wR_2 (I >2σ(I))^b	0.0379, 0.1044
R_1 , wR_2 (all data)	0.0487, 0.1115

Table S1b. Crystal data and structure refinement for $[NaSr_4SCl][Si_3S_9]$.

Empirical formula	$[NaSr_4SCl][Si_3S_9]$
largest diff. peak and hole ($e \cdot Å^{-3}$)	0.994, -1.176
Flack parameter	0.005(8)

$^{a}R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^{b}wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2a. Selected bond distances (Å) and angles (degrees) for $[NaSr_3Cl_3][SiS_4]$.

Atom-Atom	**Length (Å)**	S(5)-Na(1)-Cl(2)	93.4(2)
Na(1)-S(5)	2.735(7)	S(5)-Na(1)-S(4)#1	147.4(3)
Na(1)-S(4)#1	2.918(7)	Cl(2)-Na(1)-S(4)#1	119.2(2)
Na(1)-S(2)#4	3.147(6)	S(5)-Na(1)-Cl(3)#2	92.88(13)
Na(1)-S(2)#1	3.147(6)	Cl(2)-Na(1)-Cl(3)#2	73.58(12)
Na(1)-Cl(2)	2.794(7)	S(4)#1-Na(1)-Cl(3)#2	96.23(13)
Na(1)-Cl(3)#2	3.043(3)	S(5)-Na(1)-Cl(3)#3	92.88(13)
Na(1)-Cl(3)#3	3.043(3)	Cl(2)-Na(1)-Cl(3)#3	73.58(12)
Na(2)-Cl(3)	2.754(4)	S(4)#1-Na(1)-Cl(3)#3	96.23(13)
Na(2)-Cl(3)#7	2.754(4)	Cl(3)#2-Na(1)-Cl(3)#3	146.9(2)
Na(2)-S(6)	2.807(8)	S(5)-Na(1)-S(2)#4	83.50(17)
Na(2)-S(1)	2.897(8)	Cl(2)-Na(1)-S(2)#4	147.25(8)
Na(2)-S(3)	3.284(7)	S(4)#1-Na(1)-S(2)#4	69.22(15)
Na(2)-S(3)#7	3.284(7)	Cl(3)#2-Na(1)-S(2)#4	139.01(18)
Sr(1)-Cl(1)	3.032(4)	Cl(3)#3-Na(1)-S(2)#4	74.03(9)
Sr(1)-S(2)#11	3.091(3)	S(5)-Na(1)-S(2)#1	83.50(17)
Sr(1)-S(2)#12	3.091(3)	Cl(2)-Na(1)-S(2)#1	147.25(8)
Sr(1)-S(1)#2	3.098(5)	S(4)#1-Na(1)-S(2)#1	69.22(15)
Sr(1)-Cl(2)#8	3.116(4)	Cl(3)#2-Na(1)-S(2)#1	74.03(9)
Sr(1)-S(5)#2	3.127(4)	Cl(3)#3-Na(1)-S(2)#1	139.01(18)

Table S2a. Selected bond distances (Å) and angles (degrees) for $[NaSr_3Cl_3][SiS_4]$.

Sr(1)-Cl(4)#13	3.129(3)	S(2)#4-Na(1)-S(2)#1	64.99(15)
Sr(1)-Cl(4)#8	3.129(3)	Cl(3)-Na(2)-Cl(3)#7	141.6(3)
Sr(2)-Cl(2)	2.970(2)	Cl(3)-Na(2)-S(6)	89.51(16)
Sr(2)-Cl(3)#3	2.976(3)	Cl(3)#7-Na(2)-S(6)	89.51(16)
Sr(2)-S(2)#14	2.987(3)	Cl(3)-Na(2)-S(1)	101.14(16)
Sr(2)-S(2)#15	3.026(3)	Cl(3)#7-Na(2)-S(1)	101.14(16)
Sr(2)-Cl(3)#14	3.049(3)	S(6)-Na(2)-S(1)	145.5(3)
Sr(2)-S(6)#16	3.096(3)	Cl(3)-Na(2)-S(3)	77.61(11)
Sr(2)-S(4)#17	3.1035(12)	Cl(3)#7-Na(2)-S(3)	140.3(2)
Sr(2)-Cl(4)#7	3.249(3)	S(6)-Na(2)-S(3)	83.5(2)
Sr(3)-Cl(1)	2.937(4)	S(1)-Na(2)-S(3)	67.33(15)
Sr(3)-Cl(4)	2.977(3)	Cl(3)-Na(2)-S(3)#7	140.3(2)
Sr(3)-Cl(4)#18	2.977(3)	Cl(3)#7-Na(2)-S(3)#7	77.61(11)
Sr(3)-S(3)#13	3.029(3)	S(6)-Na(2)-S(3)#7	83.5(2)
Sr(3)-S(3)#8	3.029(3)	S(1)-Na(2)-S(3)#7	67.33(15)
Sr(3)-S(3)#8	3.029(3)	S(3)-Na(2)-S(3)#7	62.75(16)
Sr(3)-S(6)#8	3.052(4)	Cl(1)-Sr(1)-S(2)#11	135.40(8)
Sr(3)-S(4)#8	3.080(4)	Cl(1)-Sr(1)-S(2)#12	135.40(8)
Sr(4)-Cl(4)	2.949(3)	S(2)#11-Sr(1)-S(2)#12	66.33(10)
Sr(4)-Cl(1)#8	2.990(3)	Cl(1)-Sr(1)-S(1)#2	69.31(11)

Table S2a. Selected bond distances (Å) and angles (degrees) for [$NaSr_3Cl_3$][SiS_4].

Sr(4)-S(3)	3.022(3)	S(2)#11-Sr(1)-S(1)#2	131.55(8)
Sr(4)-S(5)	3.046(3)	S(2)#12-Sr(1)-S(1)#2	131.55(8)
Sr(4)-S(3)#2	3.050(3)	Cl(1)-Sr(1)-Cl(2)#8	68.98(11)
Sr(4)-Cl(3)#2	3.064(3)	S(2)#11-Sr(1)-Cl(2)#8	81.06(9)
Sr(4)-S(1)#2	3.1807(13)	S(2)#12-Sr(1)-Cl(2)#8	81.06(9)
Si(1)-S(2)	2.111(4)	S(1)#2-Sr(1)-Cl(2)#8	138.29(12)
Si(1)-S(2)#7	2.111(4)	Cl(1)-Sr(1)-S(5)#2	135.65(11)
Si(1)-S(6)	2.118(6)	S(2)#11-Sr(1)-S(5)#2	78.37(9)
Si(1)-S(4)	2.148(6)	S(2)#12-Sr(1)-S(5)#2	78.37(9)
Si(2)-S(3)	2.112(4)	S(1)#2-Sr(1)-S(5)#2	66.34(11)
Si(2)-S(3)#7	2.112(4)	Cl(2)#8-Sr(1)-S(5)#2	155.37(12)
Si(2)-S(1)	2.121(6)	Cl(1)-Sr(1)-Cl(4)#13	70.71(6)
Si(2)-S(5)	2.129(6)	S(2)#11-Sr(1)-Cl(4)#13	68.27(7)
Atom-Atom-Atom	**Angle (°)**	S(2)#12-Sr(1)-Cl(4)#13	128.89(9)
S(1)#2-Sr(1)-Cl(4)#13	96.29(7)	Cl(2)#8-Sr(1)-Cl(4)#13	69.86(6)
S(5)#2-Sr(1)-Cl(4)#13	113.91(6)	Cl(1)-Sr(1)-Cl(4)#8	70.71(6)
S(2)#11-Sr(1)-Cl(4)#8	128.89(9)	S(2)#12-Sr(1)-Cl(4)#8	68.27(7)
S(1)#2-Sr(1)-Cl(4)#8	96.29(7)	Cl(2)#8-Sr(1)-Cl(4)#8	69.86(6)
S(5)#2-Sr(1)-Cl(4)#8	113.91(6)	Cl(4)#13-Sr(1)-Cl(4)#8	131.66(11)
Cl(2)-Sr(2)-Cl(3)#3	72.16(9)	Cl(2)-Sr(2)-S(2)#14	85.24(10)

Table S2a. Selected bond distances (Å) and angles (degrees) for $[NaSr_3Cl_3][SiS_4]$.

Cl(3)#3-Sr(2)-S(2)#14	142.19(9)	Cl(2)-Sr(2)-S(2)#15	151.63(9)
Cl(3)#3-Sr(2)-S(2)#15	132.40(8)	S(2)#14-Sr(2)-S(2)#15	79.44(9)
Cl(2)-Sr(2)-Cl(3)#14	104.92(10)	Cl(3)#3-Sr(2)-Cl(3)#14	72.85(8)
S(2)#14-Sr(2)-Cl(3)#14	143.83(8)	S(2)#15-Sr(2)-Cl(3)#14	75.71(8)
Cl(2)-Sr(2)-S(6)#16	72.86(9)	Cl(3)#3-Sr(2)-S(6)#16	126.91(10)
S(2)#14-Sr(2)-S(6)#16	70.75(9)	S(2)#15-Sr(2)-S(6)#16	79.56(8)
Cl(3)#14-Sr(2)-S(6)#16	79.16(9)	Cl(2)-Sr(2)-S(4)#17	138.81(10)
Cl(3)#3-Sr(2)-S(4)#17	78.01(10)	S(2)#14-Sr(2)-S(4)#17	102.55(9)
S(2)#15-Sr(2)-S(4)#17	68.50(9)	Cl(3)#14-Sr(2)-S(4)#17	92.36(10)
S(6)#16-Sr(2)-S(4)#17	148.06(10)	Cl(2)-Sr(2)-Cl(4)#7	70.03(9)
Cl(3)#3-Sr(2)-Cl(4)#7	75.90(8)	S(2)#14-Sr(2)-Cl(4)#7	67.92(8)
S(2)#15-Sr(2)-Cl(4)#7	124.02(8)	Cl(3)#14-Sr(2)-Cl(4)#7	148.25(8)
S(6)#16-Sr(2)-Cl(4)#7	125.63(9)	S(4)#17-Sr(2)-Cl(4)#7	75.67(9)
Cl(1)-Sr(3)-Cl(4)	79.54(7)	Cl(1)-Sr(3)-Cl(4)#18	79.54(7)
Cl(4)-Sr(3)-Cl(4)#18	126.92(12)	Cl(1)-Sr(3)-S(3)#13	77.79(9)
Cl(4)-Sr(3)-S(3)#13	142.41(9)	Cl(4)#18-Sr(3)-S(3)#13	77.44(8)
Cl(1)-Sr(3)-S(3)#8	77.79(9)	Cl(4)-Sr(3)-S(3)#8	77.44(8)
Cl(4)#18-Sr(3)-S(3)#8	142.41(9)	S(3)#13-Sr(3)-S(3)#8	68.72(11)
Cl(1)-Sr(3)-S(6)#8	157.91(12)	Cl(4)-Sr(3)-S(6)#8	108.77(7)
Cl(4)#18-Sr(3)-S(6)#8	108.77(7)	S(3)#13-Sr(3)-S(6)#8	84.02(9)

Table S2a. Selected bond distances (Å) and angles (degrees) for $[NaSr_3Cl_3][SiS_4]$.

S(3)#8-Sr(3)-S(6)#8	84.02(9)	Cl(1)-Sr(3)-S(4)#8	133.44(12)
Cl(4)-Sr(3)-S(4)#8	80.11(8)	Cl(4)#18-Sr(3)-S(4)#8	80.11(8)
S(3)#13-Sr(3)-S(4)#8	136.45(7)	S(3)#8-Sr(3)-S(4)#8	136.45(7)
S(6)#8-Sr(3)-S(4)#8	68.65(11)	Cl(4)-Sr(4)-Cl(1)#8	73.80(9)
Cl(4)-Sr(4)-S(3)	133.31(9)	Cl(1)#8-Sr(4)-S(3)	77.11(9)
Cl(4)-Sr(4)-S(5)	132.07(9)	Cl(1)#8-Sr(4)-S(5)	74.66(9)
S(3)-Sr(4)-S(5)	70.98(9)	Cl(4)-Sr(4)-S(3)#2	138.57(9)
Cl(1)#8-Sr(4)-S(3)#2	147.60(9)	S(3)-Sr(4)-S(3)#2	76.02(9)
S(5)-Sr(4)-S(3)#2	79.71(8)	Cl(4)-Sr(4)-Cl(3)#2	79.21(8)
Cl(1)#8-Sr(4)-Cl(3)#2	120.24(9)	S(3)-Sr(4)-Cl(3)#2	147.48(9)
S(5)-Sr(4)-Cl(3)#2	86.66(9)	S(3)#2-Sr(4)-Cl(3)#2	77.00(8)
Cl(4)-Sr(4)-S(1)#2	79.08(9)	Cl(1)#8-Sr(4)-S(1)#2	134.56(11)
S(3)-Sr(4)-S(1)#2	97.13(9)	S(5)-Sr(4)-S(1)#2	146.57(11)
S(3)#2-Sr(4)-S(1)#2	67.00(10)	Cl(3)#2-Sr(4)-S(1)#2	88.68(10)
S(2)-Si(1)-S(2)#7	106.4(2)	S(2)-Si(1)-S(6)	112.80(17)
S(2)#7-Si(1)-S(6)	112.80(17)	S(2)-Si(1)-S(4)	108.19(17)
S(2)#7-Si(1)-S(4)	108.19(17)	S(6)-Si(1)-S(4)	108.3(2)
S(3)-Si(2)-S(3)#7	108.1(2)	S(3)-Si(2)-S(1)	108.76(17)
S(3)#7-Si(2)-S(1)	108.75(17)	S(3)-Si(2)-S(5)	112.31(16)
S(3)#7-Si(2)-S(5)	112.31(16)	S(1)-Si(2)-S(5)	106.5(3)

Symmetry transformations used to generate equivalent atoms:

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

#4 x-1,-y+1/2,z-1   #5 -x+1,-y,-z   #6 -x+1,y+1/2,-z

#7 x,-y+1/2,z   #8 -x+2,-y+1,-z+1   #9 x,-y+1/2,z+1

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

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

#16 x,y,z-1   #17 -x+2,-y,-z+1   #18 x,-y+3/2,z

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

Table S2b. Selected bond distances (Å) and angles (degrees) for $[NaSr_4SCl][Si_3S_9]$.

Atom-Atom	**Length (Å)**	S(3)#1-Na(1)-S(3)#2	119.998(7)
Na(1)-S(3)#1	2.807(3)	S(3)#1-Na(1)-S(3)	119.998(7)
Na(1)-S(3)	2.807(3)	S(3)#2-Na(1)-S(3)	119.998(7)
Na(1)-S(3)#2	2.807(3)	S(3)#1-Na(1)-Cl(4)#3	89.8(4)
Na(1)-Cl(4)#3	2.90(2)	S(3)#2-Na(1)-Cl(4)#3	89.8(4)
Na(1)-Cl(4)	2.92(2)	S(3)-Na(1)-Cl(4)#3	89.8(4)
Sr(1)-Cl(4)	2.8665(12)	S(3)#1-Na(1)-Cl(4)	90.2(4)
Sr(1)-S(4)	2.8971(17)	S(3)#2-Na(1)-Cl(4)	90.2(4)
Sr(1)-S(3)	3.099(4)	S(3)-Na(1)-Cl(4)	90.2(4)
Sr(1)-S(1)#6	3.207(3)	Cl(4)#3-Na(1)-Cl(4)	180.0
Sr(1)-S(2)#7	3.208(3)	Cl(4)-Sr(1)-S(4)	144.05(8)
Sr(1)-S(2)#6	3.324(3)	Cl(4)-Sr(1)-S(3)	85.65(15)
Sr(1)-S(3)#7	3.430(4)	S(4)-Sr(1)-S(3)	119.76(12)
Sr(1)-S(2)#8	3.504(3)	Cl(4)-Sr(1)-S(1)#6	97.66(14)
Si(1)-S(2)	2.064(4)	S(4)-Sr(1)-S(1)#6	89.18(10)
Si(1)-S(3)	2.082(4)	S(3)-Sr(1)-S(1)#6	122.99(8)
Si(1)-S(1)	2.151(4)	Cl(4)-Sr(1)-S(2)#7	74.71(6)
Si(1)-S(1)#10	2.158(4)	S(4)-Sr(1)-S(2)#7	73.66(6)
Sr(2)-S(4)	3.041(5)	S(3)-Sr(1)-S(2)#7	106.94(9)
Atom-Atom-Atom	**Angle (°)**	S(1)#6-Sr(1)-S(2)#7	128.95(9)

Table S2b. Selected bond distances (Å) and angles (degrees) for $[NaSr_4SCl][Si_3S_9]$.

Cl(4)-Sr(1)-S(2)#6	142.30(6)	S(4)-Sr(1)-S(2)#6	71.91(5)
S(3)-Sr(1)-S(2)#6	78.69(8)	S(1)#6-Sr(1)-S(2)#6	64.50(8)
S(2)#7-Sr(1)-S(2)#6	142.68(9)	Cl(4)-Sr(1)-S(3)#7	78.94(14)
S(4)-Sr(1)-S(3)#7	71.75(10)	S(3)-Sr(1)-S(3)#7	163.33(9)
S(1)#6-Sr(1)-S(3)#7	66.05(8)	S(2)#7-Sr(1)-S(3)#7	62.94(8)
S(2)#6-Sr(1)-S(3)#7	117.58(8)	Cl(4)-Sr(1)-S(2)#8	70.11(5)
S(4)-Sr(1)-S(2)#8	141.86(7)	S(3)-Sr(1)-S(2)#8	64.29(8)
S(1)#6-Sr(1)-S(2)#8	63.82(7)	S(2)#7-Sr(1)-S(2)#8	144.17(8)
S(2)#6-Sr(1)-S(2)#8	72.20(9)	S(3)#7-Sr(1)-S(2)#8	115.24(8)
S(2)-Si(1)-S(3)	113.65(18)	S(2)-Si(1)-S(1)	111.58(17)
S(3)-Si(1)-S(1)	105.40(16)	S(2)-Si(1)-S(1)#10	114.73(17)
S(3)-Si(1)-S(1)#10	101.43(16)	S(1)-Si(1)-S(1)#10	109.2(2)
S(2)#14-Sr(2)-S(2)#15	83.23(9)	S(2)#14-Sr(2)-S(2)#16	83.23(9)
S(2)#15-Sr(2)-S(2)#16	83.23(9)	S(2)#14-Sr(2)-S(3)#17	71.21(8)
S(2)#15-Sr(2)-S(3)#17	84.48(8)	S(2)#16-Sr(2)-S(3)#17	152.74(10)
S(2)#14-Sr(2)-S(3)#7	84.48(8)	S(2)#15-Sr(2)-S(3)#7	152.74(10)
S(2)#16-Sr(2)-S(3)#7	71.21(8)	S(3)#17-Sr(2)-S(3)#7	114.23(5)
S(2)#14-Sr(2)-S(3)#6	152.74(10)	S(2)#15-Sr(2)-S(3)#6	71.21(8)
S(2)#16-Sr(2)-S(3)#6	84.48(8)	S(3)#17-Sr(2)-S(3)#6	114.23(5)
S(3)#7-Sr(2)-S(3)#6	114.23(5)	S(2)#14-Sr(2)-S(4)	129.93(6)

Table S2b. Selected bond distances (Å) and angles (degrees) for $[NaSr_4SCl][Si_3S_9]$.

S(2)#15-Sr(2)-S(4)	129.93(6)	S(2)#16-Sr(2)-S(4)	129.93(6)
S(3)#17-Sr(2)-S(4)	75.85(7)	S(3)#7-Sr(2)-S(4)	75.85(7)
S(3)#6-Sr(2)-S(4)	75.85(7)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

#11 x,y,z-1 #12 -x,-y,z+1/2 #13 -x+y+1,-x+1,z

#14 -y+1,x-y,z+1 #15 -x+y+1,-x+1,z+1 #16 x,y,z+1

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

Table S3a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[NaSr_3Cl_3][SiS_4]$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	***x***	***y***	***z***	U_{eq}	**BVS**[a]
Na(1)	4189(7)	2500	1412(5)	22(2)	0.95
Na(2)	5074(9)	2500	7917(5)	34(2)	1.13
Sr(1)	9093(2)	7500	6788(1)	19(1)	2.06
Sr(2)	7802(1)	291(1)	543(1)	18(1)	2.15
Sr(3)	10811(2)	7500	2949(1)	18(1)	2.10
Sr(4)	6713(1)	4656(1)	3918(1)	20(1)	2.22
Si(1)	10605(5)	2500	10191(4)	14(1)	4.05
Si(2)	5026(5)	2500	5389(4)	13(1)	3.92
S(1)	2848(5)	2500	5704(3)	20(1)	2.21
S(2)	11177(3)	4032(2)	11237(2)	16(1)	2.16
S(3)	6299(3)	4049(2)	6136(2)	18(1)	2.26
S(4)	12072(5)	2500	9140(3)	16(1)	2.04
S(5)	4514(5)	2500	3631(3)	18(1)	2.11
S(6)	8248(5)	2500	9167(3)	17(1)	2.18
Cl(1)	11215(5)	7500	5341(3)	19(1)	0.98
Cl(2)	7408(5)	2500	1768(3)	23(1)	1.22
Cl(3)	4839(3)	4856(3)	8562(2)	22(1)	1.13
Cl(4)	9476(3)	5087(2)	3191(3)	25(1)	1.06

[a]Bond valence state was calculated using the empirical formula $V_{\mathrm{i}} = \Sigma S_{ij} = \Sigma \exp[(r_0 - r_{ij})/0.37]$, where S_{ij} is the bond valence associated with bond lengths r_{ij} and r_0.

Table S3b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for [$NaSr_4SCl$][Si_3S_9]. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	***x***	***y***	***z***	U_{eq}	**BVS**[a]
Na(1)	0	0	3526(17)	76(4)	1.17
Sr(1)	3363(1)	2535(1)	5966(2)	36(1)	2.06
Sr(2)	6667	3333	9154(2)	17(1)	2.25
Si(1)	4514(3)	3346(3)	2581(3)	15(1)	4.04
S(1)	6673(3)	5485(3)	3194(3)	21(1)	2.11
S(2)	4253(3)	3427(3)	825(3)	23(1)	2.13
S(3)	2587(3)	3247(3)	3517(3)	21(1)	2.24
S(4)	6667	3333	6540(4)	20(1)	2.14
Cl(1)	0	0	6036(6)	31(1)	1.07

[a]Bond valence state was calculated using the empirical formula $V_i = \Sigma S_{ij} = \Sigma \exp[(r_0 - r_{ij})/0.37]$, where S_{ij} is the bond valence associated with bond lengths r_{ij} and r_0.

Table S4a. Anisotropic displacement parameters (Å^2 × 10^3) for $[NaSr_3Cl_3][SiS_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2(a^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	17(4)	31(4)	17(4)	0	3(3)	0
Na(2)	46(5)	22(4)	22(4)	0	-6(4)	0
Sr(1)	17(1)	24(1)	16(1)	0	7(1)	0
Sr(2)	18(1)	17(1)	20(1)	-2(1)	9(1)	-1(1)
Sr(3)	17(1)	22(1)	13(1)	0	4(1)	0
Sr(4)	20(1)	20(1)	25(1)	4(1)	12(1)	2(1)
Si(1)	11(2)	14(2)	16(3)	0	3(2)	0
Si(2)	13(3)	14(2)	12(2)	0	3(2)	0
S(1)	19(3)	22(2)	21(3)	0	9(2)	0
S(2)	19(2)	13(2)	16(2)	-2(1)	6(1)	-3(1)
S(3)	20(2)	14(2)	18(2)	-3(1)	5(1)	2(1)
S(4)	18(3)	18(2)	14(2)	0	5(2)	0
S(5)	17(2)	21(2)	17(2)	0	7(2)	0
S(6)	17(2)	19(2)	11(2)	0	0(2)	0
Cl(1)	18(2)	24(2)	16(2)	0	6(2)	0
Cl(2)	21(3)	23(2)	24(3)	0	8(2)	0
Cl(3)	22(2)	30(2)	17(2)	-2(1)	10(1)	5(1)
Cl(4)	28(2)	16(2)	36(2)	-3(1)	19(2)	-4(1)

Table S4b. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[NaSr_4SCl][Si_3S_9]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2(a^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	73(5)	73(5)	82(9)	0	0	36(2)
Sr(1)	29(1)	32(1)	44(1)	1(1)	-5(1)	13(1)
Sr(2)	19(1)	19(1)	12(1)	0	0	9(1)
Si(1)	16(1)	15(1)	13(2)	-1(1)	2(1)	7(1)
S(1)	20(1)	21(1)	22(1)	-5(1)	1(1)	10(1)
S(2)	22(1)	40(2)	11(1)	-1(1)	3(1)	19(1)
S(3)	21(1)	21(1)	21(1)	-2(1)	9(1)	10(1)
S(4)	19(1)	19(1)	22(2)	0	0	9(1)
Cl(1)	20(1)	20(1)	52(3)	0	0	10(1)

Table S5. Space group and optical performances of some reported chalcogenide halides.

Compounds	Space group	Band gap (eV)	SHG effect (× AGS)	LIDT (× AGS)
$[KBa_4Cl][Ge_3S_{10}]$[10]	$P6_3$	3.57	0.9	12
$[NaSr_4Cl][Ge_3S_{10}]$[10]	$P6_3$	3.54	1	11
$[KSr_4Cl][Ge_3S_{10}]$[10]	$P6_3$	3.51	0.9	12
$Li[LiCs_2Cl][Ga_3S_6]$[11]	$Pna2_1$	4.18	0.7	4.1
$[RbBa_2Cl][Ga_4S_8]$[12]	$Pna2_1$	3.30	1.0	11
$[CsBa_2Cl][Ga_4S_8]$[12]	$Pna2_1$	3.35	0.9	12
$[K_3Br][PGa_3S_8]$[13]	Pm	3.85	1.2	31
$[Rb_3Br][PGa_3S_8]$[13]	Pm	3.50	2.0	29
$[Rb_3Cl][PGa_3S_8]$[13]	$Pmn2_1$	3.65	1.1	35
$[K_3Cl][PGa_3S_8]$[13]	$Pmn2_1$	3.60	1.0	37
$[Ba_4Cl_2][ZnGa_4S_{10}]$[14]	I-4	3.85	1.1	51
$[Ba_4Cl_2][HgGa_4S_{10}]$[15]	I-4	2.95	1.5	15
$[K_4Cl][CdGa_9S_{16}]$[16]	$P1$	3.14	0.9	22.6
$[K_4Cl][CdGa_9Se_{16}]$[16]	$P1$	1.72	2.4	7.7
$[Rb_3BaCl][In_8Se_{14}]$[17]	I-42d	2.02	3.2	3.2

Table S6. Dimension of covalent units, Space group and A/M ratio of reported chalcogenide halides.

Compounds	Space group	Dimension of covalent units	A/M
$[NaBa_4Cl][Ge_3S_{10}]$	$P6_3$	0D	1.67
$[NaSr_4Cl][Ge_3S_{10}]$	$P6_3$	0D	1.67
$[KSr_4Cl][Ge_3S_{10}]$	$P6_3$	0D	1.67
$[KBa_4Cl][Ge_3S_{10}]$	$P6_3$	0D	1.67
$[KBa_3Cl_2][Ge_3S_9]$	$P6_3$	0D	1.67
$[Ba_4Cl_2][Ge_3S_9]$	$P6_3$	0D	1.33
$[Ba_4Cl_2][Ge_3Se_9]$	$P6_3$	0D	1.33
$[Ba_4Cl_2][Si_3Se_9]$	$P6_3$	0D	1.33
$[Ba_4Br_2][Ge_3Se_9]$	$P6_3$	0D	1.33
$[Ba_4Br_2][Si_3Se_9]$	$P6_3$	0D	1.33
$[Sr_4Cl_2][Si_3S_9]$	$P6_3$	0D	1.33
$[LaCa_2Cl_3][GeS_4]$	$P6_3mc$	0D	3
$[Ba_2F_2][GeS_3]$	*Pnma*	0D	2
$[Ba_2F_2][GeSe_3]$	*Pnma*	0D	2
$[Ba_3Cl][GaS_4]$	*Pnma*	0D	3
$[Ba_3Br][GaS_4]$	*Pnma*	0D	3
$[Ba_3Br][GaSe_4]$	*Pnma*	0D	3
$[Ba_3Cl][GaSe_4]$	*Pnma*	0D	3
$[Ba_3Cl][AlS_4]$	*Pnma*	0D	3
$[Ba_3Br][AlS_4]$	*Pnma*	0D	3
$[Ba_3Cl][AlSe_4]$	*Pnma*	0D	3
$[Ba_3Br][AlSe_4]$	*Pnma*	0D	3
$[Ba_3Cl][InS_4]$	$I4/mcm$	0D	3
$[Ba_3Cl][InSe_4]$	$I4/mcm$	0D	3

Table S6. Dimension of covalent units, Space group and A/M ratio of reported chalcogenide halides.

Compounds	Space group	Dimension of covalent units	A/M
$[Ba_3Br][InSe_4]$	*I*4/*mcm*	0D	3
$[Ba_3F_2][GaSe_4]$	*P*2$_1$/*n*	0D	3
$[RbBa_2Cl][GeS_4]$	*P*2$_1$/*c*	0D	3
$[CsBa_2Cl][GeS_4]$	*P*2$_1$/*c*	0D	3
$[RbBa_2Cl][SnS_4]$	*P*2$_1$/*c*	0D	3
α-$[CsBa_2Cl][SnS_4]$	*P*2$_1$/*c*	0D	3
β-$[CsBa_2Cl][SnS_4]$	*I*4/*mcm*	0D	3
$[Pb_3Br_2][GeS_4]$	*I*4/*mcm*	0D	3
$[Ba_4F_3][GaS_4]$	*I*4$_1$/*a*	0D	4
$[Ba_2F_2][SnS_3]$	*Pnma*	1D	2
$[Ba_2F_2][SnSe_3]$	*Pnma*	1D	2
$[Sr_2F_2][SnS_3]$	*Pnma*	1D	2
$[Sr_2F_2][SnSe_3]$	*Pnma*	1D	2
$[Ba_3F_2][ZnSe_3]$	*Pnma*	1D	3
$[Ba_3F_2][CdSe_3]$	*Pnma*	1D	3
$[RbBa_2Cl][Ga_4S_8]$	*Pmn*2$_1$	2D	0.75
$[CsBa_2Cl][Ga_4S_8]$	*Pmn*2$_1$	2D	0.75
$[K_3Cl][Ga_3PS_8]$	*Pmn*2$_1$	2D	1
$[Rb_3Cl][Ga_3PS_8]$	*Pmn*2$_1$	2D	1
$[K_3Br][Ga_3PS_8]$	*Pm*	2D	1
$[Rb_3Br][Ga_3PS_8]$	*Pm*	2D	1
$[Cs_6Cl]_2Cs_5[Ga_{15}Ge_9Se_{48}]$	*I*4/*m*	2D	0.7
$[Cs_6Br]_2Cs_5[Ga_{15}Ge_9Se_{48}]$	*I*4/*m*	2D	0.7
$Cs_3[Cs_6Cl]_6[Ga_{53}Se_{96}]$	*R*-3*m*	2D	0.74

Table S6. Dimension of covalent units, Space group and A/M ratio of reported chalcogenide halides.

Compounds	Space group	Dimension of covalent units	A/M
$[Rb_4Cl][Cd_{11}In_9S_{26}]$	*Cmn*2$_1$	3D	0.2
$[K_4Cl][Zn_{11}In_9S_{26}]$	*Cmn*2$_1$	3D	0.2
$[K_4Cl][Cd_{11}In_9S_{26}]$	*Cmn*2$_1$	3D	0.2
$K_2[K_3BaCl][In_{18}Se_{30}]$	*P*6$_3$*cm*	3D	0.33
$Rb_2[Rb_3BaCl][In_{18}Se_{30}]$	*P*6$_3$*cm*	3D	0.33
$K[K_4Cl][In_{14}Se_{23}]$	*P*1	3D	0.36
$Rb[Rb_4Cl][In_{14}Se_{23}]$	*P*1	3D	0.36
$[K_4Cl][CdGa_9S_{16}]$	*P*1	3D	0.4
$[K_4Cl][CdGa_9Se_{16}]$	*P*1	3D	0.4
$[K_2PbCl][Ga_7S_{12}]$	*Imm*2	3D	0.43
$[K_2PbBr][Ga_7S_{12}]$	*Imm*2	3D	0.43
$[K_2PbI][Ga_7S_{12}]$	*Imm*2	3D	0.43
$[Na_2PbI][Ga_7S_{12}]$	*Imm*2	3D	0.43
$[Na_4I][Ga_9S_{15}]$	*R*3	3D	0.44
$[Rb_3BaCl][In_8Se_{14}]$	*I*-42*d*	3D	0.5
$K_2[K_4Cl][Ga_5Sn_7S_{24}]$	*P*-4	3D	0.5
$[K_4Cl][BaK_9Cl_4][In_{22}Se_{38}]$	*C*2	3D	0.63
$[K_4Cl][LiK_{10}Cl_4][In_{22}Se_{38}]$	*C*2	3D	0.68
$[KBa_3Cl_2][Ga_5Se_{10}]$	*I*-4	3D	0.8
$[RbBa_3Cl_2][Ga_5Se_{10}]$	*I*-4	3D	0.8
$[CsBa_3Cl_2][Ga_5Se_{10}]$	*I*-4	3D	0.8
$[KBa_3Cl_2][Ga_5S_{10}]$	*I*-4	3D	0.8
$[RbBa_3Cl_2][Ga_5S_{10}]$	*I*-4	3D	0.8
$[CsBa_3Cl_2][Ga_5S_{10}]$	*I*-4	3D	0.8

Table S6. Dimension of covalent units, Space group and A/M ratio of reported chalcogenide halides.

Compounds	Space group	Dimension of covalent units	A/M
$[NaBa_3Br_2][Ga_5Se_{10}]$	*I*-4	3D	0.8
$[KBa_3Br_2][Ga_5Se_{10}]$	*I*-4	3D	0.8
$[RbBa_3Br_2][Ga_5Se_{10}]$	*I*-4	3D	0.8
$[CsBa_3Br_2][Ga_5Se_{10}]$	*I*-4	3D	0.8
$[Ba_4Cl_2][ZnGa_4Se_{10}]$	*I*-4	3D	0.8
$[Ba_4Cl_2][CdGa_4Se_{10}]$	*I*-4	3D	0.8
$[Ba_4Cl_2][ZnGa_4S_{10}]$	*I*-4	3D	0.8
$[Ba_4Cl_2][HgGa_4S_{10}]$	*I*-4	3D	0.8

A = electropositive cations, M = tetrahedrally coordinated cations

Table S7. Space group and optical performances among some reported chalcogenide halides.

Compounds	Space group	SHG effect (× AGS)	Band gap (eV)
$[Sr_4Cl_2][Si_3S_9]$[18]	$P6_3$	1.1	4.22
$[KBa_3Cl_2][Ge_3S_9]$[19]	$P6_3$	0.3	3.69
$[KBa_4Cl][Ge_3S_{10}]$[10]	$P6_3$	0.9	3.57
$[NaSr_4Cl][Ge_3S_{10}]$[10]	$P6_3$	1	3.54
$[KSr_4Cl][Ge_3S_{10}]$[10]	$P6_3$	0.9	3.51
$[NaBa_4Cl][Ge_3S_{10}]$[20]	$P6_3$	0.3	3.49
$[Ba_4Br_2][Si_3Se_9]$[21]	$P6_3$	3.2	2.96
$[Ba_4Cl_2][Ge_3S_9]$[22]	$P6_3$	2.4	2.91
$[Ba_4Br_2][Ge_3Se_9]$[21]	$P6_3$	3.5	2.60
$[Ba_4Cl_2][Si_3Se_9]$[22]	$P6_3$	0.5	1.89
$[Ba_4Cl_2][Ge_3Se_9]$[22]	$P6_3$	0.5	1.76
$[NaSr_4SCl][Si_3S_9]$[This work]	**$P6_3$**	**0.8**	**4.43**

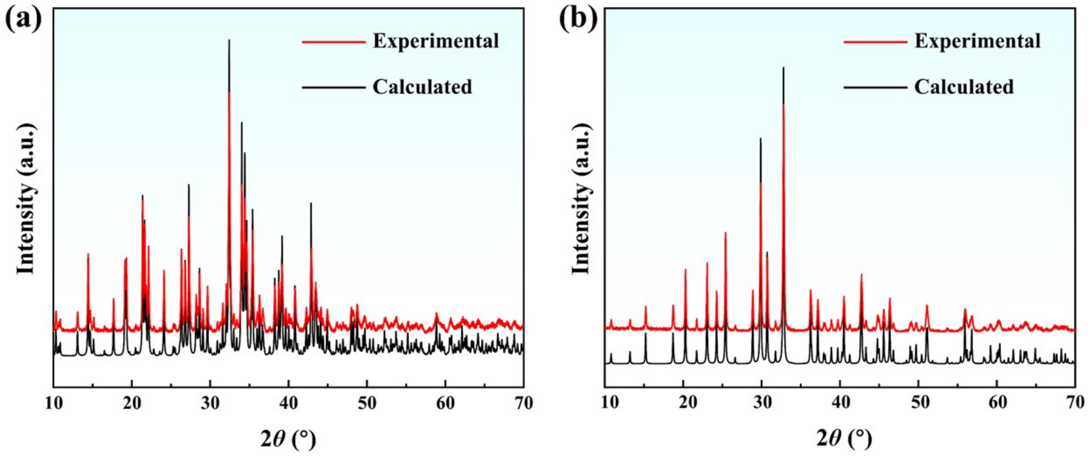

Fig. S1 PXRD patterns of (a) $[NaSr_3Cl_3][SiS_4]$ and (b) $[NaSr_4SCl][Si_3S_9]$.

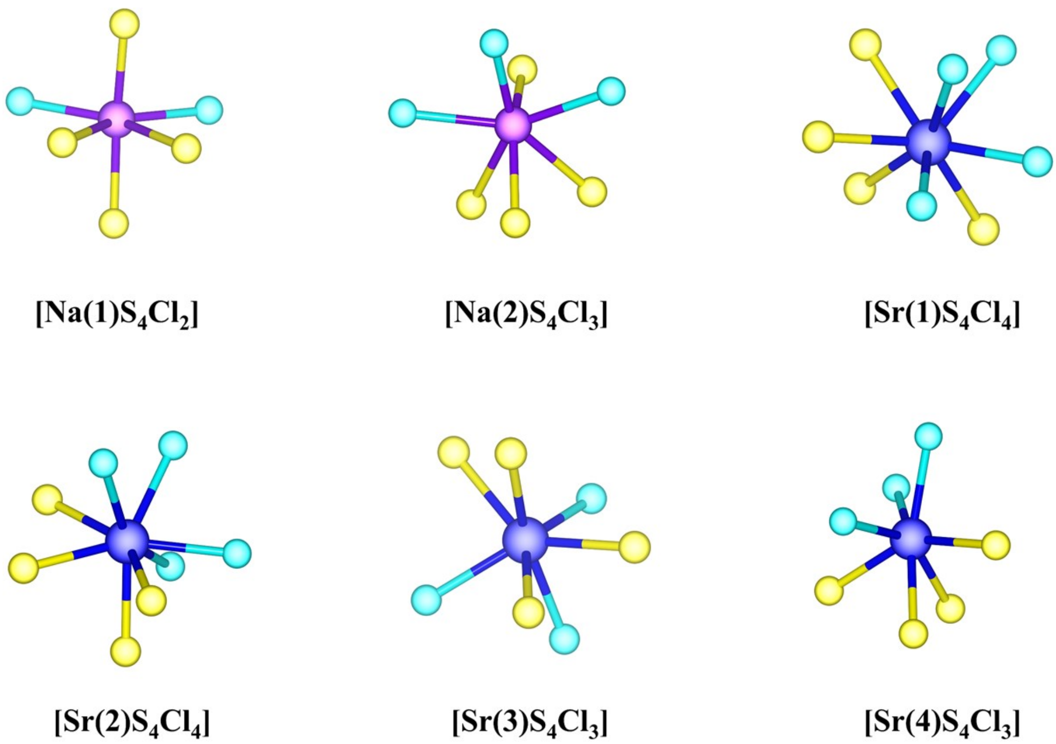

Fig. S2 The coordination environments of Na and Sr atoms in $[NaSr_3Cl_3][SiS_4]$.

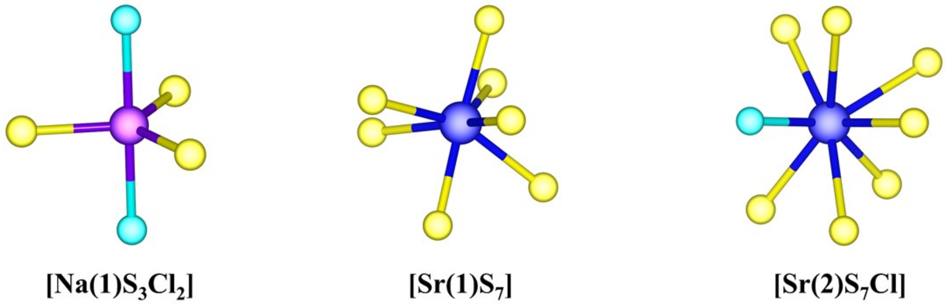

Fig. S3 The coordination environments of Na and Sr atoms in $[NaSr_4SCl][Si_3S_9]$.

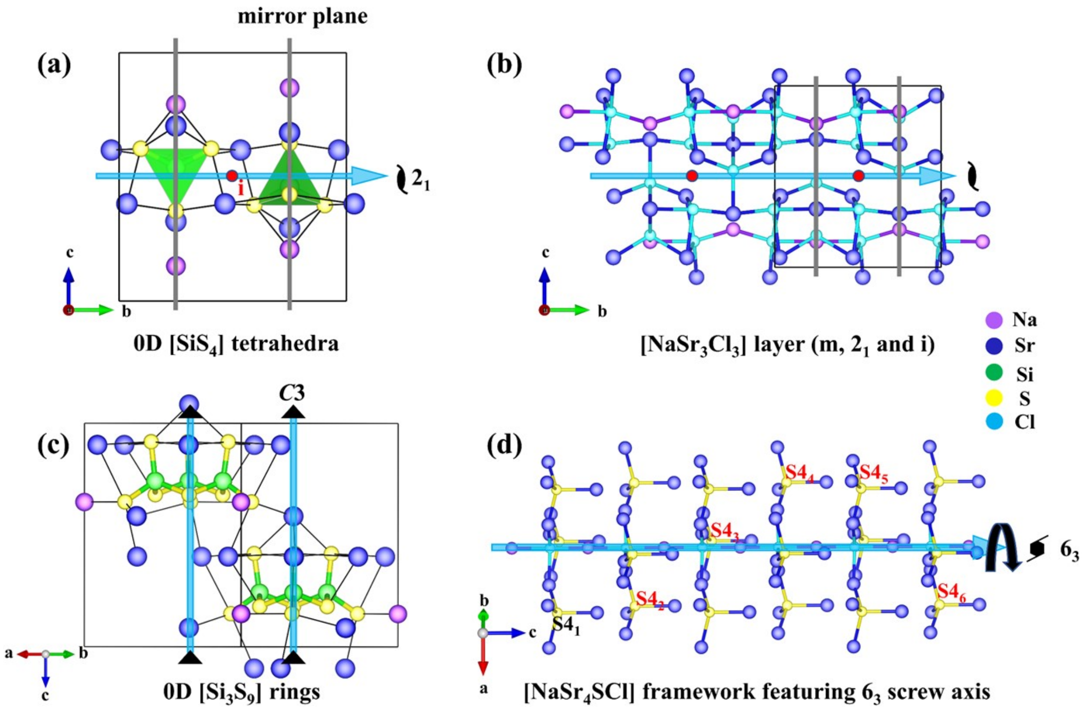

Fig. S4 (a) the coordination environments of [SiS_4] tetrahedra; (b) [$NaSr_3Cl_3$] layer with m, 2_1 screw axis and i; (c) the coordination environments of [Si_3S_9] rings; (d) [$NaSr_4SCl$] framework featuring 6_3 screw axis.

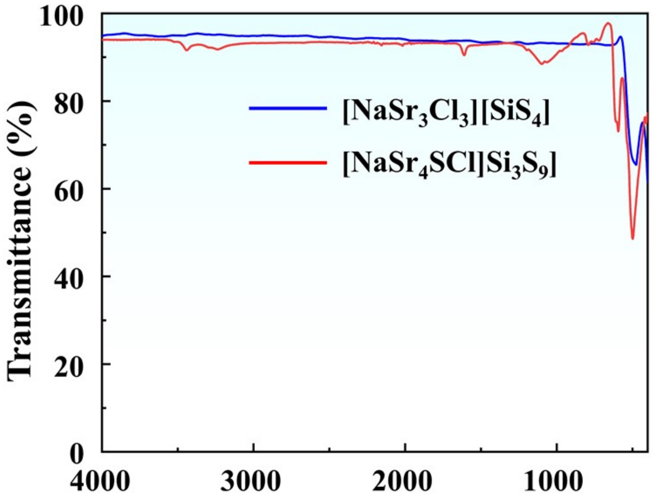

Fig. S5 The FTIR spectrum of $[NaSr_3Cl_3][SiS_4]$ and $[NaSr_4SCl][Si_3S_9]$.

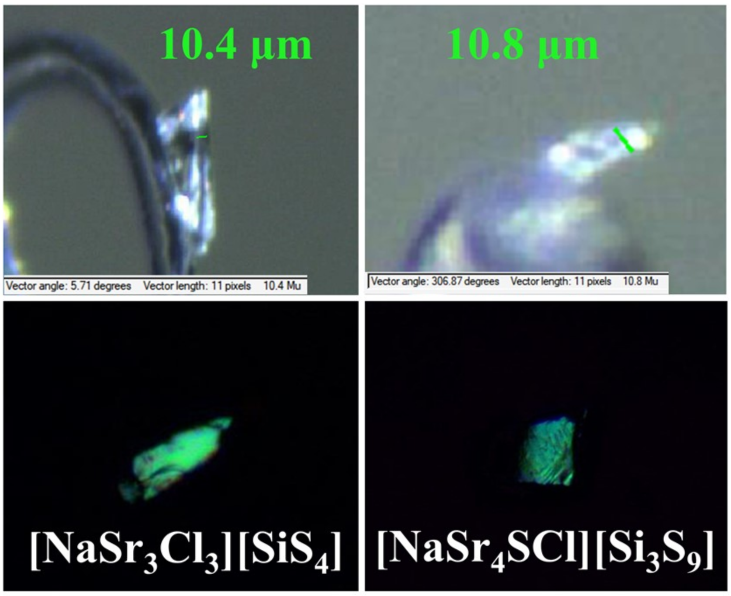

Fig. S6 The thickness of the test crystal and the interference state under cross-polarized light.

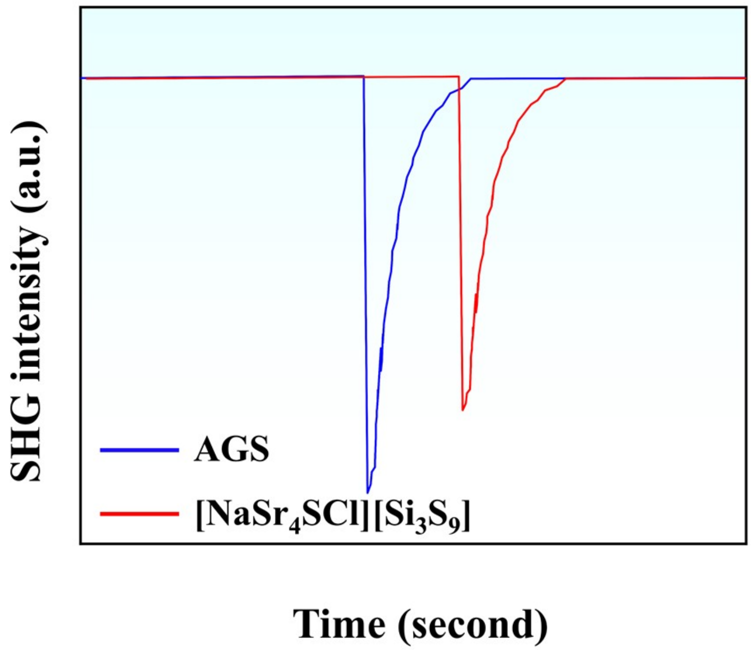

Fig. S7 The SHG signals for $[NaSr_4SCl][Si_3S_9]$ and AGS in the exact particle sizes.

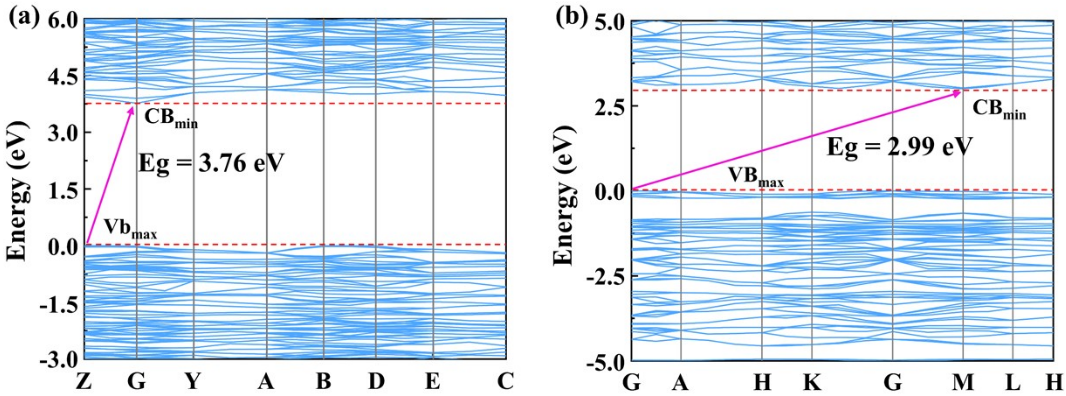

Fig. S8 The electronic band structure of (a) $[NaSr_3Cl_3][SiS_4]$ and (b) $[NaSr_4SCl][Si_3S_9]$.

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