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$[Sr_4Cl_2][Si_3S_9]$: Ultrawide-bandgap salt-inclusion thiosilicate nonlinear optical material with unprecedented tri-polymerized $[Si_3S_9]$ clusters

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1. Synthesis of Title Compound

All the reagents were directly purchased from the Beijing Hawke Technology Co., Ltd. The whole preparation process is completed in an Ar-filled glovebox.

The synthesis of $[Sr_4Cl_2][Si_3S_9]$ was carried out with the stoichiometric ratio ($SrS:SrCl_2:Si:S=3:1:3:6$). We firstly put the raw material into a graphite crucible and then put the crucible into a flame-sealed silica tube with 10^{-3} Pa to eliminate the corrosion problem between the quartz tube and the raw material. The silica tube was heated to 850 °C and kept at this temperature for about 50 hours and slowly reduced to ambient temperature over a period of 3 days. Finally, the high yield (>95%) of $[Sr_4Cl_2][Si_3S_9]$ crystals were obtained and they were stable in air within half of year.

The SEM-EDS test of the crystal was performed with a Hitachi TM4000Plus scanning electron microscope, which shows that four chemical elements (Sr, Si, S and Cl) were contained in a ratio of approximately 4.198 : 3.584 : 9.952 : 2.266 (Figure S3).

2. Structural Refinement and Crystal Data

Selected high-quality crystal of $[Sr_4Cl_2][Si_3S_9]$ was used for data collection by a Bruker D8 VENTURE diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 296 K. Its crystal structure was solved by direct method and refined using the SHELXTL program package.[1] Absorption correction was performed using the multi-scan method. [2] Reasonable anisotropic thermal parameters were obtained for all atoms by anisotropic refinement and extinction correction. PLATON was also used to check the final structures and no other symmetries were found.[3] Refinement parameters and data were detailed in Table S1.

3. Property Characterization

3.1 Powder X-ray Diffraction

Powder X-ray diffraction (XRD) patterns of title compounds were collected on a Bruker D2 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 10-70° with a step size of 0.02° and a fixed counting time of 1s/step.

3.2 UV−Vis−Near-IR (NIR) Diffuse-Reflectance Spectra

Diffuse-reflectance spectra were measured by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 200−1100 nm at room temperature. The absorption spectra were converted from the reflection spectra *via* the Kubelka−Munk function.

3.3 IR and Raman Spectra

The Infrared spectrum was carried out on a Shimadzu IR Affinity Fourier transform infrared spectrometer in the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}. The crystals were mixed with KBr in a ratio of approximately 1:100 as the sample for measurement. The sample was dried and ground into a fine powder and then pressed into a transparent sheet. Finally, the sheet was loaded into the sample chamber and the IR spectral data were recorded.

Hand-picked crystals were first placed on object slides and then Raman spectra were recorded by a 532 nm laser using a LABRAM HR Evolution spectrometer equipped with a CCD detector. The integration time was set to 5 seconds.

3.4 Second-harmonic Generation Measurements

The powder SHG response was studied by the Kurtz and Perry method [4] with Q-switch laser (2.09 μm, 3 Hz, 50 ns) of different particle sizes, including 38−55, 55−88, 88−105, 105−150, 150−200, and 200−250 μm. The $AgGaS_2$ crystal was ground and sieved into the same size range as the reference.

3.5 LDT Measurements

The LDTs of title compounds were evaluated on powder sample (150−200 μm) with a pulsed YAG laser (1.06 μm, 10 ns, 10 Hz). Similar size of $AgGaS_2$ is chosen as the reference. The judgment criterion is as follows: with increasing laser energy, the color

change of the powder sample is constantly observed by optical microscope to determine the damage threshold. To adjust different laser beams, an optical concave lens is added into the laser path. The damage spot is measured by the scale of optical microscope.

3.6 Thermal Properties

The thermogravimetric analysis (TG) was performed using a NETZSCH STA449F3 thermal analyzer and the title compound was heated from 50°C to 950°C at a rate of 8°C/min under air conditions.

3.7 Computational Description

In order to further investigate the relationship of structure–property, the electronic structure of title compound was studied by density functional theory (DFT) based on ab initio calculations.[5] The exchange-correlation potential was calculated using Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme.[6] To achieve energy convergence, a plane-wave basis set energy cutoff was 720 eV within normal-conserving pseudo-potential (NCP)[7]. As important parameters for NLO crystal, SHG coefficients were also calculated.[8] Owing to the discontinuity of exchange correlation energy, the experimental value is usually larger than that of calculated band gap. Thus, scissors operators are used to make the conduction bands agree with the experimental values.

4. Tables and Figures

Table S1. Crystal data and structure refinement for title compound.

Empirical formula	$[Sr_4Cl_2][Si_3S_9]$
formula weight	794.19
crystal system	Hexagonal
space group	$P6_3$
cell parameter a (Å)	9.4397(8)
cell parameter c (Å)	11.5555(11)
Z, V (Å^3) (Volume)	2, 891.73(17)
D_c (g/cm^3) (calculated density)	2.958
μ (mm^{-1}) (absorption coefficient)	13.429
goodness-of-fit on F^2	0.997
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0356, 0.0454
R_1, wR_2 (all data)	0.0272, 0.0437
absolute structure parameter	0.018(8)
largest diff. peak and hole (e·Å^{-3})	0.516, –0.438

[a] $R_1 = F_o - F_c / F_o$ and $wR_2 = [w (F_o^2 - F_c^2)^2 / wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma (F_o^2)$

Table S2. Link modes of SiS_4 units in 197 known thiosilicates.

Compounds	Space group	Link modes
$Na_2Si_2S_5$	*Cmcm*	Si_4S_{10}
$Cs_2ZnSi_3S_8$	*P*-1	1D chain
$Rb_2ZnSi_3S_8$	*P*-1	1D chain
Cu_2SiS_3	*Cc*	1D chain
$Cs_4Si_2S_6$	*C*2/*m*	Si_2S_6(edge-sharing)
$Rb_4Si_2S_6$	*C*2/*m*	Si_2S_6(edge-sharing)
Ag_2SiS_3	$P2_1/c$	Si_2S_6(edge-sharing)
$Li_2Mg_2Si_2S_6$	*P*31*m*	Si_2S_6(Si-Si)
$Cu_4NiSi_2S_7$	*C*2	Si_2S_7
Sr_2SiS_4	$P2_1/m$	SiS_4
$SrCu_2SiS_4$	$P3_121$	SiS_4
$SrNa_2SiS_4$	*R*3*c*	SiS_4
$SrLi_2SiS_4$	*I*4-2*m*	SiS_4
$SrAg_2SiS_4$	*I*4-2*m*	SiS_4
$EuCu_2SiS_4$	$P3_121$	SiS_4
Cu_2PbSiS_4	$P3_221$	SiS_4
Cu_2FeSiS_4	$Pmn2_1$	SiS_4
α-Cu_2ZnSiS_4	$Pmn2_1$	SiS_4
β-Cu_2ZnSiS_4	*Pn*	SiS_4
Cu_2MgSiS_4	$Pmn2_1$	SiS_4
Cu_2CdSiS_4	$Pmn2_1$	SiS_4
Cu_2HgSiS_4	$Pmn2_1$	SiS_4
Cu_2MnSiS_4	$Pmn2_1$	SiS_4
Cu_2CoSiS_4	*I*4-2*m*	SiS_4
Li_2CdSiS_4	$Pmn2_1$	SiS_4
Li_2HgSiS_4	$Pmn2_1$	SiS_4
Li_2ZnSiS_4	$Pna2_1$	SiS_4
Ag_2ZnSiS_4	*Pn*	SiS_4
Ag_2FeSiS_4	*Pc*	SiS_4
$Na_2Hg_3Si_2S_8$	*P*4-*c*2	SiS_4
Pb_2SiS_4	$P2_1/c$	SiS_4

$Ce_3(SiS_4)_2Br$	*C*2/*c*	SiS_4
$Ce_3(SiS_4)_2I$	*C*2/*c*	SiS_4
$Ce_3(SiS_4)_2Cl$	*C*2/*c*	SiS_4
$La_3(SiS_4)_2I$	*C*2/*c*	SiS_4
$(La_2Ce)(SiS_4)_2I$	*C*2/*c*	SiS_4
$(La_{2.2}Ce_{0.8})(SiS_4)_2I$	*C*2/*c*	SiS_4
$(La_{2.5}Ce_{0.5})(SiS_4)_2I$	*C*2/*c*	SiS_4
$(La_{2.8}Ce_{0.2})(SiS_4)_2I$	*C*2/*c*	SiS_4
$(La_{2.9}Ce_{0.1})(SiS_4)_2I$	*C*2/*c*	SiS_4
$(La_{2.97}Ce_{0.03})(SiS_4)_2I$	*C*2/*c*	SiS_4
$(La_{2.99}Ce_{0.01})(SiS_4)_2I$	*C*2/*c*	SiS_4
$Pr_3(SiS_4)_2I$	*C*2/*c*	SiS_4
$Nd_3(SiS_4)_2I$	*C*2/*c*	SiS_4
$Sm_3(SiS_4)_2I$	*C*2/*c*	SiS_4
$Tb_3(SiS_4)_2I$	*C*2/*c*	SiS_4
$Gd_3(SiS_4)_2Br$	*C*2/*c*	SiS_4
$La_3(SiS_4)_2Br$	*C*2/*c*	SiS_4
$Nd_3(SiS_4)_2Br$	*C*2/*c*	SiS_4
$Pr_3(SiS_4)_2Br$	*C*2/*c*	SiS_4
$Sm_3(SiS_4)_2Br$	*C*2/*c*	SiS_4
$La_3(SiS_4)_2Cl$	*C*2/*c*	SiS_4
$Ce_3(SiS_4)_2Cl$	*C*2/*c*	SiS_4
$Pr_3(SiS_4)_2Cl$	*C*2/*c*	SiS_4
$Ba_2(SiS_4)$	*Pnma*	SiS_4
$KCeSiS_4$	$P2_1$	SiS_4
$KYSiS_4$	$P2_1$	SiS_4
$KLaSiS_4$	$P2_1$	SiS_4
$KEuSiS_4$	$P2_1$	SiS_4
$KYbSiS_4$	$P2_1$	SiS_4
$KPrSiS_4$	$P2_1$	SiS_4
$KNdSiS_4$	$P2_1$	SiS_4
$CsPrSiS_4$	$P2_1$	SiS_4
$CsNdSiS_4$	$P2_1$	SiS_4

Na_4SiS_4	$P2_12_12_1$	SiS_4
$RbTbSiS_4$	$P2_1$	SiS_4
$RbHoSiS_4$	$P2_1$	SiS_4
$RbDySiS_4$	$P2_1$	SiS_4
$RbPrSiS_4$	$P2_1$	SiS_4
$RbGdSiS_4$	$P2_1$	SiS_4
$RbNdSiS_4$	$P2_1$	SiS_4
$CsDySiS_4$	$P2_1$	SiS_4
$CsErSiS_4$	$P2_1$	SiS_4
$CsEuSiS_4$	$P2_1$	SiS_4
$CsGdSiS_4$	$P2_1$	SiS_4
$CsHoSiS_4$	$P2_1$	SiS_4
$CsSmSiS_4$	$P2_1$	SiS_4
$CsTbSiS_4$	$P2_1$	SiS_4
$CsTmSiS_4$	$P2_1$	SiS_4
$RbEuSiS_4$	$P2_1$	SiS_4
$RbCeSiS_4$	*Pnma*	SiS_4
$CsLaSiS_4$	*Pnma*	SiS_4
$RbLaSiS_4$	*Pnma*	SiS_4
$CsCeSiS_4$	*Pnma*	SiS_4
$KLaSiS_4$	$P2_1/m$	SiS_4
$Ce_4(SiS_4)_3$	*R*3*c*	SiS_4
$BaLa_2Si_2S_8$	*R*-3*c*	SiS_4
$Ba(La_{0.94}Ce_{0.06})_2Si_2S_8$	*R*-3*c*	SiS_4
$CeDyPbSi_2S_8$	*R*-3*c*	SiS_4
$CeErPbSi_2S_8$	*R*-3*c*	SiS_4
$CeSmPbSi_2S_8$	*R*-3*c*	SiS_4
$CeTbPbSi_2S_8$	*R*-3*c*	SiS_4
$CePrPbSi_2S_8$	*R*-3*c*	SiS_4
$CeHoPbSi_2S_8$	*R*-3*c*	SiS_4
$LaCePbSi_2S_8$	*R*-3*c*	SiS_4
$LaErPbSi_2S_8$	*R*-3*c*	SiS_4
$LaDyPbSi_2S_8$	*R*-3*c*	SiS_4

$PrErPbSi_2S_8$	*R*-3*c*	SiS_4
$LaTbPbSi_2S_8$	*R*-3*c*	SiS_4
$PrDyPbSi_2S_8$	*R*-3*c*	SiS_4
$PrSmPbSi_2S_8$	*R*-3*c*	SiS_4
$PrYPbSi_2S_8$	*R*-3*c*	SiS_4
$PrTbPbSi_2S_8$	*R*-3*c*	SiS_4
$PrHoPbSi_2S_8$	*R*-3*c*	SiS_4
$LaYPbSi_2S_8$	*R*-3*c*	SiS_4
$La_{2.1}Pb_{0.9}(SiS_4)_2$	*R*-3*c*	SiS_4
Li_2PbSiS_4	*I*-42*m*	SiS_4
$Ce_2Pb(SiS_4)_2$	*R*-3*c*	SiS_4
$Pr_2Pb(SiS4)_2$	*R*-3*c*	SiS_4
$Nd_2Pb(SiS_4)_2$	*R*-3*c*	SiS_4
Tl_2PbSiS_4	$P2_1/c$	SiS_4
$RbSiBiS_4$	$P2_1/c$	SiS_4
$CsSiBiS_4$	$P2_1/c$	SiS_4
$KBiSiS_4$	$P2_1/c$	SiS_4
$SiSn_2S_4$	$P2_1/c$	SiS_4
$Pr_6Si_4S_{17}$	*P*-1	SiS_4
$Nd_6Si_4S_{17}$	*P*-1	SiS_4
$Sm_6Si_4S_{17}$	*P*-1	SiS_4
$Ce_6Si_4S_{17}$	*P*-1	SiS_4
Ce_2SiS_5	$P2_1$/c	SiS_4
Ba_3SiS_5	*Pnma*	SiS_4
Cu_8SiS_6	$Pmn2_1$	SiS_4
$Sm_3ClS_2(SiS_4)$	*Pnma*	SiS_4
$Nd_3ClS_2(SiS_4)$	*Pnma*	SiS_4
$Ag_8(SiS_4)S_2$	$Pna2_1$	SiS_4
Hg_4SiS_6	*Cc*	SiS_4
Cd_4SiS_6	*Cc*	SiS_4
$CeYPbSi_2S_8$	*R*-3*c*	SiS_4
$La_3Sb_{0.33}SiS_7$	$P6_3$	SiS_4
$Pr_3Sb_{0.33}SiS_7$	$P6_3$	SiS_4

$La_3Al_{0.44}Si_{0.93}S_7$	$P6_3$	SiS4
$Gd_3Cd_{0.50}SiS_7$	$P6_3$	SiS4
$Y_3Pd_{0.50}SiS_7$	$P6_3$	SiS4
$Al_{0.33}Sm_3SiS_7$	$P6_3$	SiS_4
$In_{0.33}Sm_3SiS_7$	$P6_3$	SiS_4
$Gd_3Cd_{0.5}SiS_7$	$P6_3$	SiS_4
$Sm_3Ag_{0.77}SiS_7$	$P6_3$	SiS_4
La_3CuSiS_7	$P6_3$	SiS_4
Y_3CuSiS_7	$P6_3$	SiS_4
Ce_3CuSiS_7	$P6_3$	SiS_4
Nd_3CuSiS_7	$P6_3$	SiS_4
Pr_3CuSiS_7	$P6_3$	SiS_4
Sm_3CuSiS_7	$P6_3$	SiS_4
Tb_3CuSiS_7	$P6_3$	SiS_4
Dy_3CuSiS_7	$P6_3$	SiS_4
Er_3CuSiS_7	$P6_3$	SiS_4
Ho_3CuSiS_7	$P6_3$	SiS_4
Gd_3CuSiS_7	$P6_3$	SiS_4
La_3AgSiS_7	$P6_3$	SiS_4
Ce_3AgSiS_7	$P6_3$	SiS_4
Nd_3AgSiS_7	$P6_3$	SiS_4
Pr_3AgSiS_7	$P6_3$	SiS_4
Sm_3AgSiS_7	$P6_3$	SiS_4
$La_3Ag_{0.9}SiS_7$	$P6_3$	SiS_4
$Ce_3Ag_{0.82}SiS_7$	$P6_3$	SiS_4
$Pr_3Ag_{0.85}SiS_7$	$P6_3$	SiS_4
$Nd_3Ag_{0.81}SiS_7$	$P6_3$	SiS_4
$La_3Cr_{0.5}SiS_7$	$P6_3$	SiS_4
$Y_3Cr_{0.5}SiS_7$	$P6_3$	SiS4
$La_3Cd_{0.5}SiS_7$	$P6_3$	SiS_4
$LaSmPbSi_2S_8$	*R*-3*c*	SiS_4
$LaHoPbSi_2S_8$	*R*-3*c*	SiS_4
$(Ag_{0.56}Li_{1.44})In_2(SiS_6)$	*Cc*	SiS_4

$(Ag_{0.88}Li_{1.12})In_2(SiS_6)$	*Cc*	SiS_4
$Li_2In_2SiS_6$	*Cc*	SiS_4
$Na_2In_2SiS_6$	*Cc*	SiS_4
$Cu_2In_2SiS_6$	*Cc*	SiS_4
$Ag_2In_2SiS_6$	*Cc*	SiS_4
$ZnY_6Si_2S_{14}$	$P6_3$	SiS_4
$Y_6MgSi_2S_{14}$	$P6_3$	SiS_4
$FeSm_6Si_2S_{14}$	$P6_3$	SiS_4
$La_6ZnSi2S_{14}$	$P6_3$	SiS_4
$La_6MnSi_2S_{14}$	$P6_3$	SiS_4
$Ce_6MnSi_2S_{14}$	$P6_3$	SiS_4
$La_6In_{0.67}Si_2S_{14}$	$P6_3$	SiS_4
$La_6MgSi_2S_{14}$	$P6_3$	SiS_4
$La_6NiSi_2S_{14}$	$P6_3$	SiS_4
$La_6Sn_{0.5}Si_2S_{14}$	$P6_3$	SiS_4
$La_6CoSi_2S_{14}$	$P6_3$	SiS_4
$Dy_6MnSi_2S_{14}$	$P6_3$	SiS_4
$Er_6MnS_{14}Si_2$	$P6_3$	SiS_4
$Y_6FeSi_2S_{14}$	$P6_3$	SiS_4
$Gd_6MnSi_2S_{14}$	$P6_3$	SiS_4
$Nd_6MnSi_2S_{14}$	$P6_3$	SiS_4
$Pr_6MnSi_2S_{14}$	$P6_3$	SiS_4
$Sm_6MnSi_2S_{14}$	$P6_3$	SiS_4
$Tm_6MnSi_2S_{14}$	$P6_3$	SiS_4
$Y_6MnSi_2S_{14}$	$P6_3$	SiS_4
$La_6Cu_2(SiS_4)_2S_6$	$P6_3$	SiS_4
$La_6FeSi_2S_{14}$	$P6_3$	SiS_4
$La_6PdSi_2S_{14}$	$P6_3$	SiS_4
$NaY_3S_3(SiS_4)$	$P6_3$	SiS_4
$Gd_3(CuS_3)(SiS_4)$	$P6_3$	SiS_4
$CuCe_3S_3(SiS_4)$	$P6_3$	SiS_4
$NaSm_3S_3(SiS_4)$	$P6_3$	SiS_4
$Ba_8Si_2US_{14}$	$C2/m$	SiS_4

Table S3. The optical band gap and SHG response of the reported IR NLO chalcohalides (E_g > 3.0 eV).

Compounds	E_g**(eV)**	d_{ij} **(×AGS)**	**LDT(×AGS)**	**PM/NPM**	**Ref.**
$[Sr_4Cl_2][Si_3S_9]$	**4.22**	**1.2**	**12**	**PM**	**This work**
$Li[LiCs_2Cl][Ga_3S_6]$	4.18	0.7	4.1	PM	[9]
$[CsBa_3Cl_2][Ga_5S_{10}]$	3.96	0.9	6.7	PM	[10]
$[RbBa_3Cl_2][Ga_5S_{10}]$	3.95	0.93	6.5	PM	[10]
$[KBa_3Cl_2][Ga_5S_{10}]$	3.93	0.95	6.3	PM	[10]
$[Ba_4Cl_2][ZnGa_4S_{10}]$	3.85	1.1	51	PM	[11]
$K_2Ba_3Ge_3S_9Cl_2$	3.69	0.34	28.8	N/A	[12]
$[Rb_3Cl][Ga_3PS_8]$	3.65	1.1	37	PM	[13]
$[K_3Cl][Ga_3PS_8]$	3.6	1	39	PM	[13]
$[KBa_4Cl][Ge_3S_{10}]$	3.57	0.82	N/A	NPM	[14]
$[NaSr_4Cl][Ge_3S_{10}]$	3.54	1.08	N/A	NPM	[14]
$[KSr_4Cl][Ge_3S_{10}]$	3.51	0.91	N/A	NPM	[14]
$NaBa_4Ge_3S_{10}Cl$	3.49	0.33	20	N/A	[15]
$[CsBa_2Cl][Ga_4S_8]$	3.35	0.9-1.0	11-12	PM	[16]
$[RbBa_2Cl][Ga_4S_8]$	3.3	0.9-1.0	11-12	PM	[16]
$[KBa_3Cl_2][Ga_5Se_{10}]$	3.25	0.9	9.7	NPM	[17]
$[K_4Cl][CdGa_9S_{16}]$	3.14	0.9	22.6	PM	[18]
$[Ba_4Cl_2][ZnGa_4Se_{10}]$	3.08	1.6	17	NPM	[19]
$CsHg_3P_2S_8Cl$	3	0.8	N/A	PM	[20]

*AGS = $AgGaS_2$

Table S4. LDTs of title compound and $AgGaS_2$ (as the reference).

Compounds	damage energy (mJ)	spot diameter (mm)	LDT (MW/cm^2)	LDT (× AGS)*
$AgGaS_2$	0.92	0.5	4.69	1
$[Sr_4Cl_2][Si_3S_9]$	10.70	0.5	54.49	~12

*AGS = $AgGaS_2$

Table S5. Dipole moment of SiS_4 in the $[Sr_4Cl_2][Si_3S_9]$.

Dipole Moment					
Unit	***x*(a)**	***y*(b)**	***z*(c)**	**Magnitude**	
				Debye	**$\times 10^{-4}$esu·cm/Å^3**
$[Sr_4Cl_2][Si_3S_9]$					
SiS_4	0.00	0.00	13.20	13.20	0.03

Table S6. Property comparison of the $[Ae_4X_2][M^{IV}_3Q_9]$ system.

Compounds	**Space group**	E_g**(eV)**	d_{ij}**(× AGS)**	**LDT(× AGS)**	**Ref.**
$[Sr_4Cl_2][Si_3S_9]$	$P6_3$	4.22	1.2	12	**This work**
$Ba_4Ge_3S_9Cl_2$	$P6_3$	2.91	2.4	N/A	[21]
$Ba_4Si_3Se_9Cl_2$	$P6_3$	1.76	0.5	N/A	[21]
$Ba_4Ge_3Se9Cl_2$	$P6_3$	1.89	0.5	N/A	[21]
$Ba_4Si_3Se_9Br_2$	$P6_3$	2.96	3.2	N/A	[22]
$Ba_4Ge_3Se_9Br_2$	$P6_3$	2.60	3.5	N/A	[22]

*AGS = $AgGaS_2$

Table S7. Property comparison of the reported NLO chalcohalides.

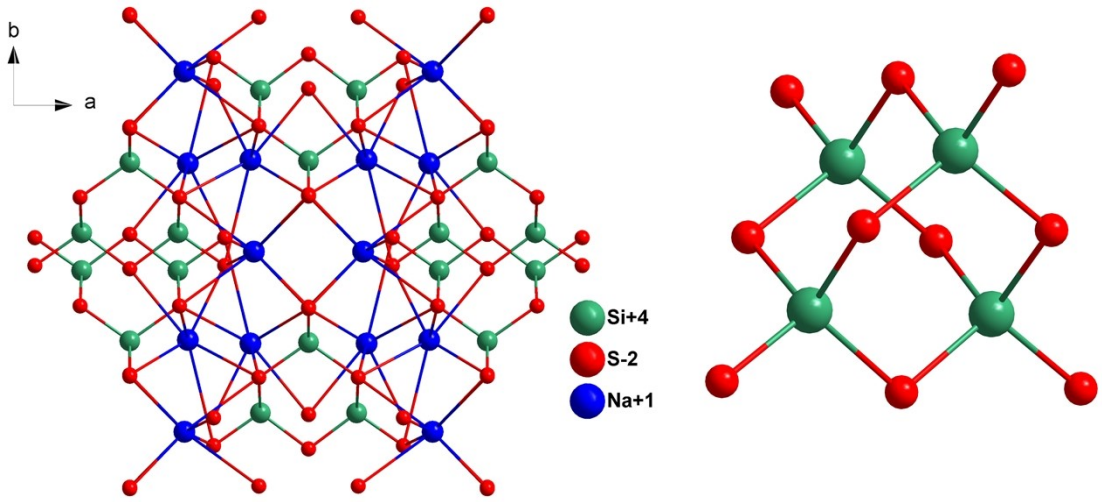
No.	Compounds	E_g(eV)	d_{ij} (×AGS)	LDT(×AGS)	PM/NPM	Ref.
1	$Li[LiCs_2Cl][Ga_3S_6]$	4.18	0.7	4.1	PM	[9]
2	$[CsBa_3Cl_2][Ga_5S_{10}]$	3.96	0.9	6.7	PM	[10]
3	$[RbBa_3Cl_2][Ga_5S_{10}]$	3.95	0.93	6.5	PM	[10]
4	$[KBa_3Cl_2][Ga_5S_{10}]$	3.93	0.95	6.3	PM	[10]
5	$[Ba_4Cl_2][ZnGa_4S_{10}]$	3.85	1.1	51	PM	[11]
6	$K_2Ba_3Ge_3S_9Cl_2$	3.69	0.34	28.8	N/A	[12]
7	$[Rb_3Cl][Ga_3PS_8]$	3.65	1.1	37	PM	[13]
8	$[K_3Cl][Ga_3PS_8]$	3.6	1	39	PM	[13]
9	$[KBa_4Cl][Ge_3S_{10}]$	3.57	0.82	N/A	NPM	[14]
10	$[NaSr_4Cl][Ge_3S_{10}]$	3.54	1.08	N/A	NPM	[14]
11	$[KSr_4Cl][Ge_3S_{10}]$	3.51	0.91	N/A	NPM	[14]
12	$NaBa_4Ge_3S_{10}Cl$	3.49	0.33	20	N/A	[15]
13	$[CsBa_2Cl][Ga_4S_8]$	3.35	0.9-1.0	11-12	PM	[16]
14	$[RbBa_2Cl][Ga_4S_8]$	3.3	0.9-1.0	11-12	PM	[16]
15	$[KBa_3Cl_2][Ga_5Se_{10}]$	3.25	0.9	9.7	NPM	[17]
16	$[K_4Cl][CdGa_9S_{16}]$	3.14	0.9	22.6	PM	[18]
17	$[Ba_4Cl_2][ZnGa_4Se_{10}]$	3.08	1.6	17	NPM	[19]
18	$CsHg_3P_2S_8Cl$	3	0.8	N/A	PM	[20]
19	$[Ba_4Cl_2][HgGa_4S_{10}]$	2.95	1.5	15	N/A	[23]
20	$Ba_4Ge_3S_9Cl_2$	2.91	2.4	N/A	NPM	[21]
21	$Ag_5PS_4Cl_2$	2.71	2.5	3.8	PM	[24]
22	$[Rb_4Cl][Cd_{11}In_9S_{26}]$	2.32	0.23	4.9	N/A	[25]
23	$La_6Cd_{0.75}Ga_2S_{11.5}Cl_{2.5}$	2.28	0.8	N/A	N/A	[26]
24	Cu_6PS_5Cl	2.22	2	N/A	N/A	[27]
25	Ag_6PS_5Cl	2.01	2.7	N/A	N/A	[27]
26	$[K_4Cl][CdGa_9Se_{16}]$	1.72	2.4	N/A	PM	[18]
27	$Ba_4Ge_3Se_9Cl_2$	1.89	1	N/A	NPM	[21]
28	$Ba_4Si_3Se_9Cl_2$	1.76	1	N/A	NPM	[21]
29	$La_6Cd_{0.75}Ga_2Se_{11.5}Cl_{2.5}$	1.65	0.1	N/A	N/A	[26]

*AGS = $AgGaS_2$

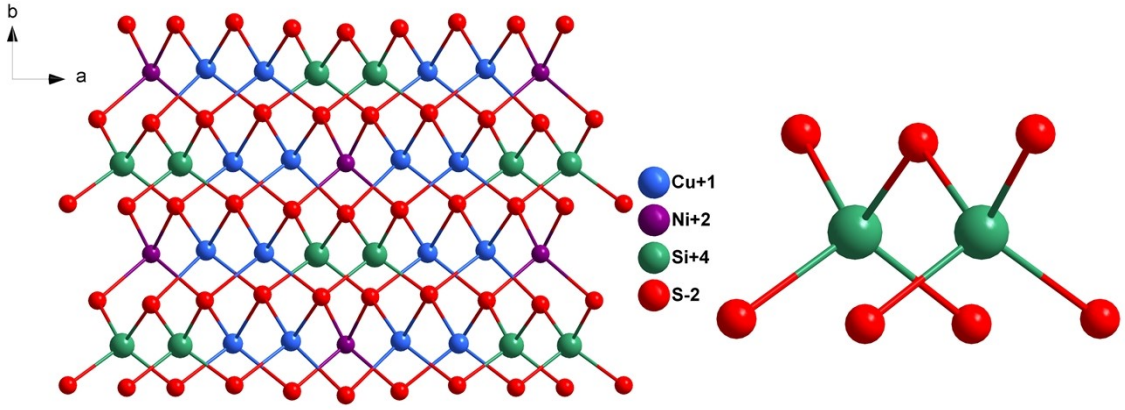
Table S8. Property comparison of the reported NLO thiosilicates.

No.	Compounds	E_g(eV)	d_{ij}(×AGS)	LDT(×AGS)	PM/NPM	Ref.
1	$SrLi_2SiS_4$	3.94	0.4	21	PM	[28]
2	Li_2ZnSiS_4	3.9	1.1	10	PM	[29]
3	$SrNa_2SiS_4$	3.87	0.4	17	PM	[28]
4	Li_2CdSiS_4	3.76	1	N/A	PM	[30]
5	$BaGa_2SiS_6$	3.75	1	N/A	PM	[31]
6	$Li_2In_2SiS_6$	3.61	1	N/A	N/A	[32]
7	β-Cu_2ZnSiS_4	3.2	1.2	N/A	N/A	[33]
8	$SrCu_2SiS_4$	3.04	0.78	8	PM	[28]
9	α-Cu_2ZnSiS_4	3	1.2	N/A	N/A	[33]
10	$Na_2Hg_3Si_2S_8$	2.86	1.3	4.5	PM	[34]
11	Cd_4SiS_6	2.75	1.3	N/A	N/A	[35]
12	Li_2HgSiS_4	2.68	0.8	3	NPM	[36]
13	$Na_2In_2SiS_6$	2.47	4.3	6.9	PM	[37]
14	$SrAg_2SiS_4$	2.08	0.6	N/A	N/A	[38]
15	$La_6PdSi_2S_{14}$	1.41	3.7	3	PM	[39]

*AGS = $AgGaS_2$



(a)



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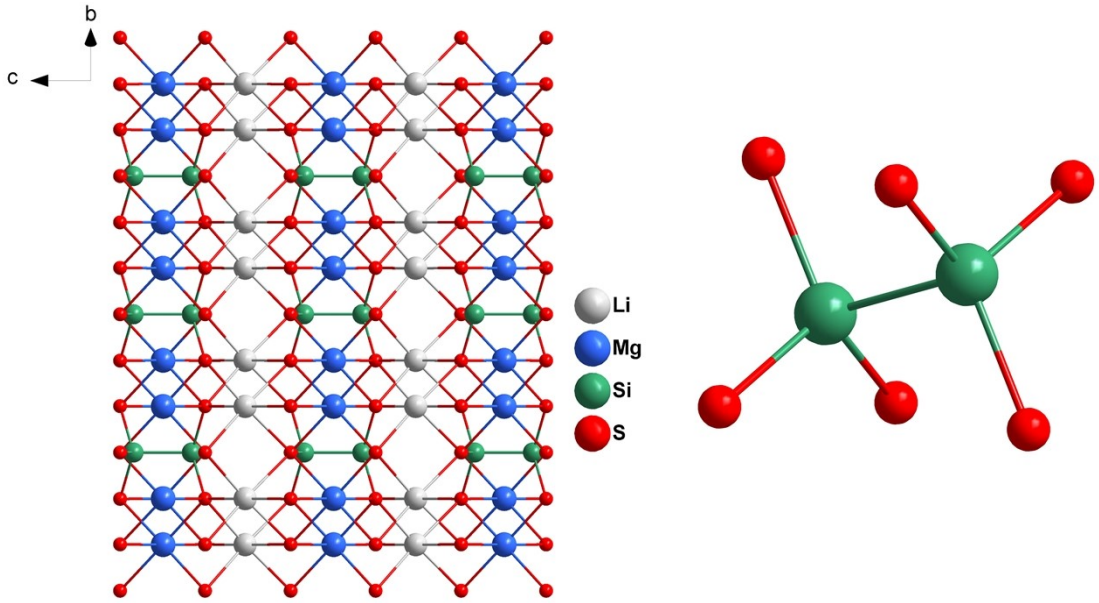

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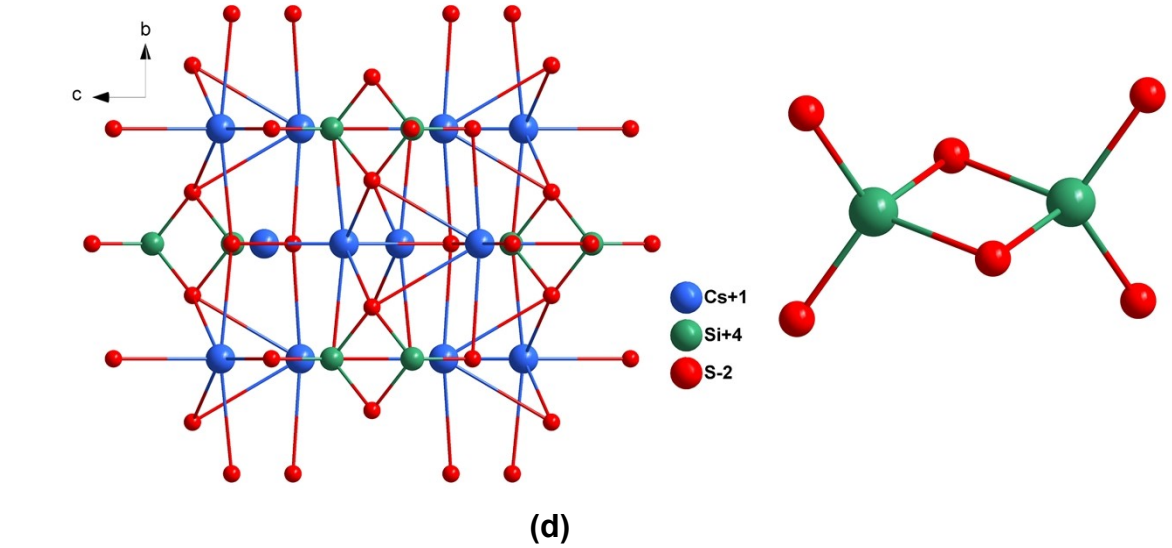

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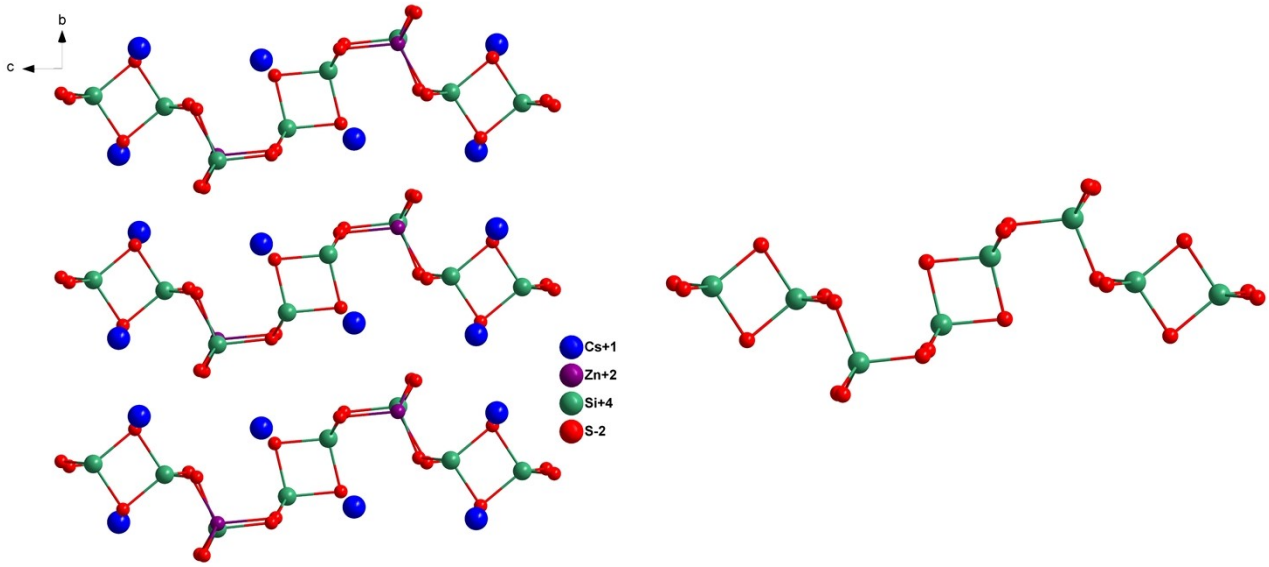


(e)

Fig. S1. The whole structures and link modes of SiS_4 units in (a) $Na_2Si_2S_5$; (b) $Cu_4NiSi_2S_7$; (c) $Li_2MgSi_2S_6$; (d) $Cs_4Si_2S_6$ and (e) $Cs_2ZnSi_3S_8$.

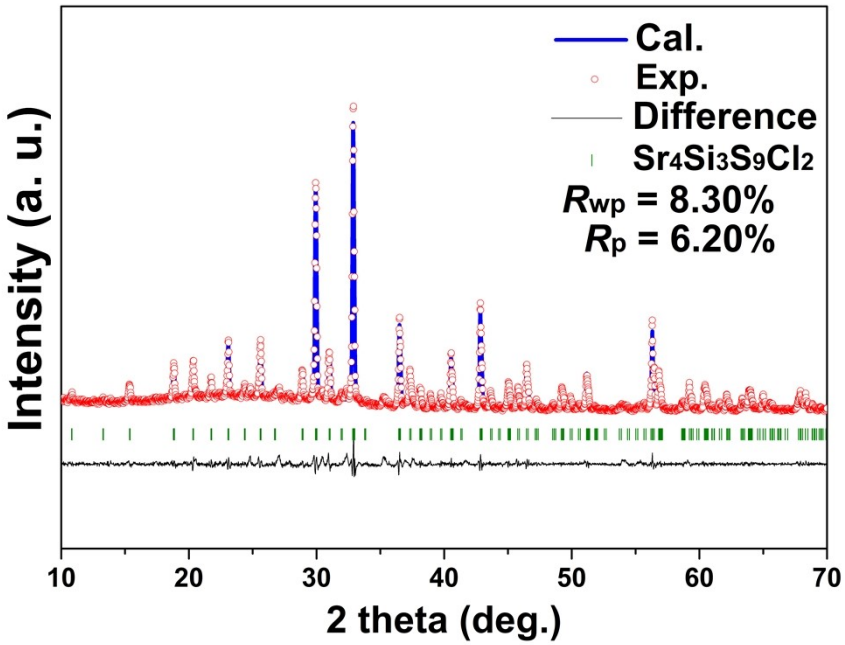
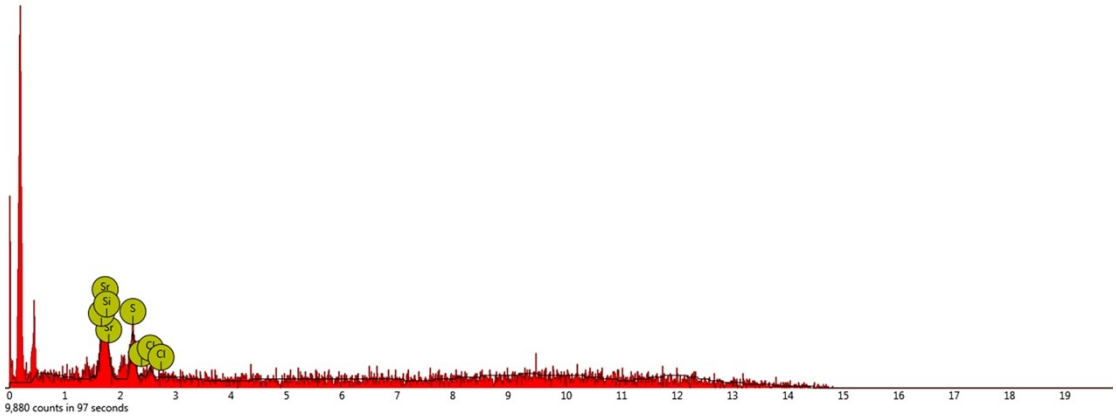


Fig. S2. Powder XRD patterns of title compound.



Element	Weight%	Atomic%	Formula
Sr	42.38	20.99	4.198
Si	11.60	17.92	3.584
S	36.77	49.76	9.952
Cl	9.26	11.33	2.266

Formula:$Sr_{4.198}Si_{3.584}S_{9.952}Cl_{2.266}$

Fig. S3. The SEM-EDS diagram of $[Sr_4Cl_2][Si_3S_9]$.

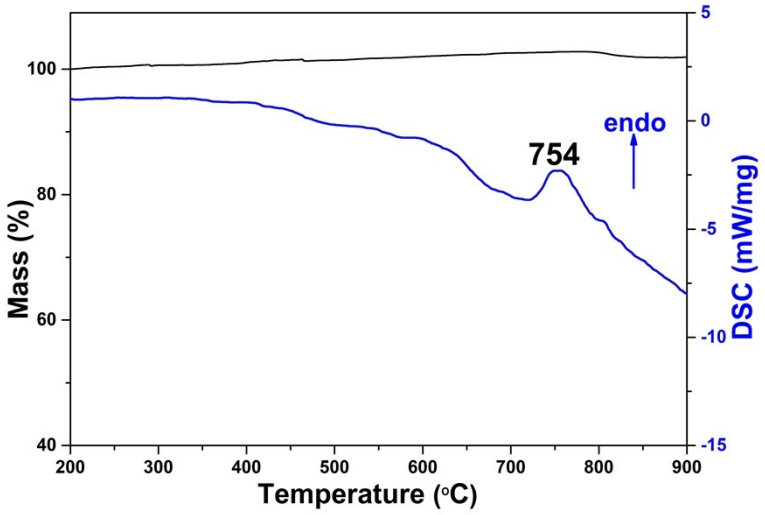


Fig. S4. The TG and DSC curves of $[Sr_4Cl_2][Si_3S_9]$.

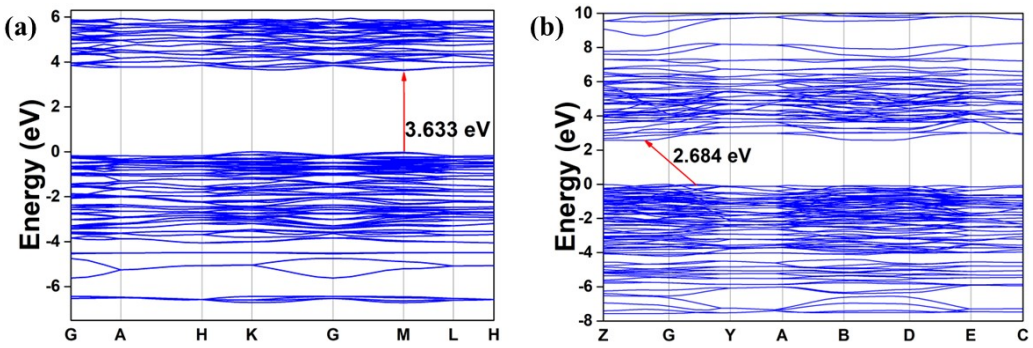


Fig. S5. Band structures of (a) $[Sr_4Cl_2][Si_3S_9]$ and (b) Sr_2SiS_4.

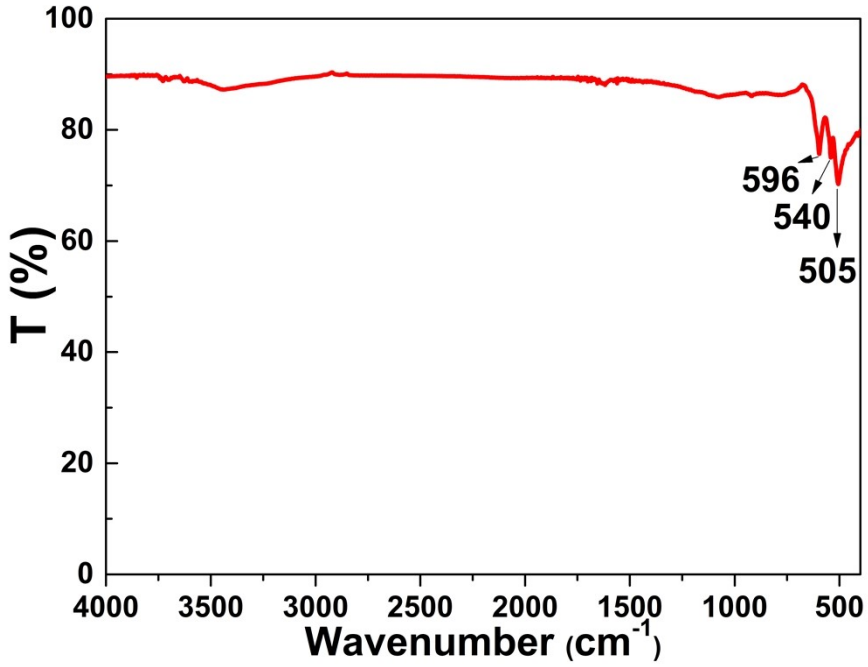


Fig. S6. IR spectrum of $[Sr_4Cl_2][Si_3S_9]$.

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