

**New family of quaternary thiosilicates  $\text{SrA}_2\text{SiS}_4$  (A = Li, Na, Cu) as promising  
infrared nonlinear optical crystals**

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## 1. Synthesis of Title Compounds

All the binary sulfides as initial reagents including SrS, Ag<sub>2</sub>S, Cu<sub>2</sub>S, Li<sub>2</sub>S and SiS<sub>2</sub>, with high purity ( $\geq 99.9\%$ ) were purchased from the Beijing Hawk Science & Technology Co., Ltd without further purification. The whole preparation process is completed in an Ar-filled glovebox because of their instability in the air. In order to prepare the targeted products, we have chosen many of different ratio of raw materials and the high yield was appeared with the ratio of SrS : A<sub>2</sub>S : SiS<sub>2</sub> at 1:3:1. Their spontaneous crystallization were completed in the vacuum-sealed silica tubes. Firstly, the tube was heated to 600 °C in 30 h and kept at this temperature for about 100 h, then quickly down to room temperature. The above products were ground and then loaded into the vacuum-sealed silica tubes. They were further sintered again at 1000 °C for 10 days and slowly down to room temperature with 5°C/h. Finally, many high quality colorless crystals with millimetre-level were found in the tubes after washed with N, N-dimethylformamide (DMF) solvent and they are stable in the air within several weeks.

## 2. Structural Refinement and Crystal Data

Selected high-quality crystals were used for data collections on a Bruker SMART APEX II 4K CCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296 K. The crystal structures were solved by direct method and refined using the SHELXTL program package.<sup>[1]</sup> Multi-scan method was used for absorption correction.<sup>[2]</sup> Rational anisotropic thermal parameters for all atoms were obtained by the anisotropic refinement and extinction correction. PLATON was also used to check the final structures and no other symmetries were found.<sup>[3]</sup> Detail refinement parameters and data were shown 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 K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature. The  $2\theta$  range was  $10\text{--}70^\circ$  with a step size of  $0.02^\circ$  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  $200\text{--}2600 \text{ nm}$  at room temperature.

#### **3.3 Second-harmonic Generation Measurement**

Through the Kurtz and Perry method,<sup>[4]</sup> powder SHG responses of title compounds were investigated by a Q-switch  $2.09 \mu\text{m}$  laser with different particle sizes, including  $38\text{--}55$ ,  $55\text{--}88$ ,  $88\text{--}105$ ,  $105\text{--}150$ ,  $150\text{--}200$ , and  $200\text{--}250 \mu\text{m}$ . The AgGaS<sub>2</sub> crystal was ground and sieved into the same size range as the reference.

#### **3.4 LDT Measurement**

The LDTs of title compounds were evaluated on powder sample ( $150\text{--}200 \mu\text{m}$ ) with a pulsed YAG laser. Similar size of AgGaS<sub>2</sub> is chosen as the reference. 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.

#### **3.5 Computational Description**

In order to further investigate the relationship of structure–property, the electronic structures of title compounds were studied by density functional theory (DFT) based on ab initio calculations.<sup>[5]</sup> The exchange-correlation potential was calculated using Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme.<sup>[6]</sup> The following orbital electrons were treated as valence electrons, Li:  $2s^1$ , Na:  $2p^6 3s^1$ , Cu:  $4p^6 4d^{10} 5s^1$ , Sr:  $4s^2 4p^6 5s^2$ , Si:  $3s^2 3p^2$ , S:  $3s^2 3p^4$ . To achieve energy convergence, a plane-wave basis set energy cutoff was  $720 \text{ eV}$  within normal-conserving pseudo-potential (NCP)<sup>[7]</sup>. As important parameters for NLO crystals, SHG coefficients were also calculated with suitable scissors operators.<sup>[8]</sup>

#### 4. Tables and Figures

**Table S1.** Crystal data and structure refinement for title compounds.

**Table S2.** Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for title compounds.

**Table S3** Structural comparison in  $I_2$ -AE- $M^{IV}$ - $Q_4$  ( $I$  = monovalent cations: Cu, Ag, Na, Li; AE = Ba, Sr;  $M^{IV}$  = Si, Ge, Sn; Q = S, Se) system.

**Table S4.** Distortion degree  $\Delta d = 2 - (c/a)$  in the Li-based CL sulfides.

**Table S5.** LDTs of title compounds and AgGaS<sub>2</sub> (as the reference)

**Table S6.** Comparison on optical parameters of known sulfides in the  $I_2$ -AE- $M^{IV}$ - $S_4$  system ( $I$  = Li, Na, Cu, Ag; AE = Ba, Sr;  $M^{IV}$  = Si, Ge, Sn).

**Figure S1.** SHG density of SrNa<sub>2</sub>SiS<sub>4</sub> (a), SrLi<sub>2</sub>SiS<sub>4</sub> (b) and SrCu<sub>2</sub>SiS<sub>4</sub> (c).

**Table S1.** Crystal data and structure refinement for title compounds.

Empirical formula	SrLi <sub>2</sub> SiS <sub>4</sub>	SrNa <sub>2</sub> SiS <sub>4</sub>	SrCu <sub>2</sub> SiS <sub>4</sub>
formula weight	257.83	289.93	371.03
crystal system	Tetragonal	Trigonal	Trigonal
space group	$\bar{I}42m$	$R3c$	$P3_12_1$
cell parameter $a$ (Å)	6.469(3)	23.486(3)	6.0710(3)
cell parameter $c$ (Å)	7.689(7)	6.8764(19)	15.139(2)
$Z, V$ (Å <sup>3</sup> ) (Volume)	2, 321.8(4)	18, 3284.7(13)	3, 483.22(8)
$D_c$ (g/cm <sup>3</sup> ) (calculated density)	2.661	2.638	3.825
$\mu$ (mm <sup>-1</sup> ) (absorption coefficient)	9.723	8.697	16.140
goodness-of-fit on $F^2$	0.711	1.084	0.833
$R_1, wR_2$ ( $I > 2\sigma(I)$ ) <sup>a</sup>	0.0132, 0.0283	0.0403, 0.1031	0.0224, 0.0364
$R_1, wR_2$ (all data)	0.0143, 0.0288	0.0507, 0.1084	0.0265, 0.0372
absolute structure parameter	0.009(8)	0.023(8)	0.010(13)
largest diff. peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	0.278, -0.188	1.727, -0.667	0.545, -0.442

<sup>[a]</sup> $R_1 = F_o - F_c / F_o$  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** Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for title compounds.

<b>SrLi<sub>2</sub>Si<sub>4</sub></b>					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>BVS</i>
Sr1	10000	10000	10000	10(8)	1.923
Si1	10000	10000	5000	8(0)	4.121
Li1	10000	5000	7500	23(2)	0.986
S1	8094(4)	8094(4)	6567(2)	10(8)	2.005
<b>GII (vu)</b>					<b>0.051</b>
<b>SrNa<sub>2</sub>Si<sub>4</sub></b>					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>BVS</i>
Sr1	4710(8)	6575(5)	-579(0)	19(7)	1.916
Na1	6615(2)	7945(2)	-1038(7)	21(3)	1.185
Na2	6890(4)	7301(4)	4052(1)	68(2)	0.885
Si1	5230(3)	6665(2)	4385(5)	7(5)	3.937
S1	5817(4)	6687(2)	-3204(4)	18(5)	1.968
S2	4391(5)	6736(0)	-4721(5)	19(1)	1.849
S3	4835(4)	5772(8)	2785(4)	18(5)	2.134
S4	5821(6)	7418(1)	2360(5)	29(7)	1.959
<b>GII (vu)</b>					<b>0.113</b>
<b>SrCu<sub>2</sub>Si<sub>4</sub></b>					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>BVS</i>
Sr1	0	4477(5)	1666(7)	10(6)	1.836
Si1	2819(3)	0	3333(3)	5(8)	4.077
Cu1	4067(2)	791(8)	773(3)	17(4)	1.079
S1	4796(2)	271(2)	2223(0)	8(5)	1.998
S2	2349(2)	3242(2)	3279(1)	8(8)	2.038
<b>GII (vu)</b>					<b>0.071</b>

GII can be derived from the bond valence concepts, which represents the tension of lattice parameters and is always used to evaluate the rationality of structure. The value of GII in a reliable structure should be limited at 0.05–0.2 in general. **As for title compounds, calculated GII values are 0.051–0.113 vu, which illustrates that their crystal structures are reasonable.**

**Table S3.** Structural comparison in  $I_2\text{-AE-M}^{\text{IV}}\text{-Q}_4$  ( $I$  = monovalent cations: Cu, Ag, Na, Li; AE = Ba, Sr;  $\text{M}^{\text{IV}}$  = Si, Ge, Sn; Q = S, Se) system.

compounds	Crystal system	Space group	compounds	Crystal system	Space group
BaAg <sub>2</sub> GeS <sub>4</sub>	tetragonal	$I\bar{4}2m$	BaAg <sub>2</sub> GeSe <sub>4</sub>	orthorhombic	$I222$
BaAg <sub>2</sub> SiSe <sub>4</sub>	tetragonal	$I\bar{4}2m$	BaAg <sub>2</sub> SnSe <sub>4</sub>	orthorhombic	$I222$
			BaAg <sub>2</sub> SnS <sub>4</sub>	orthorhombic	$I222$
BaCu <sub>2</sub> GeS <sub>4</sub>	trigonal	$P3_12_1$	BaCu <sub>2</sub> GeSe <sub>4</sub>	trigonal	$P3_12_1$
BaCu <sub>2</sub> SnS <sub>4</sub>	trigonal	$P3_22_1$	BaCu <sub>2</sub> SnSe <sub>4</sub>	orthorhombic	$Ama2$
			BaCu <sub>2</sub> SiSe <sub>4</sub>	trigonal	$P3_22_1$
BaNa <sub>2</sub> GeS <sub>4</sub>	trigonal	$R3c$	BaNa <sub>2</sub> GeSe <sub>4</sub>	trigonal	$R3c$
BaNa <sub>2</sub> SnS <sub>4</sub>	tetragonal	$I\bar{4}2d$	BaNa <sub>2</sub> SnSe <sub>4</sub>	trigonal	$R3c$
BaLi <sub>2</sub> GeS <sub>4</sub>	tetragonal	$I\bar{4}2m$	BaLi <sub>2</sub> GeSe <sub>4</sub>	tetragonal	$I\bar{4}2m$
BaLi <sub>2</sub> SnS <sub>4</sub>	tetragonal	$I\bar{4}2m$	BaLi <sub>2</sub> SnSe <sub>4</sub>	tetragonal	$I\bar{4}2m$
			BaLi <sub>2</sub> SiSe <sub>4</sub>	tetragonal	$I\bar{4}2m$
SrCu <sub>2</sub> GeS <sub>4</sub>	trigonal	$P3_2$	SrCu <sub>2</sub> GeSe <sub>4</sub>	orthorhombic	$Ama2$
SrCu <sub>2</sub> SnS <sub>4</sub>	trigonal	$P3_1$	SrCu <sub>2</sub> SnSe <sub>4</sub>	orthorhombic	$Ama2$
SrNa <sub>2</sub> GeS <sub>4</sub>	trigonal	$R3c$	SrLi <sub>2</sub> GeS <sub>4</sub>	tetragonal	$I\bar{4}2m$
SrNa <sub>2</sub> SnS <sub>4</sub>	trigonal	$R3c$	SrLi <sub>2</sub> SnS <sub>4</sub>	tetragonal	$I\bar{4}2m$
<b>SrNa<sub>2</sub>SiS<sub>4</sub></b>	<b>trigonal</b>	<b><math>R3c</math></b>	<b>SrCu<sub>2</sub>SiS<sub>4</sub></b>	<b>trigonal</b>	<b><math>P3_12_1</math></b>
<b>SrLi<sub>2</sub>SiS<sub>4</sub></b>	<b>tetragonal</b>	<b><math>I\bar{4}2m</math></b>			



**Table S4.** Distortion degree  $\Delta d = 2-(c/a)$  in the Li-based CL sulfides.

	PbLi <sub>2</sub> GeS <sub>4</sub>	EuLi <sub>2</sub> GeS <sub>4</sub>	BaLi <sub>2</sub> GeS <sub>4</sub>	SrLi <sub>2</sub> GeS <sub>4</sub>	BaLi <sub>2</sub> SnS <sub>4</sub>	SrLi <sub>2</sub> SnS <sub>4</sub>	SrLi <sub>2</sub> SiS <sub>4</sub>
$\Delta d$ (Å)	0.810	0.824	0.790	0.815	0.792	0.811	0.811

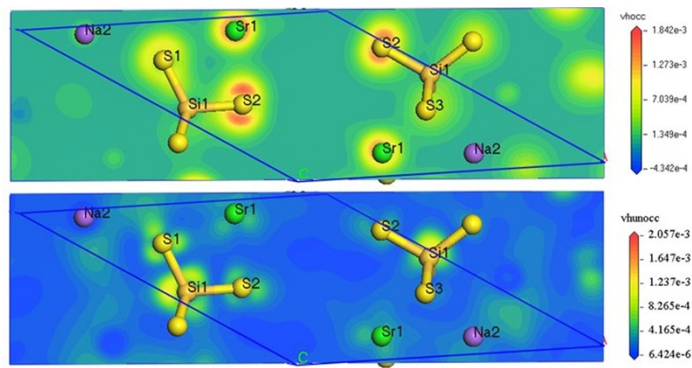
**Table S5.** LDTs of title compounds and AgGaS<sub>2</sub> (as the reference)

compounds	damage energy (mJ)	spot diameter (mm)	LDT (MW/cm <sup>2</sup> )	LDT (× AGS)*
AgGaS <sub>2</sub>	0.58	0.5	29.6	1
SrLi <sub>2</sub> SiS <sub>4</sub>	12.03	0.5	614.2	21
SrNa <sub>2</sub> SiS <sub>4</sub>	9.85	0.5	504	17
SrCu <sub>2</sub> SiS <sub>4</sub>	4.60	0.5	235	8
*AGS		=		AgGaS <sub>2</sub>

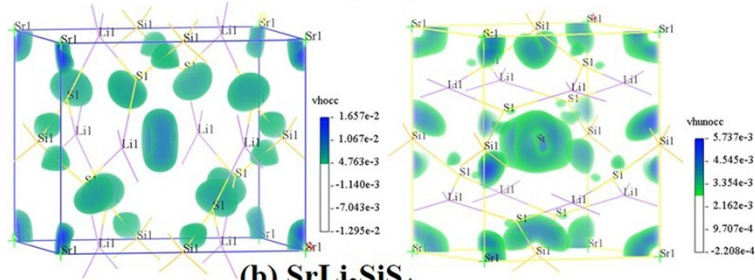
**Table S6.** Comparison on optical parameters of known compounds in the  $I_2$ -AE- $M^{IV}$ - $S_4$  system ( $I = \text{Li, Na, Cu, Ag}$ ; AE = Ba, Sr;  $M^{IV} = \text{Si, Ge, Sn}$ ).

	$E_g$ (eV)	$d_{ij}$ ( $\times$ AGS)	LDT ( $\times$ AGS)*
BaLi <sub>2</sub> GeS <sub>4</sub>	3.66	0.5	11
BaLi <sub>2</sub> SnS <sub>4</sub>	3.07	0.7	6.5
BaNa <sub>2</sub> GeS <sub>4</sub>	3.70	0.3	8
BaNa <sub>2</sub> SnS <sub>4</sub>	3.27	0.5	5
SrLi <sub>2</sub> GeS <sub>4</sub>	3.75	0.5	10
SrLi <sub>2</sub> SnS <sub>4</sub>	3.1	0.8	5
SrNa <sub>2</sub> GeS <sub>4</sub>	3.80	0.5	10
SrNa <sub>2</sub> SnS <sub>4</sub>	3.12	0.8	6
BaAg <sub>2</sub> GeS <sub>4</sub>	2.02	1.7	3.2
BaAg <sub>2</sub> SnS <sub>4</sub>	1.77	0.4	1.5
BaCu <sub>2</sub> GeS <sub>4</sub>	2.47	0.3	1
BaCu <sub>2</sub> SnS <sub>4</sub>	1.96	0.3	1
<b>SrLi<sub>2</sub>SiS<sub>4</sub></b>	<b>3.94</b>	<b>0.4</b>	<b>21</b>
<b>SrNa<sub>2</sub>SiS<sub>4</sub></b>	<b>3.87</b>	<b>0.4</b>	<b>17</b>
<b>SrCu<sub>2</sub>SiS<sub>4</sub></b>	<b>3.04</b>	<b>0.7</b>	<b>8</b>

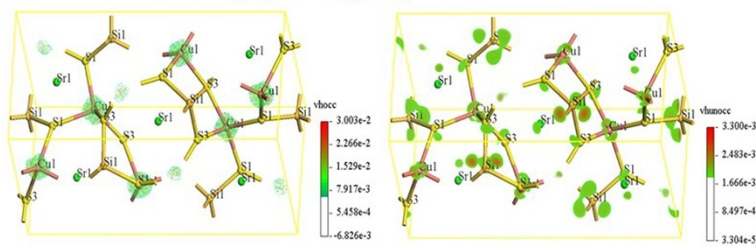
\*AGS = AgGaS<sub>2</sub>



(a)  $\text{SrNa}_2\text{SiS}_4$



(b)  $\text{SrLi}_2\text{SiS}_4$



(c)  $\text{SrCu}_2\text{SiS}_4$

**Figure S1.** SHG density of  $\text{SrNa}_2\text{SiS}_4$  (a),  $\text{SrLi}_2\text{SiS}_4$  (b) and  $\text{SrCu}_2\text{SiS}_4$  (c).

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