

**Concurrently wide bandgaps and good nonlinear optical responses in $A_2SrM^{IV}S_4$
($A = Li, Na$; $M^{IV} = Ge, Sn$) as new potential infrared nonlinear optical materials**

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1. Synthesis of Title Compounds

All the reagents were directly purchased from the Shanghai Aladdin Biochemistry Technology Co., Ltd. In view of the air-unstable Na metal and SrS powder, the whole preparation process is completed in an Ar-filled glovebox.

Li₂SrGeS₄ and Na₂SrGeS₄. A mixture of Li or Na (2 mmol, 0.014 or 0.046 g), SrS (1 mmol, 0.120 g), Ge (1 mmol, 0.072 g), and S (3 mmol, 0.096 g) was firstly loaded into a graphite crucible that avoids the reaction between alkali metals and silica tube, then put it into the silica tube and flame-sealed under 10⁻³ Pa. The tube was heated to 850 °C in 30 h and kept at this temperature for about 100 h, then slowly down to ambient temperature by 5 days. N, N-dimethylformamide (DMF) solvent was chosen to wash the products. Finally, many millimeter-level colorless crystals for Li₂SrGeS₄ and Na₂SrGeS₄ were found and stable in air after several months, respectively.

Li₂SrSnS₄ and Na₂SrSnS₄. The stoichiometric proportion and temperature controlling curve of title thiogermanates are similar to those of thioannates excepted for the maximum reaction temperature (~750 °C). After the reaction and carefully washed with DMF, pale-yellow crystals of Li₂SrSnS₄ and Na₂SrSnS₄ were appeared in the tubes and are stable in air.

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 α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. The crystal structures were solved by direct method and refined using the SHELXTL program package.^[1] Multi-scan method was used for absorption correction.^[2] 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.^[3] 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 α radiation ($\lambda = 1.5418 \text{ \AA}$) 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 IR spectra

IR spectra were performed on a Shimadzu IR Affinity-1 FTIR spectrometer in the wavenumber range from 400 to 4000 cm^{-1} . The powder samples were mixed with dried KBr and were then pressed into discs for measurement.

3.3 UV–Vis–Near-IR (NIR) Diffuse-Reflectance Spectra

Diffuse-reflectance spectra were measured by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 200–2600 nm at room temperature. The absorption spectra were converted from the reflection spectra *via* the Kubelka–Munk function.

3.4 Second-harmonic Generation Measurements

Through the Kurtz and Perry method,^[4] powder SHG responses of title compounds were investigated by a Q-switch laser (2.09 μm , 3 Hz, 50 ns) with different particle sizes, including 38–55, 55–88, 88–105, 105–150, 150–200, and 200–250 μm . The AgGaS₂ 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 AgGaS₂ 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 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.^[5] The exchange-correlation potential was calculated using Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme.^[6] The following orbital electrons were treated as valence electrons, Li: $2s^1$, Na: $2p^6 3s^1$, Sr: $4s^2 4p^6 5s^2$, Ge: $4s^2 4p^2$, Sn: $5s^2 5p^2$, S: $3s^2 3p^4$. To achieve energy convergence, a plane-wave basis set energy cutoff was 720 eV within normal-conserving pseudo-potential (NCP),^[7] and the Monkhorst–Pack scheme was $7 \times 7 \times 7$ in the Brillouin Zone (BZ) of the primitive cell are chosen for $\text{Li}_2\text{SrGeS}_4$ and $\text{Li}_2\text{SrSnS}_4$, besides, a plane-wave basis set energy cutoff of 770 eV and Monkhorst–Pack scheme of $4 \times 4 \times 4$ are chosen for $\text{Na}_2\text{SrGeS}_4$ and $\text{Na}_2\text{SrSnS}_4$. As important parameters for NLO crystals, 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. Figures and Tables

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

Table S2. Structures, $\Delta d=(d(\text{longest})-d(\text{shortest}))$, $\Delta\theta=(\theta(\text{largest})-\theta(\text{smallest}))$ for IS_4 tetrahedra in the $I_2\text{-AE-M}^{\text{IV}}\text{-S}_4$ (I = monovalent cations: Cu, Ag, Na, Li; AE = Ba, Sr; M^{IV} = Ge, Sn) system with different M^{IV} atoms.

Table S3. Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for $\text{Li}_2\text{SrGeS}_4$.

Table S4. Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for $\text{Li}_2\text{SrSnS}_4$.

Table S5. Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for $\text{Na}_2\text{SrGeS}_4$.

Table S6. Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for $\text{Na}_2\text{SrSnS}_4$.

Table S7. Calculated structural distortion degree $\Delta d = 2-(c/a)$ and interlayer spacing (d) with different divalent cations (M^{II}) in the Li-based compressed CL sulfides.

Table S8. LDTs of title compounds and AgGaS_2 (as the reference)

Table S9. Experimental optical parameters of 8 IR NLO compounds in the A-AE- M^{IV} -S system (A = Li, Na; AE = Ba, Sr; M^{IV} = Ge, Sn).

Figure S1. Powder XRD patterns of before and after melting for title compounds.

Figure S2. IR spectra of title compounds.

Figure S3. Band structures of title compounds: (a) $\text{Li}_2\text{SrGeS}_4$, (b) $\text{Li}_2\text{SrSnS}_4$, (c) $\text{Na}_2\text{SrGeS}_4$, (d) $\text{Na}_2\text{SrSnS}_4$.

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

Empirical formula	Li ₂ SrGeS ₄	Li ₂ SrSnS ₄	Na ₂ SrGeS ₄	Na ₂ SrSnS ₄
formula weight	302.33	348.43	334.43	380.53
crystal system	Tetragonal	Tetragonal	Trigonal	Trigonal
space group	$I\bar{4}2m$	$I\bar{4}2m$	$R3c$	$R3c$
cell parameter <i>a</i> (Å)	6.5420(15)	6.659(5)	23.5427(14)	23.838(4)
cell parameter <i>c</i> (Å)	7.751(3)	7.918(12)	6.9458(8)	7.115(2)
<i>Z</i> , <i>V</i> (Å ³) (Volume)	2, 331.73(17)	2, 351.1(6)	18, 3334.0(5)	18, 3501.7(13)
<i>D_c</i> (g/cm ³) (calculated density)	3.027	3.296	2.998	3.248
μ (mm ⁻¹) (absorption coefficient)	13.694	12.216	12.385	11.139
goodness-of-fit on <i>F</i> ²	1.295	0.802	1.088	1.101
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0225, 0.0563	0.0099, 0.0224	0.0318, 0.0895	0.0351, 0.0948
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0225, 0.0563	0.0100, 0.0244	0.0335, 0.0901	0.0363, 0.0955
absolute structure parameter	0.04(3)	0.015(16)	0.011(12)	0.019(19)
largest diff. peak and hole (e ⁻ ·Å ⁻³)	0.346, -1.392	0.267, -0.207	1.198, -0.768	1.401, -0.705

^[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. Structures, $\Delta d=(d(\text{longest})-d(\text{shortest}))$, $\Delta\theta=(\theta(\text{largest})-\theta(\text{smallest}))$ for IS_4 tetrahedra in the $I_2\text{-AE-M}^{\text{IV}}\text{-S}_4$ (I = monovalent cations: Cu, Ag, Na, Li; AE = Ba, Sr; M^{IV} = Ge, Sn) system with different M^{IV} atoms.

compounds	Crystal system	Space group	Structural change	$\Delta d(\text{\AA})/\Delta\theta(\text{deg.})$
$\text{Ag}_2\text{BaGeS}_4$	tetragonal	$I\bar{4}2m$	<i>Biaxial to Uniaxial</i>	0, 51.12
$\text{Ag}_2\text{BaSnS}_4$	orthorhombic	$I222$		0.297, 75.38
$\text{Cu}_2\text{BaGeS}_4$	trigonal	$P3_121$	<i>Mirror symmetry</i>	0.114, 39.09
$\text{Cu}_2\text{BaSnS}_4$	trigonal	$P3_221$		0.112, 38.27
$\text{Na}_2\text{BaGeS}_4$	trigonal	$R3c$	<i>Uniaxial to Uniaxial</i>	0.513, 92.52
$\text{Na}_2\text{BaSnS}_4$	tetragonal	$I\bar{4}2d$		0.193, 97.87
$\text{Cu}_2\text{SrGeS}_4$	trigonal	$P3_2$	<i>Mirror symmetry</i>	0.179, 40.24
$\text{Cu}_2\text{SrSnS}_4$	trigonal	$P3_1$		0.188, 37.83
$\text{Li}_2\text{BaGeS}_4$	tetragonal	$I\bar{4}2m$	<i>Isomorphism</i>	0, 51.28
$\text{Li}_2\text{BaSnS}_4$	tetragonal	$I\bar{4}2m$		0, 55.72
$\text{Na}_2\text{SrGeS}_4$	trigonal	$R3c$	<i>Isomorphism</i>	0.517, 105.56
$\text{Na}_2\text{SrSnS}_4$	trigonal	$R3c$		0.571, 103.40
$\text{Li}_2\text{SrGeS}_4$	tetragonal	$I\bar{4}2m$	<i>Isomorphism</i>	0, 53.58
$\text{Li}_2\text{SrSnS}_4$	tetragonal	$I\bar{4}2m$		0, 57.13

Table S3 Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for Li₂SrGeS₄.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>BVS</i>
Sr1	0	10000	0	10(1)	2.188
Ge1	0	10000	5000	6(1)	4.143
Li1	0	5000	2500	24(4)	0.973
S1	1957(2)	8044(2)	3377(2)	9(1)	2.069
GII (vu)					0.124

Table S4 Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for Li₂SrSnS₄.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>BVS</i>
Sr1	0	0	5000	12(1)	2.050
Sn1	0	0	10000	8(1)	4.199
Li1	0	5000	7500	22(2)	0.955
S1	2066(1)	2066(1)	8287(1)	12(1)	2.039
GII (vu)					0.107

Table S5 Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for Na₂SrGeS₄.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>BVS</i>
Sr(1)	6754(1)	1945(1)	1533(1)	17(1)	2.215
Na(1)	5393(2)	43(1)	1052(4)	17(1)	1.185
Na(2)	3544(3)	636(3)	7805(9)	72(2)	0.892
Ge(1)	4783(1)	1441(1)	1518(1)	12(1)	4.090
S(1)	5712(1)	2312(1)	2473(3)	16(1)	2.005
S(2)	4274(1)	1849(1)	-151(3)	16(1)	2.040
S(3)	4185(1)	829(1)	3967(3)	15(1)	2.099
S(4)	4960(1)	847(1)	-566(3)	28(1)	2.087
GII (vu)					0.122

Table S6 Atomic coordinates, isotropic displacement parameters, bond valence sums (BVS) and global instability index (GII) for Na₂SrSnS₄.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>BVS</i>
Sn(1)	38(1)	1900(1)	1175(1)	14(1)	4.171
Sr(1)	-1398(1)	95(1)	1190(2)	20(1)	2.021
Na(1)	1271(3)	3307(3)	-3258(8)	25(1)	1.137
Na(2)	-414(6)	2695(5)	4944(16)	85(3)	0.804
S(1)	76(2)	970(1)	91(5)	17(1)	1.883
S(2)	31(2)	2548(2)	-1346(4)	18(1)	2.102
S(3)	-931(2)	1456(2)	2988(5)	19(1)	2.178
S(4)	828(2)	2501(2)	3456(5)	30(1)	2.023
GII (vu)					0.134

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. While the value of GII is less than 0.05 vu (valence unit), the tension of structure is not proper, whereas the value of GII is larger than 0.2 vu, its structure is not stable. Thus, 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 0.107–0.134 vu, which illustrates that their crystal structures are reasonable.**

Table S7. Calculated structural distortion degree $\Delta d = 2-(c/a)$ and interlayer spacing (d) with different divalent cations (M^{II}) in the Li-based compressed CL sulfides.

Compound	a (Å)	c (Å)	c/a	Δd (Å)	d (Å)	radius of M^{II} (Å)
Li_2PbGeS_4	6.522	7.760	1.190	0.810	2.5205	1.43
Li_2EuGeS_4	6.544	7.696	1.176	0.824	2.5180	1.39
Li_2BaGeS_4	6.638	8.033	1.210	0.790	2.5497	1.56
Li_2SrGeS_4	6.542	7.751	1.185	0.815	2.5160	1.40
Li_2BaSnS_4	6.774	8.185	1.208	0.792	2.7696	1.56
Li_2SrSnS_4	6.659	7.918	1.189	0.811	2.7133	1.40

Table S8. LDTs of title compounds and AgGaS₂ (as the reference)

compounds	damage energy (mJ)	spot diameter (mm)	LDT (MW/cm ²)	LDT (× AGS)*
AgGaS ₂	0.58	0.5	29.6	1
Li ₂ SrGeS ₄	5.72	0.5	292	~10
Li ₂ SrSnS ₄	3.04	0.5	155	~5
Na ₂ SrGeS ₄	5.90	0.5	301	~10
Na ₂ SrSnS ₄	3.43	0.5	175	~6
*AGS		=		AgGaS ₂

Table S9. Experimental optical parameters of eight IR NLO compounds in the A-AE- M^{IV} -S system (A = Li, Na; AE = Ba, Sr; M^{IV} = Ge, Sn).

	E_g (eV)	d_{ij} (\times AGS)	LDT (\times AGS)*
Li_2BaGeS_4	3.66	0.5	11
Li_2BaSnS_4	3.07	0.7	6.5
Na_2BaGeS_4	3.70	0.3	8
Na_2BaSnS_4	3.27	0.5	5
Li_2SrGeS_4	3.75	0.5	10
Li_2SrSnS_4	3.1	0.8	5
Na_2SrGeS_4	3.80	0.5	10
Na_2SrSnS_4	3.12	0.8	6

*AGS = AgGaS₂

Based on the empirical rule of Miller, the NLO coefficient (d_{ij}) can be approximately reduced as the following equation:^[9]

$$d_{ij} = dp(108/E_g)^{3/2}$$

where d_{ij} is the NLO coefficient, d is a dimensionless constant depending only on crystal structure, p is the cation-anion bond dipole moment, E_g is the optical bandgap. From the above equation, it shows that d_{ij} has an inverse relationship with E_g and can be also determined by the structural distortion and arrangement of the NLO-active unit. Moreover, a high LDT commonly corresponds to a wide E_g in one material. Based on the critical demand (high LDT and large d_{ij}) of excellent IR NLO crystals, thus, two parameters (E_g and d_{ij}) should satisfy the balanced condition.

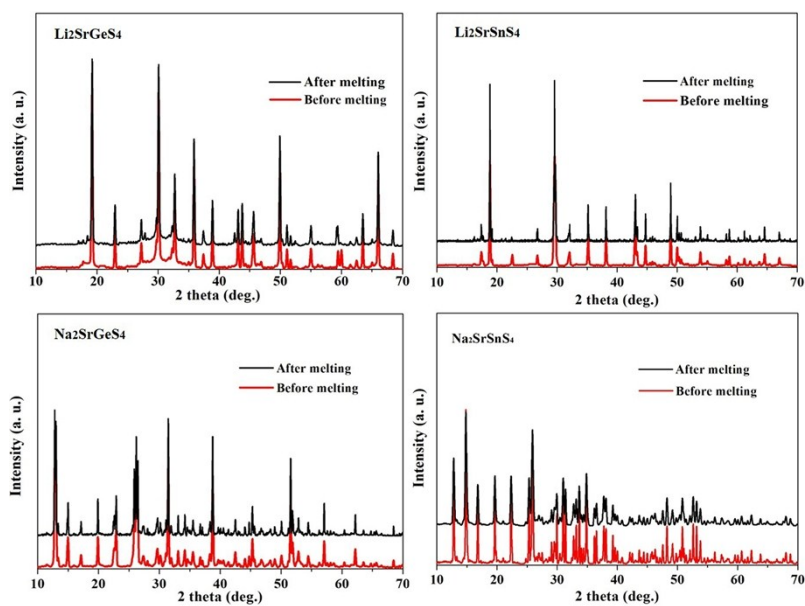


Figure S1. Powder XRD patterns of before and after melting for title compounds.

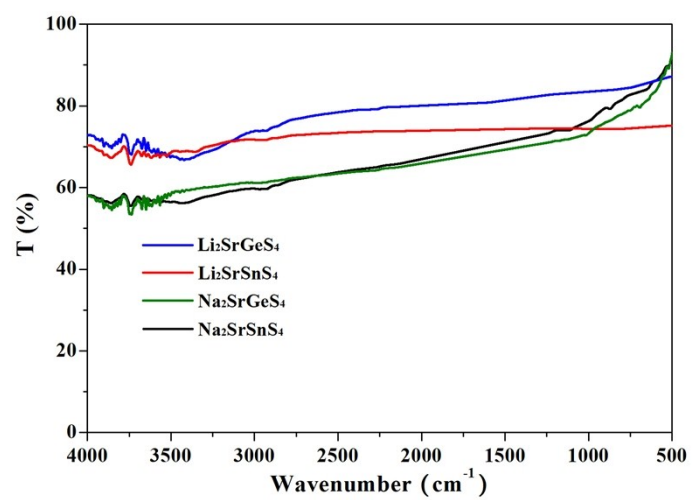


Figure S2. IR spectra of title compounds.

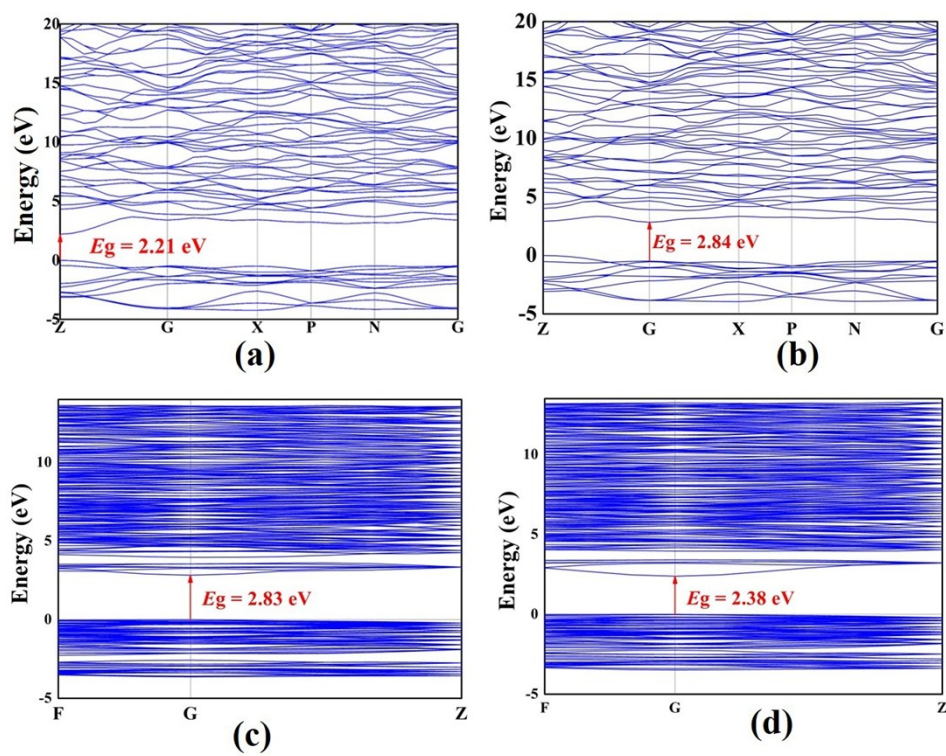


Figure S3. Band structures of title compounds: (a) $\text{Li}_2\text{SrGeS}_4$, (b) $\text{Li}_2\text{SrSnS}_4$, (c) $\text{Na}_2\text{SrGeS}_4$, (d) $\text{Na}_2\text{SrSnS}_4$.

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