Coordinated regulation on critical physiochemical performances activated from mixed tetrahedral anionic ligands in new series of $Sr_6A_4M_4S_{16}$ (A = Ag, Cu; M = Ge, Sn) nonlinear optical materials

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1. Synthesis of Title Compounds

All the binary sulfides as initial reagents including SrS, Ag_2S, Cu_2S, GeS_2 and SnS_2, with high purity (≥ 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 most of them are not stable in the air. Targeted products were prepared under stoichiometric ratio of raw materials 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 900 °C for 10 days and slowly down to room temperature with 5°C/h. Finally, many millimetre-level high-quality crystals with yellow color for thiogermanides or red color for thiostannates were found in the tubes after washed with N, N−dimethylformamide (DMF) solvent, respectively. They are stable in the air within several weeks. The polycrystalline samples for measurement are obtained with grinding the submillimeter single-crystals into powder samples.

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 Kα radiation (λ = 0.71073 Å) 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. Targeted crystals were refined by single-crystal X-ray crystallography with the exact formula according to the structural refinement of previously reported $Ba_6Ag_{2.67+4\delta}Sn_{4.33-\delta}S_{16-x}Se_x$ compounds.[3] And final formula are further determined by the assisting determination of EDX elemental analysis (ICONE plus, Shimadzu), for instance, $Sr_{6.2}Ag_{1.9}Cu_2Ge_{3.9}S_{15.6}$, $Sr_{5.8}Ag_{4.0}Ge_{4.4}S_{15.4}$, $Sr_{5.9}Ag_4Sn_{4.1}S_{15.2}$, and $Sr_{6.3}Cu_{3.7}Sn_{4.0}S_{16.2}$, which are in agreement with final formula. PLATON was also used to check the final structures and no other symmetries were found.[4] 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 Dandong Haoyuan DX-27mini 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 200−2000 nm at room temperature.

3.3 Raman Spectra

Hand-picked crystals were firstly put on an object slide, and then a LABRAM HR Evolution spectrometer equipped with a CCD detector by a 532 nm laser was used to record the Raman spectra. The integration time was set to be 5 s.

3.4 Second-harmonic Generation Measurement

Powder SHG responses of title compounds were investigated by a Q-switch 2.09 μm laser at 38-55 μm particle size. The $AgGaS_2$ crystal was ground and sieved into the same size range as the reference.

Based on the empirical rule of Miller,[5] SHG response can be approximately reduced as the following equation:

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

where d_{ij} is the SHG response, 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 can be concluded that d_{ij} has an inverse relationship with E_g and also been determined by the structural distortion and arrangement of the NLO-active units.

3.5 LDT Measurement

The LDTs of title compounds were evaluated on powder sample with a pulsed YAG laser. Similar size of $AgGaS_2$ 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.

4. Tables and Figures

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

Table S2. LDTs of title compounds and $AgGaS_2$ (as the reference).

Table S3. Comparison on optical parameters of cubic analogues and title compounds with $AgGaS_2$ (AGS) as the reference. *AGSe = $AgGaSe_2$, LN = $LiNbO_3$.

Fig. 1 EDX diagrams of title compounds.

Table S1 Structure refinement and crystal data for title compounds.

Empirical formula	$Sr_6Ag_2Cu_2Ge_4S_{16}$	$Sr_6Ag_4Ge_4S_{16}$	$Sr_6Cu_4Sn_4S_{16}$	$Sr_6Ag_4Sn_4S_{16}$
fw	1671.86	1760.52	1767.60	1944.92
crystal system		*cubic*		
space group		$I\bar{4}3d$		
$a = b = c$ (Å)	14.030(5)	14.0925(15)	13.982(3)	14.2219(4)
Z, V (Å^3)	4, 2762(3)	4, 2798.8(9)	4, 2733.7(15)	4, 2876.6(2)
D_c (g/cm^3)	4.021	4.178	4.295	4.491
μ (mm^{-1})	19.857	19.476	19.442	18.243
GOF on F^2	1.105	1.098	1.181	1.232
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0552, 0.1404	0.0181, 0.0469	0.0692, 0.2000	0.0414, 0.1303
R_1, wR_2 (all data)	0.0574, 0.1430	0.0183, 0.0470	0.0772, 0.2079	0.0453, 0.1330
absolute structure parameter	0.027(16)	0.00(2)	0.06(4)	0.05(6)
largest diff. peak and hole (e Å^{-3})	2.128, –1.214	0.408, –0.751	4.299, –2.369	1.802, –1.628

[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. LDTs of title compounds and $AgGaS_2$ (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
$Sr_6Ag_2Cu_2Ge_4S_{16}$	2.6	0.5	133	4.5
$Sr_6Ag_4Ge_4S_{16}$	2.6	0.5	133	4.5
$Sr_6Cu_4Sn_4S_{16}$	1.2	0.5	61	2.0
$Sr_6Ag_4Sn_4S_{16}$	1.2	0.5	61	2.0

*AGS = $AgGaS_2$

Table S3. Comparison on optical parameters of cubic analogues and title compounds with $AgGaS_2$ (AGS) as the reference. *AGSe = $AgGaSe_2$, LN = $LiNbO_3$.

	Z	*Site occupancy*	E_g (eV)	d_{ij} (AGS)
$Sr_6Ag_2Cu_2Ge_4S_{16}$	4	Ag/Cu (0.6667:0.3333)	2.76	1.1, @2090 nm
$Sr_6Ag_4Ge_4S_{16}$	4	Ag (0.6667+0.3333)	2.62	1.3, @2090 nm
$Sr_6Cu_4Sn_4S_{16}$	4	Cu (0.6667+0.3333)	2.07	1.5, @2090 nm
$Sr_6Ag_4Sn_4S_{16}$	4	Ag (0.6667+0.1667+0.1667)	1.94	2.0, @2090 nm
$Ba_6Ag_4Sn_4S_{16}$	4	Ag (0.739+0.140+0.156)	2.37	~AGSe, @800 nm
$Ba_6Ag_{3.92}Sn_{4.02}S_{16}$	4	Ag (0.747+0.135+0.149)	1.85	~AGSe, @800 nm
$Ba_6Ag_{3.21}Sn_{4.2}S_{16}$	4	Ag (0.857+0.071+0.069)	1.58	~AGSe, @800 nm
$Ba_6Ag_{3.57}Sn_{4.11}S_{9.53}Se_{6.47}$	4	Ag (0.780+0.111+0.112)	1.44	2.7×AGSe, @800 nm
$Ba_6Ag_{3.63}Sn_{4.09}Se_{16}$	4	Ag (0.762+0.107+0.133)	1.27	1.5×AGSe, @800 nm
$Na_2Ba_7Sn_4S_{16}$	4	Na/Ba (0.6667:0.3333)	2.5	1.0, @2090 nm
$Li_2Ba_7Sn_4S_{16}$	4	Li/Ba (0.6667:0.3333)	2.3	1.0, @2090 nm
$Na_2Ba_7Sn_4Se_{16}$	4	Na/Ba (0.6667:0.3333)	2.1	1.0, @2090 nm
$Li_2Ba_7Sn_4Se_{16}$	4	Li/Ba (0.6667:0.3333)	1.75	1.0, @2090 nm
$Ba_3CdSn_2S_8$	8	Cd (0.6667)	2.75	0.8, @2090 nm
$Ba_6Ag_2CdSn_4S_{16}$	4	Ag/Cd (0.6667:0.3333)	2.7	5.3, @2050 nm
$Ba_6Li_2CdSn_4S_{16}$	4	Li/Cd (0.6667:0.3333)	3.02	7.6, @2050 nm
$Ba_6Li_2ZnSn_4S_{16}$	4	Li/Zn (0.6667:0.3333)	3.3	5.2, @2050 nm
$Ba_6Ag_2ZnSn_4S_{16}$	4	Ag/Zn (0.6667:0.3333)	2.85	2.6, @2050 nm
$Ba_6Li_{2.67}Sn_{4.33}S_{16}$	4	Li/Sn (0.89:0.11)	2.23	1.45, @2050 nm
$Ag_{0.5}Pb_{1.75}GeS_4$	16	Ag1/Pb1= 0.6667:0.1667	1.83	-
$Ag_{0.5}Pb_{1.75}GeSe_4$	16	Ag1/Pb1= 0.6667:0.1667	1.51	-
$Cu_{0.5}Pb_{1.75}GeS_4$	16	Cu1/Pb1= 0.6667:0.1667	1.48	-
$Na_{0.5}Pb_{1.75}GeSe_4$	16	Na1/Pb1= 0.6667:0.1667	1.60	-
$Na_{1.5}Pb_{0.75}PSe_4$	16	Na1/Pb1=0.5:0.5 + 50%Na2	2.09	-
$Na_{0.5}Pb_{1.75}GeS_4$	16	Pb2/Na2= 0.167:0.333	2.08	7-8×LN, @3500 nm
$Li_{0.5}Pb_{1.75}GeS_4$	16	Pb2/Li2= 0.167:0.333	1.95	-

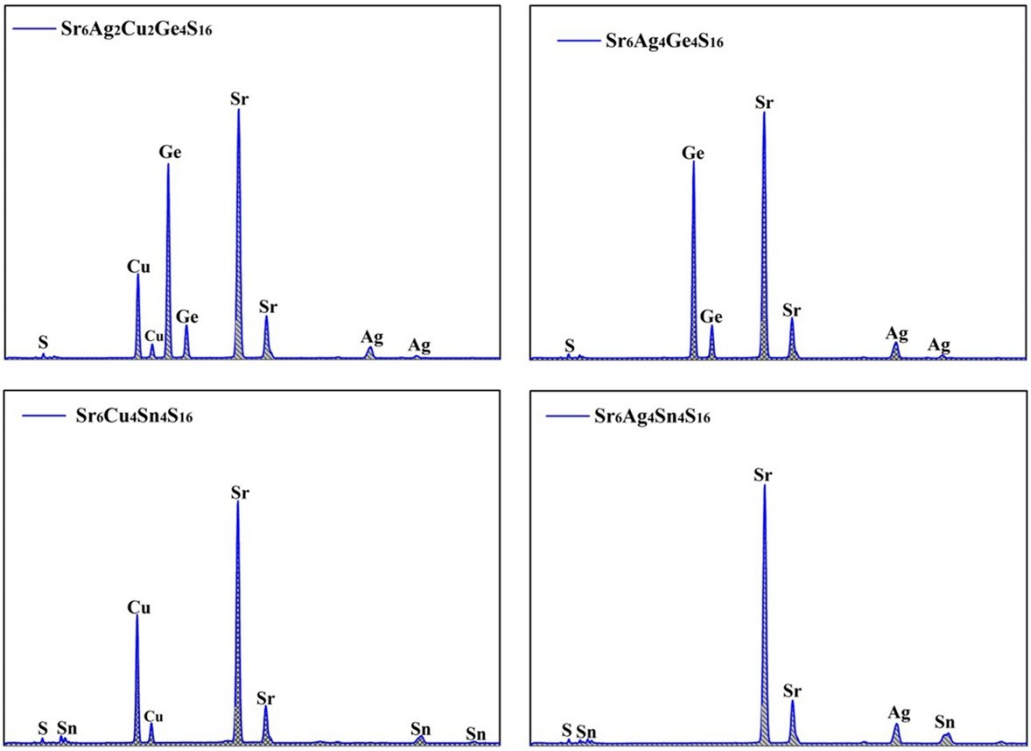

Fig. 1 EDX diagrams of title compounds.

5. References

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