Electronic Supplementary Information

$Sr_5ZnGa_6S_{15}$: a new quaternary non-centrosymmetric semiconductor with a 3D framework structure displaying excellent nonlinear optical performance

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1. Experimental Section

1.1 Materials and Instruments

All of the chemicals were obtained from commercial sources and used without further purification. Sr granule (3N), Zn shot (4N), Ga ingot (5N), and S powder (5N) were purchased from Alfa-Aesar. Energy dispersive X-ray (EDX, Oxford INCA) spectra were performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an X-ray spectroscope. Powder X-ray diffraction (PXRD) patterns of polycrystalline material were collected on a Rigaku Mini-Flex II powder diffractometer by using Cu-K_α radiation (λ = 1.5416 Å) in the range of 10–60° (2Θ) with a step size of 0.02°. The UV–Vis–NIR diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 950 UV–Vis spectrophotometer at room temperature in the wavelength range of 190−2500 nm and $BaSO_4$ was used as a standard (100% reflectance). The absorption

spectrum was calculated from the reflection spectra using the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, where α was the absorption coefficient, S was the scattering coefficient, and R was the reflectance.[1] The IR data was measured by a Perkin-Elmer Spectrum on an FT-IR spectrophotometer in the range of 2.5−25 μm. Powder sample was ground with KBr and pressed into a transparent pellet for the measurement. The thermal stability analyses were carried out with a NETZSCH STA 449C simultaneous analyser and heated from 300 to 1373 K at a heating rate of 10 K/min under a constant flow of nitrogen atmosphere.

The measurements of second-harmonic generation (SHG) were carried out on the sieved powder samples (a series of distinct particle size ranges: 30−46, 46−74, 74−106, 106−150, 150−210 μm) by using the modified Kurtz-NLO system with a 2050 nm Q-switched laser. Microcrystalline $AgGaS_2$ (AGS) served as the standard (AGS single crystals supplied from Anhui Institute of Optics and Fine Mechanics Chinese Academy of Sciences). The laser induced damage threshold (LIDT) was measured on powder samples (grounded crystals placed between two glass sheets), with the high-power laser source (1064 nm, 8 ns, 1 Hz). The title compound and AGS were sieved into the same particle size range (150–210 μm). The energy of the laser emission was gradually increased until the colour of the sample changed. The power of laser beam was measured by a Nova II sensor with a PE50-DIF-C energy sensor, and the size of the damage spot was measured by a Vernier caliper.

1.2 Syntheses

Title compound was first obtained as a by-product on attempting to synthesize "$SrZn_2Ga_2S_6$" in an evacuated fused silica tube with Sr/Zn/Ga/S in molar ratio 1:2:2:6 and total weight of ca. 500 mg was shown by single-crystal structure determination and elemental analysis to have the formula $Sr_5ZnGa_6S_{15}$ (**SZGS**). Subsequently, numerous explorations were made to get a pure phase by adjusting experimental conditions including loading ratio, starting reactant and annealing temperature, however, the highest yields of target products were about 85%. In a

typical reaction, the mixtures of Sr/Zn/Ga/S in molar ratio of 5:4:4:15 and total weight of 0.5g was heated to 1323K in a rate of 15K/h and kept at that temperature for 72 h, then cooled at a slow rate of 3K/h to 523 K and finally cooled to room temperature naturally. Light-orange and transparent crystals of **SZGS** with good quality were obtained, the by-products whitish powder of ZnS and SrS. Because of their distinguishable shapes and colour, we were easy to manually pick considerable numbers of crystals, and all properties reported here were measured on single crystals of **SZGS**. The purity of target product was confirmed by PXRD study, in which the experimental PXRD pattern is in good agreement with the simulated data based on the single-crystal XRD model (Fig. S1). The crystals of **SZGS** were stable in the air for several months.

1.3 Crystal Structure Determinations

High-optical quality title crystal was selected for the single-crystal XRD collection. All diffraction data were collected at room temperature on a Mercury 70 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The absorption correction was done and structures were solved by direct methods[2] and refined by full-matrix least-squares fitting on F^2 by *SHELX*–2014 program package.[3] All of the non-hydrogen atoms were refined with anisotropic thermal parameters and the coordinates were standardized using *STRUCTURE TIDY*.[4] As we know, it is difficult to distinguish Zn and Ga atoms by diffraction data because their X-ray scattering factors are similar, but the identity can be assigned according to the valence bond sum (VBS) method, $V_i = \sum S_{ij}$, where the bond valence (S_{ij}) is calculated by $S_{ij} = \exp[(R_{ij}–d_{ij})/0.37]$, d_{ij} is bond length between nearest neighboring atoms i–j, and R_{ij} is the tabulated parameter.[5] We therefore determine Zn and Ga atoms according to the VBS and valence balance. Similar assignment was found in $Pb_5ZnGa_6S_{15}$ compound.[6] The atomic coordinates and isotropic displacement parameters are listed in Table S2, and the selected bond distances are shown in Table S3.

2. Computational Sections

Theoretical studies were performed by the density functional theory (DFT)[7a] with the generalized gradient approximation (GGA)[7b] as implemented in the Vienna ab initio simulation package (VASP).[7c] The plane-wave basis with projector augmented wave (PAW)[7d,e] potentials was used to represent the core electrons. The plane-wave cut-off energy of 600 eV was chosen for all calculations and denser κ-point grids of 0.02 $Å^{-1}$ were carried out in the optical property calculations. For calculating the optical properties, scissors operators were applied for title compound and AGS. The second-order nonlinear susceptibility $\chi^{abc}(-2\omega,\omega,\omega)$ was calculated through the so-called length-gauge formalism.[8] The specific parameter settings as described in our previously reported papers.[9]

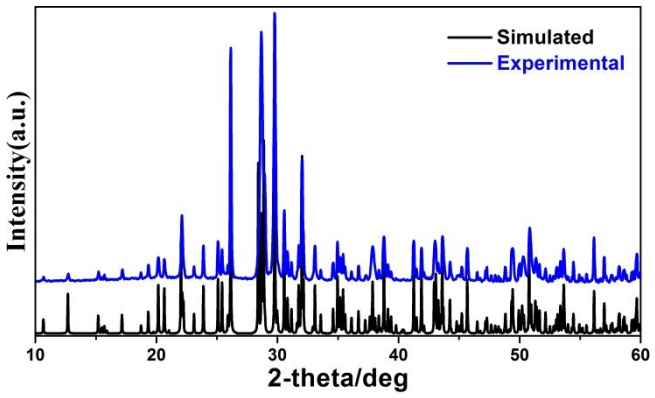
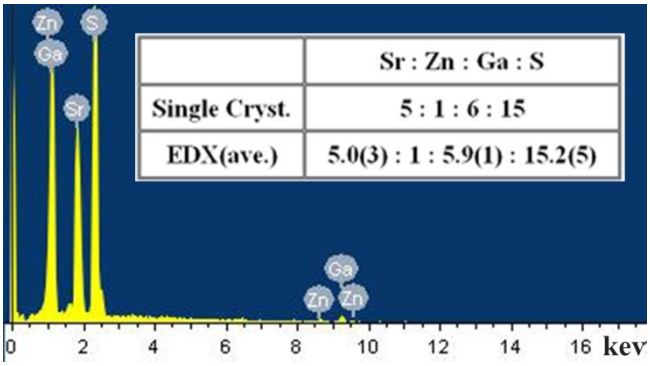


Fig. S1 Experimental (blue) and simulated (black) PXRD patterns of **SZGS.**



	Sr : Zn : Ga : S
Single Cryst.	5 : 1 : 6 : 15
EDX(ave.)	5.0(3) : 1 : 5.9(1) : 15.2(5)

Fig. S2 EDX result of **SZGS.**

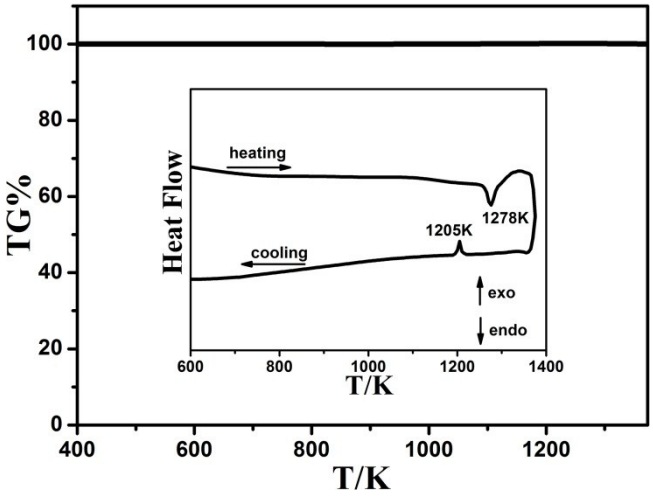


Fig. S3 TG and DSC (inset) diagrams of **SZGS.**

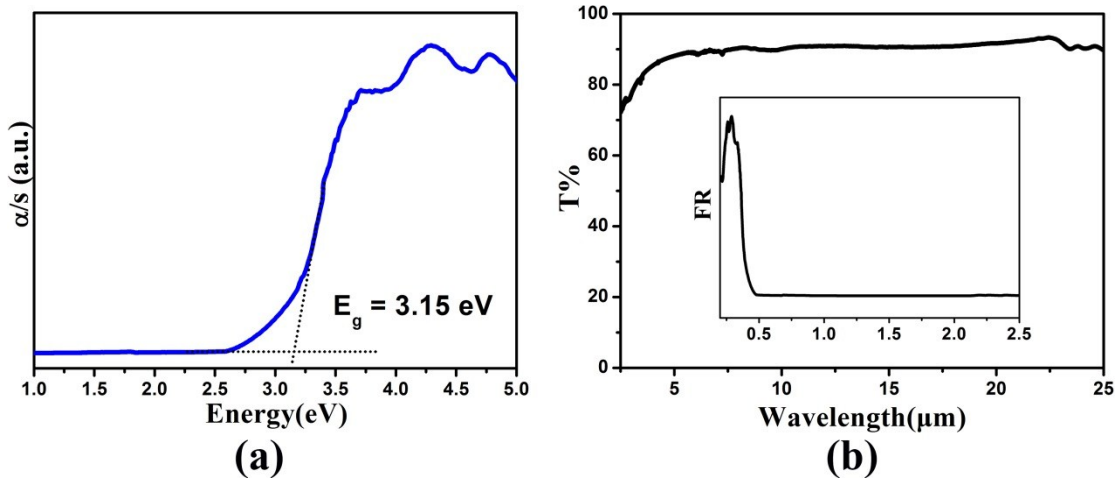


Fig. S4 Property measurements on **SZGS**: (a) solid-state UV–Vis–NIR optical absorption spectra, (b) reflection (inset) and FT–IR spectra.

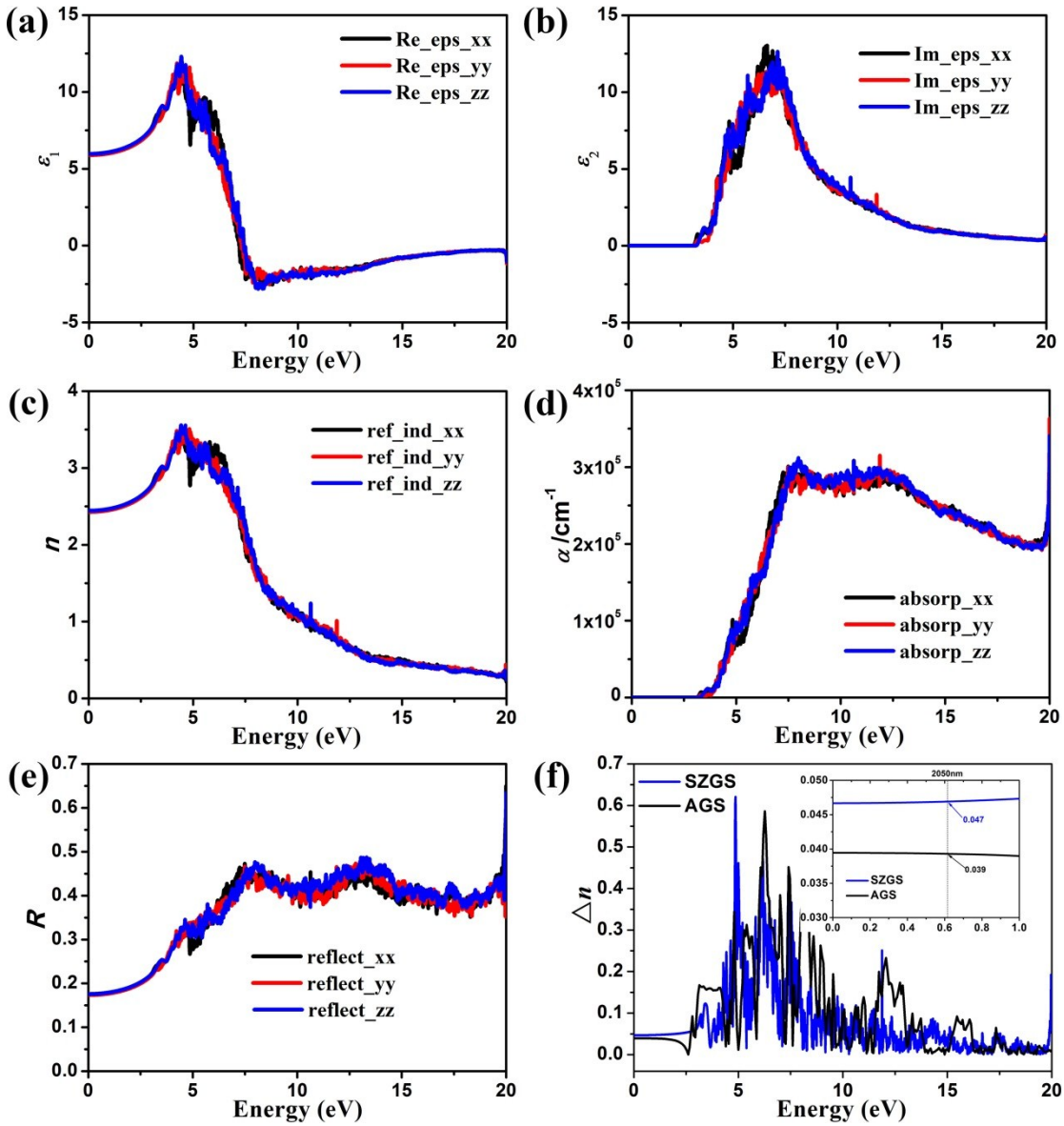


Fig. S5. Energy dependences of the real part ε_1 (a) and imaginary part ε_2 (b) of **SZGS**. The calculated (c) refractive index (n), (d) absorption coefficient (α), (e) reflectivity (R) and (f) birefringence (Δn) of **SZGS**.

Table S1. Properties comparison of the well-known MFIR NLO chalcogenides with wide band-gap (E_g > 3.0 eV) and phase-matching behavior, $AgGaS_2$ (AGS) as reference.

Compounds	E_g **(eV)**	d_{ij} **(×AGS)**	**LIDT**	**Ref.**
$LiGaS_2$	4.15	0.4 × AGS	11 × AGS	10
$BaAl_4S_7$	3.95	0.5 × AGS	10 × AGS	11
Li_2ZnSiS_4	3.90	1.1 × AGS	10 × AGS	12
$BaGa_2SiS_6$	3.75	1.0 × AGS	n/a	13
Na_2BaGeS_4	3.70	0.3 × AGS	8 × AGS	14
Li_2BaGeS_4	3.66	0.5 × AGS	11 × AGS	15
$Li_2Ga_2GeS_6$	3.65	0.8 × AGS	n/a	16
$Li_2In_2SiS_6$	3.61	1.0 × AGS	n/a	17
$LiInS_2$	3.57	0.5 × AGS	2.5 × AGS	18
$BaGa_4S_7$	3.54	1.0 × AGS	3 × AGS	19
$Ba_6Zn_7Ga_2S_{16}$	3.50	0.5 × AGS	28 × AGS	20
$Li_2In_2GeS_6$	3.45	1.0 × AGS	n/a	17
$LiZnPS_4$	3.44	0.8 × AGS	n/a	21
$BaAl_4Se_7$	3.40	0.3 × AGS	n/a	22
$LiGaSe_2$	3.34	0.7 × AGS	n/a	10
Na_2BaSnS_4	3.27	0.5 × AGS	5 × AGS	14
Li_2CdSnS_4	3.26	0.1 × AGS	n/a	23
$Na_2ZnGe_2S_6$	3.25	0.9 × AGS	6 × AGS	24
$BaGa_2GeS_6$	3.23	1.0 × AGS	n/a	13
$Na_2CdGe_2S_6$	3.21	0.8 × AGS	n/a	25
Li_2CdGeS_4	3.15	2.0 × AGS	10 × AGS	26
$SnGa_4S_7$	3.10	1.3 × AGS	19 × AGS	27
$PbGa_4S_7$	3.08	1.1 × AGS	n/a	28
Li_2MnGeS_4	3.07	0.5 × AGS	40 × AGS	29
$Zn_3(PS_4)_2$	3.07	0.9 × AGS	n/a	21
Li_2BaSnS_4	3.07	0.7 × AGS	6.5 × AGS	15
$AgGaS_2$(AGS)	**2.64**	**1.0 × AGS**	**1.0 × AGS**	30

Table S2. Atomic coordinates and equivalent isotropic displacement parameters of $Sr_5ZnGa_6S_{15}$.

Atom	*Wyckoff*	*x*	*y*	*z*	$U_{(eq)}$*
Sr1	4*b*	0.25	0.65146(8)	0.4285(2)	0.0173(3)
Sr2	8*c*	0.11546(4)	0.15213(5)	0.4688(2)	0.0161(2)
Sr3	8*c*	0.11584(4)	0.36507(5)	0.0072(2)	0.0128(2)
Zn	4*a*	0	0	0	0.0063(3)
Ga1	8*c*	0.52798(4)	0.30612(5)	0.4533(2)	0.0097(2)
Ga2	8*c*	0.66027(4)	0.03336(5)	0.0197(2)	0.0110(2)
Ga3	4*b*	0.25	0.46802(8)	0.0444(2)	0.0132(3)
Ga4	4*b*	0.25	0.30410(7)	0.3925(2)	0.0104(3)
S1	8*c*	0.0814(2)	0.0039(2)	0.2250(4)	0.0109(5)
S2	8*c*	0.0019(2)	0.4043(2)	0.2595(4)	0.0109(5)
S3	8*c*	0.5044(2)	0.1944(2)	0.3004(4)	0.0112(5)
S4	8*c*	0.6281(2)	0.3009(2)	0.4814(4)	0.0132(5)
S5	8*c*	0.1579(2)	0.3407(2)	0.5128(4)	0.0125(5)
S6	8*c*	0.1648(2)	0.5169(2)	0.1880(4)	0.0122(5)
S7	4*b*	0.25	0.3391(2)	0.0335(5)	0.0114(6)
S8	4*b*	0.25	0.1807(2)	0.4372(6)	0.0115(7)
S9	4*b*	0.25	0.0063(2)	0.1836(5)	0.0110(7)

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond lengths (Å) of $Sr_5ZnGa_6S_{15}$.

Zn–S1 × 2	2.298(2)	Sr1–S8	3.199(4)
Zn–S2 × 2	2.284(2)	Sr1–S6 × 2	3.431(3)
Ga1–S2	2.244(2)	Sr1–S7	3.449(4)
Ga1–S4	2.251(2)	Sr2–S3	2.980(3)
Ga1–S3	2.272(2)	Sr2–S6	3.006(2)
Ga1–S3	2.291(2)	Sr2–S8	3.065(2)
Ga2–S6	2.251(3)	Sr2–S4	3.153(3)
Ga2–S5	2.275(2)	Sr2–S1	3.167(2)
Ga2–S1	2.279(3)	Sr2–S4	3.302(3)
Ga2–S9	2.364(2)	Sr2–S2	3.348(3)
Ga3–S6 × 2	2.283(3)	Sr2–S5	3.545(2)
Ga3–S7	2.329(3)	Sr3–S3	3.006(2)
Ga3–S9	2.343(4)	Sr3–S4	3.013(2)
Ga4–S5 × 2	2.292(2)	Sr3–S7	3.047(2)
Ga4–S7	2.314(4)	Sr3–S2	3.076(3)
Ga4–S8	2.244(3)	Sr3–S1	3.153(2)
Sr1–S4 × 2	2.883(2)	Sr3–S6	3.158(2)
Sr1–S9	3.061(4)	Sr3–S5	3.238(3)
Sr1–S8	3.093(4)	Sr3–S5	3.304(3)

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