Supporting Information

The first quaternary rare-earth oxythiogermanate with second-harmonic generation and ferromagnetic behaviors

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1. Experimental Section

1) Synthesis.

All the raw materials including Eu metal (99.95 %), GeO₂ powder (99.99 %), S powder (99.99 %), B powder (99.99 %) and KI flux (99 %) were commercially purchased without further purification. Single crystals of Eu₃GeOS₄ were synthesized by traditional high-temperature solid-state reactions using a 500 mg mixture of starting materials Eu, GeO₂, S and B with the molar ratios of 3 : 1 : 4 : 1, and additional 500 mg KI as flux. All of the reactants were placed in a glovebox in which the level of H₂O and O₂ was kept under 0.1 ppm. These reagents were loaded into quartz tubes and sealed after vacuuming. The tubes were placed in a furnace, heated from room temperature to 1148 K in one day with several intermediate equilibrated temperatures aiming to homogenize the reactive system and prevent quartz tube's broken, and kept at 1148 K for 5 days, and then cooled down to 673 K with a rate of 4 K/h before turning off the furnace. The product was ultrasonically washed using distilled water and alcohol to remove the flux. After then, millimeter-level red block crystals of Eu₃GeOS₄ (Fig. S1) were obtained. The crystals are stable in air and water and can be picked out manually under a light microscope for the following characterizations and physical measurements.

2) X-Ray Crystallography Analysis

Power X-Ray Diffraction (PXRD) Characterization. The purity of the sample was confirmed by the powder X-ray diffraction (PXRD) analysis with Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 100 mA on Bruker D8 Advance diffractometer. The experimental PXRD data was collected in 2θ varying from 20° to 80° with a scan speed of 2 °/min at room temperature. The simulated one was generated from single-crystal diffraction data using Mercury v3.8 program. The simulated and experimental patterns of Eu₃GeOS₄ are displayed in Fig. S2.

Single-Crystal X-Ray Diffraction (SXRD) Characterization. Single crystal X-ray diffraction data of Eu₃GeOS₄ was collected on a Bruker D8 QUEST single crystal X-ray diffractometer, which was equipped with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) at 296 K. The crystal structure was determined via Direct Methods and refined by full-matrix least-squares fitting on F^2 using the SHELXTL program package.^{1,2} The detailed

data of crystal refinement, atoms positions and bond distances are summarized in Tables S1–S3, respectively. The CIF document of Eu_3GeOS_4 was also deposited with the CCDC number of 2216613.

Semi-quantitative energy dispersive X-ray spectroscopy (EDS) analyses were obtained using a field emission scanning electron microscope (SEM) equipped with an energy-dispersive Xray analyzer, as shown in Fig. S3. EDS data were collected using an accelerating voltage of 20 keV with a 30 s accumulation time. The EDS data on several single crystals of Eu₃GeOS₄ indicates that Eu, Ge, O, and S elements coexist, and their molar ratios are close to the chemical formula except for the content of O element. The oxygen content is inaccurate because of the oxygen-containing substrate and the small atomic mass of oxygen element.

3) UV-vis-NIR Diffuse and Infrared (IR) Reflectance Spectra. The UV-vis-NIR spectrum for the powder sample of Eu₃GeOS₄ was measured on a computer-controlled Cary 5000 UV-vis-NIR spectrometer with data collected in the wavelength range of 200–1200 nm at room temperature. A BaSO₄ plate was used as the standard for comparison. The Kubelka–Munk function was used to calculate the absorption spectrum form the reflection spectrum.^{3,4} The Fourier-transform infrared (FT-IR) spectrum was measured using a TENSOR27 FT-IR spectrophotometer in the range of 4000–400 cm⁻¹. Powdery sample was pressed into a pellet with KBr as the background for measurement.

4) Thermal analysis. The thermostability of Eu_3GeOS_4 was measured through thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis using a TGA-DSC-1-1000 (STARE) thermal analyzer under N₂ flow. A 15 mg grounded multicrystalline powder sample was placed on the sample side of the detector with an empty crucible on the reference side. The sample of Eu_3GeOS_4 was heated from room temperature to 1000 °C at a heating rate of 15 °C· min⁻¹.

5) Magnetic Susceptibility Measurement. Temperature-dependent magnetic susceptibility of Eu₃GeOS₄ was measured using a Quantum Design PPMS from 2 to 300 K in an applied magnetic field of 1000 Oe. The polycrystalline powdery samples were secured in a gel capsule. Raw magnetization data was collected for the holder contribution and converted to molar

susceptibility ($\chi_m = M/H$; emu/mol). For Eu₃GeOS₄, field sweep for the same specimen was done at 2 K up to applied magnetic field of 70 kOe.

6) Second-Harmonic Generation (SHG) and Laser-Induced Damage Threshold (LIDT) Measurements. The SHG responses of Eu₃GeOS₄ were investigated by the modified Kurtz–Perry Powder SHG system with a laser radiation of 2100 nm at 10 Hz.⁵ Hand-picked multicrystalline samples along with AGS as reference were sieved into several particle ranges (25–45, 45–75, 75–110, 110–150, 150–200 and 200–250 μ m) for the SHG measurements. The SHG signals were collected by a photomultiplier tube and the peaks appeared on the oscilloscope.

The LIDTs of Eu₃GeOS₄ and AgGaS₂ with a distinct particle range of 75–110 μ m were measured through the single-pulse measurement method.⁶ The damage spot occurring on the surface of the title crystals was radiated by a high-power 1064 nm pulse laser (10 ns and 1 Hz repetition), and then the radius of the damaged spot area and corresponding laser energy E were recorded. The laser-induced damage threshold was calculated from the equation of I (threshold) = $E/(\pi r^2 \tau_p)$, where E is the energy of a single pulse, r is the spot radius, and τ_p is the pulse width. 7) Calculation Details. On the basis of density functional theory (DFT), first-principles electronic structure calculations were carried out by applying the CASTEP package.⁷ The calculation model was built from the single-crystal diffraction data of Eu₃GeOS₄ and no further geometry optimization was performed. The exchange-correlation function LDA (local density approximation) was chosen and a plane wave basis with ultrasoft pseudopotential was used. The configurations of the valence electrons are 4f⁷5d⁰6s² for Eu, 4s²4p² for Ge, 2s²2p⁴ for O, and 3s²3p⁴ for S. The cut off energy of plane waves was set as 480 eV. The threshold was set at 10^{-5} eV, and Monkhorst-Pack k-points meshes were $3 \times 1 \times 4$ in the Brillouin Zone to achieve energy convergence. Moreover, in order to describe the localized f-orbitals in RE atoms, the LDA + U method was adopted by setting the on-site orbital dependent Hubbard U energy as U_{f} = 6 eV. To match the measured value, a proper scissor operator was used to correct the conduction band energy. The refractive indices *n* and the birefringence Δn were deduced from the imaginary and the real parts of the dielectric function, which were calculated on the strength

of the electronic band structure and determined by means of the Kramers–Kronig transform.^{8,} Moreover, the second-order susceptibilities can be derived from the first-order nonresonant susceptibility in the low-frequency region.

2. Tables and Figures

Empirical formula	Eu ₃ GeOS ₄
Formula weight	672.71
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	$Pca2_1$
$a/ m \AA$	11.7433(6)
$b/{ m \AA}$	5.9456(3)
$c/{ m \AA}$	11.6103(6)
$V/Å^3$	810.64(7)
Ζ	4
$ ho_{ m calc}~ m g/cm^3$	5.512
μ/mm^{-1}	27.504
F(000)	1172.0
2 heta range/°	6.854 to 52.97
Goodness-of-fit on F^2	1.072
R1, ^{<i>a</i>} wR2 $[I \ge 2\sigma (I)]^b$	0.0140, 0.0282
R1, ^{<i>a</i>} wR2 (all data) ^{<i>b</i>}	0.0143, 0.0283
$\Delta ho_{ m max}/\Delta ho_{ m min}$ / e Å ⁻³	0.58/-0.91
Flack parameter	0.116(18)

Table S1. Crystal data and structure refinement for Eu₃GeOS₄.

^{*a*}R1= $||F_o| - |F_c||/|F_o|$. ^{*b*}wR2 = $[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

Table S2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (U_{eq}^{a} , Å² × 10³) for Eu₃GeOS₄.

Atom	x	у	Z	$U_{ m eq}/{ m \AA}^2$
Eu(1)	190.0(3)	4154.3(5)	2416.1(3)	8.3 (1)
Eu(2)	2693.0(3)	6009.4(5)	6009.4(5)	8.3(1)
Eu(3)	2990.4(3)	360.1(5)	2476.1(4)	8.4(1)
Ge(1)	47.7(7)	67.3(16)	0.0(9)	5.6(1)
S(1)	1867.5(13)	961(3)	157.1(18)	9.1(4)
S(2)	2676.0(13)	5214(3)	2580.6(18)	7.3(3)
S(3)	4989.1(14)	3639(3)	112.5(19)	9.1(3)
S(4)	5496.9(15)	844(3)	3219.8(16)	8.8(4)
O(1)	4206(4)	-1510(8)	1002(4)	8.3(10)

 $^{a}U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Bond	Length/Å	Bond	Length/Å
Eu(1)–S(2)	2.9926(16)	Eu(2)–O(1) ⁹	2.556(5)
Eu(1)–S(2) ⁷	2.9822(16)	Ge(1)–S(1)	2.2098(17)
$Eu(1)-S(3)^{6}$	3.153(2)	$Ge(1)-S(3)^5$	2.2083(18)
Eu(1)–S(3) ⁷	2.988(2)	$Ge(1)-S(4)^8$	2.212(2)
Eu(1)–S(4) ⁵	3.1357(18)	$Ge(1)-O(1)^5$	1.751(4)
Eu(1)–S(4) ⁷	3.1375(17)	Eu(3)–S(1) ⁶	3.138(2)
Eu(1)–O(1) ⁵	2.550(5)	Eu(3)–S(1)	3.019(2)
Eu(2)–S(1)	3.1561(17)	$Eu(3)-S(2)^3$	3.0843(15)
Eu(2)–S(1) ⁹	3.1018(18)	Eu(3)–S(2)	2.9119(15)
Eu(2)–S(2)	2.966(2)	Eu(3)–S(4) ⁵	3.1357(18)
$Eu(2)-S(2)^8$	2.948(2)	Eu(3)–S(4)	3.0810(18)

Table S3. Bond Lengths for Eu₃GeOS₄.

Bond	Length/Å	Bond	Length/Å
Eu(2)–S(3)	3.0433(16)	Eu(3–O(1)	2.491(5)
Eu(2)–S(3) ⁷	3.1827(16)		

Symmetry codes: ¹1/2+*x*, -*y*, +*z*; ²1/2+*x*, 1-*y*, +*z*; ³1/2-*x*, -1+*y*, 1/2+*z*; ⁴+*x*, -1+*y*, +*z*; ⁵-1/2+*x*, -*y*, +*z*; ⁶1/2-*x*, +*y*, 1/2+*z*; ⁷-1/2+*x*, 1-*y*, +*z*; ⁸1/2-*x*, +*y*, -1/2+*z*; ⁹+*x*, 1+*y*, +*z*.

Table S4. Known A_3BCD_4 (A = Alkali or alkaline earth metal, B = group 13 or 14 metal, C = halogen, D = chalcogen) compounds and their derivatives.

Compound	Space group	Reference
Eu_3GeOS_4	$Pca2_1$	this work
$Ba_3GaS_4X (X = Cl, Br)$	Pnma	9
Ba_3GaSe_4X (X = Cl, Br)	Pnma	9,10
Ba ₃ GaS ₄ I	Стст	11
Ba ₃ InS ₄ Cl	I4/mcm	12
Ba_3InSe_4X (X = Cl, Br)	I4/mcm	9,10
$NaBa_2SnS_4Cl$	I4/mcm	13
KBa ₂ SnS ₄ Cl	I4/mcm	13
KBa_2SnS_4Br	Pnma	13
α -ABa ₂ MS ₄ Cl (A = Rb, Cs; M= Ge, Sn)	$P2_{1}/c$	14
β -CsBa ₂ SnS ₄ Cl	I4/mcm	13
Hg_3AsQ_4X (Q = S or Se; X = Cl, Br, or I)	$P6_3mc$	15
$Ba_3(FeS_4)X (X = Cl, Br)$	Pnma	16
Ba ₃ (FeSe ₄)Br	Pnma	16
Ba ₃ (FeS ₄)I	Стст	17

Compound	Damage energy /mJ	Spot area /cm ²	Damage threshold MW/cm ²	Relative value
Eu ₃ GeOS ₄	4.61	0.015393804	29.94711378	8.86
AGS	0.52	0.015393804	3.377982466	1

Table S5. Measured LIDTs of Eu₃GeOS₄ and AGS for their powder samples (75–110 μ m).

Table S6. Summary of reported NLO oxychalcogenides

	Compound	Createl system	En a co guoun	E (aV)	SHG response	LIDT	Reference
	Compound	Crystal system	Space group	$\mathbf{E}_{\mathbf{g}}(\mathbf{ev})$	@ 2.1 µm		
1	$Sr_4Pb_{1.5}Sb_5O_5Se_8$	monoclinic	<i>Cm</i> (no. 8)	0.92	$0.25 \times \text{AgGaS}_2$	N/A^b	18
2	$Sr_6Cd_2Sb_6O_7Se_{10}$	monoclinic	<i>Cm</i> (no. 8)	1.55	$1.8 \times AgGaS_2$	N/A	19
3	$Sr_6Cd_2Sb_6O_7S_{10}$	monoclinic	<i>Cm</i> (no. 8)	1.89	$4 \times \text{AgGaS}_2$	N/A	20
4	Ba ₃ Ge ₂ O ₄ Te ₃	trigonal	<i>R</i> 3 <i>m</i> (no. 160)	2.08	$0.6 \times AgGaSe_2$	$1.3 \times AGSe$	21
5	$Sm_3NbS_3O_4$	orthorhombic	<i>Pna</i> 2 ₁ (no. 33)	2.68	$0.3 imes AgGaS_2$	12.5 × AGS	22
6	$Gd_3NbS_3O_4$	orthorhombic	<i>Pna</i> 2 ₁ (no. 33)	2.74	$0.4 \times \text{AgGaS}_2$	$4.5 \times AGS$	22
7	Sr ₂ CoGe ₂ OS ₆	tetragonal	$P\bar{42}_{1}m$ (no. 113)	2.77	~0.34 × AGS	$2.13 \times AGS$	23
8	Sr ₃ Ge ₂ O ₄ Se ₃	trigonal	<i>R</i> 3 <i>m</i> (no. 160)	2.96	$0.8 imes AgGaS_2$	N/A	24
9	Ca ₂ GeGa ₂ OS ₆	tetragonal	$P\bar{42}_{1}m$ (no. 113)	3.15	$2.1 imes AgGaS_2$	$9.7 \times AGS$	25
10	Sr ₂ GeGa ₂ OS ₆	tetragonal	$P\bar{42}_{1}m$ (no. 113)	3.15	$1.7 \times AgGaS_2$	$13.4 \times AGS$	25
11	SrGeOSe ₂	orthorhombic	$P2_12_12_1$ (no. 19)	3.16	$1.3 \times AgGaS_2$	$36 \times AGS$	26
12	BaGeOSe ₂	orthorhombic	$P2_12_12_1$ (no. 19)	3.2	$1.1 \times AgGaS_2$	N/A	27
13	Sr ₃ [SnOSe ₃][CO ₃]	orthorhombic	<i>Pmn</i> 2 ₁ (no. 31)	3.46	$\sim 1 \times \text{AgGaS}_2$	$12 \times AGS$	28
14	Sr ₂ MnGe ₂ OS ₆	tetragonal	$P\bar{42}_1m$ (no. 113)	3.51	$0.3 imes AgGaS_2$	$17.4 \times AGS$	29
15	$Sr_2ZnSn_2OS_6$	tetragonal	$P\bar{42}_1m$ (no. 113)	3.52	$0.7 imes AgGaS_2$	~10 × AGS	30
16	Sr ₂ CdGe ₂ OS ₆	tetragonal	$P\bar{42}_1m$ (no. 113)	2.95	$1.3 \times AgGaS_2$	$5.6 \times AGS$	25

		Compound Constal system Space group F (sV)			SHG response	LIDT	Reference
	Compound	Crystal system	Space group	E _g (ev)	@ 2.1 µm		
	Sr ₂ CdGe ₂ OS ₆	tetragonal	$P\bar{42}_1m$ (no. 113)	3.13	$0.7 imes AgGaS_2$	N/A	31
	Sr ₂ CdGe ₂ OS ₆	tetragonal	$P\bar{42}_1m$ (no. 113)	3.62	$0.8 imes AgGaS_2$	19.2 × AGS	29
18	CaZnOS	hexagonal	<i>P</i> 6 ₃ <i>mc</i> (no. 186)	3.71	$100 \times SiO_2$	N/A	24
19	$K_2Ba_{0.5}Ga_9O_2S_{13}$	hexagonal	<i>Р</i> ⁶ (по. 174)	3.72	$0.5 imes AgGaS_2$	$17 \times AGS$	32
20	Sr ₂ ZnGe ₂ OS ₆	tetragonal	$P\bar{42}_1m$ (no. 113)	3.0	$0.3 \times AgGaS_2$	$13.7 \times AGS$	25
	Sr ₂ ZnGe ₂ OS ₆	tetragonal	$P\bar{42}_1m$ (no. 113)	3.30	$0.6 \times AgGaS_2$	N/A	31
	Sr ₂ ZnGe ₂ OS ₆	tetragonal	<i>P</i> 42 ₁ <i>m</i> (no. 113)	3.73	$0.6 imes AgGaS_2$	$20.6 \times AGS$	29
21	SrZn ₂ OS ₂	orthorhombic	<i>Pmn</i> 2 ₁ (no. 31)	3.86	$2 \times \text{KDP}$	N/A	33
22	$Sr_5Ga_8O_3S_{14}$	orthorhombic	<i>P</i> 2 ₁ 2 ₁ 2 (no. 18)	3.9	$0.8 imes AgGaS_2$	N/A	34
23	$Ba_2SnSSi_2O_7$	tetragonal	<i>P4bm</i> (no. 100)	2.4	$2 \times SiO_2$	N/A	35
	$Ba_2SnSSi_2O_7$	tetragonal	<i>P4bm</i> (no. 100)	4.05	$0.6 imes AgGaS_2$	N/A	36
24	SrGeOS ₂	orthorhombic	$P2_12_12_1$ (no. 19)	3.9	$0.4 imes AgGaS_2$	N/A	37
	SrGeOS ₂	orthorhombic	$P2_12_12_1$ (no. 19)	4.36	$0.71 \times \text{KDP}$	~1.2 × KDP	38
25	BaGeOS ₂	orthorhombic	$P2_12_12_1$ (no. 19)	4.1	$0.5 imes AgGaS_2$	N/A	37
	BaGeOS ₂	orthorhombic	$P2_12_12_1$ (no. 19)	4.43	1.07 × KDP	~1.2 × KDP	38
26	La3Ga3Ge2S3O10	hexagonal	<i>P62c</i> (no. 190)	4.7	$2 \times \text{KDP}$	N/A	39
27	α-Na ₃ PO ₃ S	trigonal	<i>R</i> 3 <i>c</i> (no. 161)	N/A	$200 \times SiO_2$	N/A	40
	α-Na ₃ PO ₃ S	trigonal	<i>R</i> 3 <i>c</i> (no. 161)	5.29	$1.7 \times \text{KDP}$	N/A	41

Note: N/A indicates no data available.

Structural unit	EuOS ₆	GeOS ₃	Total
Dipole moment	0.3764313	0.2305719	0.5823504



Fig. S1 Photographs of Eu₃GeOS₄ crystals.



Fig. S2 Powder X-ray diffraction pattern for Eu₃GeOS₄.



Fig. S3 The EDS analysis of Eu₃GeOS₄. Inset: Atomic concentration for elements.



Fig. S4 The 3D structure of Eu_3GeOS_4 viewed along the *b*-axis.



Fig. S5 The crystal structure of Pb₃GeO₅ (*P*2₁).



Fig. S6 Structure map for A_3 -B-C₄-D (A = Alkali or alkaline earth metal, B = group 13 or 14 metal, C = halogen, D = chalcogen) compounds based on the elements' radius ratios.



Fig. S7 UV-vis-NIR diffuse reflectance spectrum of Eu₃GeOS₄.



Fig. S8 FT-IR spectrum of Eu₃GeOS₄.







local function; (d) COHP analysis of the selected interactions; e) calculated energy-dependent SHG tensors; f) frequency-dependent birefringence Δn .

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