Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Support information

Li-free Ternary Sulphide $Cs_5Ga_9S_{16}$ with Excellent Nonlinear Optical Performance Similar to Classic $LiGaS_2$

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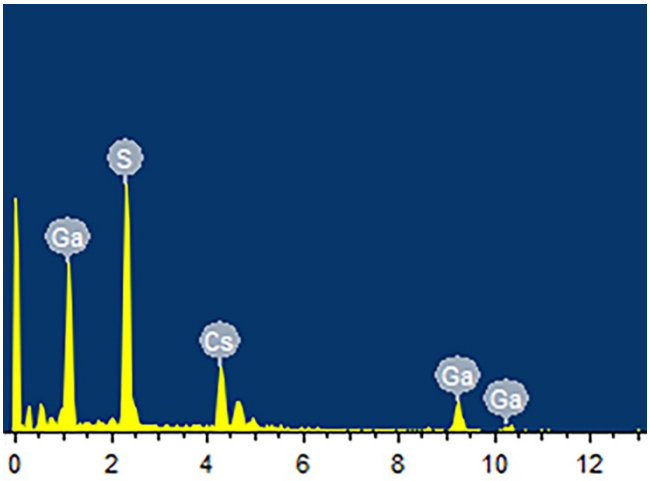

Fig. S1 EDS of single-crystal of $Cs_5Ga_9S_{16}$.

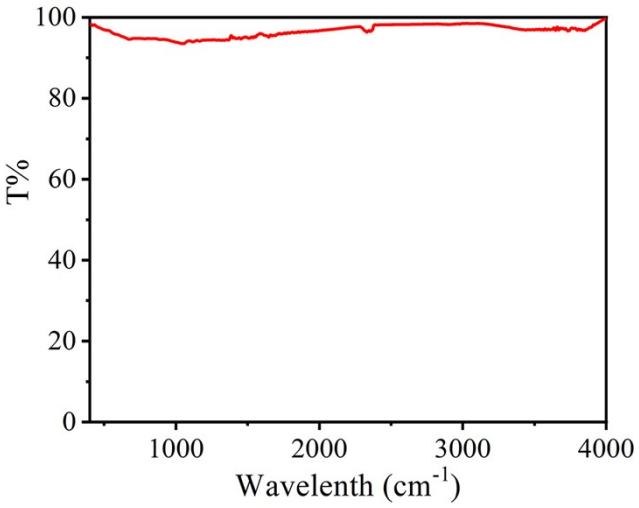

Fig. S2 IR spectrum of $Cs_5Ga_9S_{16}$.

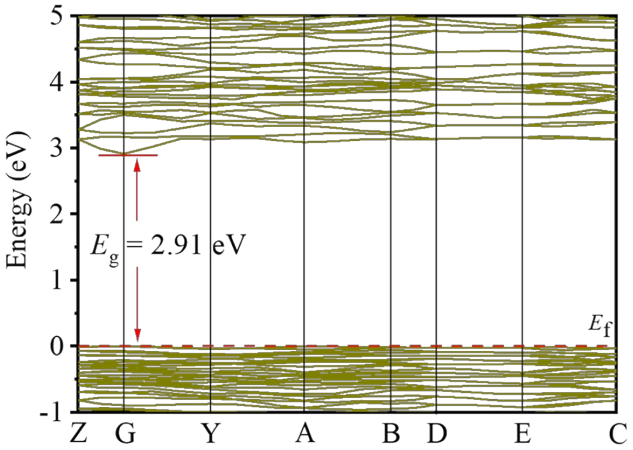

Fig. S3 Electronic band structure of $Cs_5Ga_9S_{16}$.

Table S1. Crystallographic data and structure refinement results of $Cs_5Ga_9S_{16}$.

Empirical formula	$Cs_5Ga_9S_{16}$
Fw	1805.15
Temperature (K)	293(2)
Space group	*Pc*
a (Å)	9.4067(11)
b (Å)	9.6983(11)
c (Å)	19.3949(18)
α (°)	90.00
β (°)	107.912(5)
γ (°)	90.00
Volume (Å^3)	1683.6(3)
Z	2
ρ_{calcd} (g cm^{-3})	3.561
μ (mm^{-1})	13.401
GOF on F^2	1.040
$R_1{}^a$ [$I >= 2\sigma(I)$]	0.0289
$wR_2{}^b$ [$I >= 2\sigma(I)$]	0.0606
$R_1{}^a$ [all data]	0.0301
$wR_2{}^b$ [all data]	0.0616
Dr_{max}/Dr_{min} (e Å^{-3})	1.01/-1.12
Flack	-0.017(11)

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^bwR = (\Sigma(w(F_o{}^2-F_c{}^2)^2)/\Sigma(w(F_o{}^2)^2))^{1/2}$

Table 2. Atomic coordinates, equivalent isotropic displacement parameters (Å^2) of $Cs_5Ga_9S_{16}$.

Atom	*x*	*y*	*Z*	$U_{(eq)}$
Cs1	10004.8(6)	9158.9(6)	9999.0(3)	25.40(14)
Cs2	7021.2(7)	8973.3(6)	2654.0(3)	29.93(15)
Cs3	5289.2(7)	9019.3(6)	5229.8(3)	30.31(15)
Cs4	3783.7(7)	4307.2(6)	6357.7(4)	31.59(15)
Cs5	1115.4(6)	4437.9(7)	8759.5(3)	29.93(15)
Ga1	9679.8(9)	7823.2(9)	7242.7(4)	12.35(18)
Ga2	9558.7(9)	6813.5(9)	5443.2(5)	13.52(19)
Ga3	8728.6(9)	3994.0(9)	6101.8(5)	13.14(19)
Ga4	7012.0(10)	4253.5(9)	9208.7(5)	14.74(19)

Atom	*x*	*y*	*Z*	$U_{(eq)}$
Ga5	6694.2(9)	6991.9(9)	7996.1(4)	12.81(18)
Ga6	5289.3(9)	6832.7(9)	9766.0(5)	13.67(19)
Ga7	3162.6(9)	8636.4(9)	8546.5(5)	14.44(19)
Ga8	3101.0(9)	8321.2(9)	6706.5(5)	12.54(18)
Ga9	1298.3(9)	8913.7(9)	2175.5(5)	14.78(19)
S1	9240(2)	9793(2)	6618.3(11)	17.5(4)
S2	9151(2)	5496(2)	9990.8(11)	14.5(4)
S3	9103(2)	7735(2)	8276.6(11)	18.1(4)
S4	8406(2)	6366(2)	6305.0(11)	13.5(4)
S5	8010(2)	7891(2)	4465.2(11)	18.4(4)
S6	6767(2)	2580(2)	5883.9(11)	19.1(4)
S7	6710(3)	4672(2)	8045.2(12)	24.3(5)
S8	5815(2)	8180(2)	8849.8(10)	14.3(4)
S9	5475(2)	7659(2)	6866.8(11)	17.0(4)
S10	5027(2)	4564(2)	9587.4(13)	22.1(5)
S11	3106(2)	9365(2)	1659.8(13)	21.5(5)
S12	3011(2)	7781(2)	9600.3(11)	18.0(4)
S13	2276(3)	9210(2)	3397.9(12)	29.1(6)
S14	2213(2)	7215(2)	7559.5(10)	13.2(4)
S15	1915(2)	7395(2)	5599.8(11)	19.3(4)
S16	760(2)	3390(2)	7000.8(11)	18.9(4)

Table S3. Selected bond distances (Å) for $Cs_5Ga_9S_{16}$.

Bond	**Length**	**Bond**	**Length**
Ga1-S1	2.231(2)	Ga7-S8	2.421(2)
Ga1-S3	2.234(2)	Ga7-S12	2.251(2)
Ga1-S4	2.324(2)	Ga7-S13	2.234(2)
Ga1-S14	2.346(2)	Ga7-S14	2.305(2)
Ga2-S2	2.393(2)	Ga8-S9	2.252(2)
Ga2-S4	2.296(2)	Ga8-S11	2.246(2)
Ga2-S5	2.261(2)	Ga8-S14	2.331(2)
Ga2-S15	2.216(2)	Ga8-S15	2.277(2)
Ga3-S2	2.361(2)	Ga9-S1	2.281(2)
Ga3-S4	2.369(2)	Ga9-S11	2.265(2)
Ga3-S6	2.232(2)	Ga9-S13	2.282(2)
Ga3-S16	2.233(2)	Ga9-S16	2.293(2)
Ga4-S2	2.434(2)	S1-Ga9	2.281(2)
Ga4-S5	2.274(2)	S2-Ga2	2.393(2)
Ga4-S7	2.223(2)	S2-Ga3	2.361(2)

Ga4-S10	2.227(2)	S5-Ga4	2.274(2)
Ga5-S3	2.279(2)	S6-Ga6	2.259(2)
Ga5-S7	2.252(2)	S11-Ga8	2.246(2)
Ga5-S8	2.366(2)	S13-Ga7	2.234(2)
Ga5-S9	2.233(2)	S14-Ga1	2.3460(19)
Ga6-S6	2.259(2)	S15-Ga2	2.216(2)
Ga6-S8	2.377(2)	S16-Ga3	2.233(2)
Ga6-S10	2.229(2)	S16-Ga9	2.293(2)
Ga6-S12	2.263(2)		

Table S4. Selected bond angles (°) for $Cs_5Ga_9S_{16}$.

∠Atom-Atom-Atom	Angle	∠Atom-Atom-Atom	Angle
∠S1-Ga1-S3	117.68(9)	∠S9-Ga5-S3	108.40(8)
∠S1-Ga1-S4	97.54(8)	∠S9-Ga5-S7	109.00(9)
∠S1-Ga1-S14	111.17(8)	∠S9-Ga5-S8	111.15(8)
∠S3-Ga1-S4-	118.04(8)	∠S6-Ga6-S8	111.76(8)
∠S3-Ga1-S14	105.23(8)	∠S6-Ga6-S12	108.07(8)
∠S4-Ga1-S14	106.83(7)	∠S10-Ga6-S6	113.82(9)
∠S4-Ga2-S2	91.82(7)	∠S10-Ga6-S8	117.71(8)
∠S5-Ga2-S2	97.81(8)	∠S10-Ga6-S12	108.94(9)
∠S5-Ga2-S4	111.82(8)	∠S12-Ga6-S8	94.36(8)
∠S15-Ga2-S2	109.22(8)	∠S12-Ga7-S8	93.47(7)
∠S15-Ga2-S4	128.66(8)	∠S12-Ga7-S14	114.66(9)
∠S15-Ga2-S5	110.88(9)	∠S13-Ga7-S8	121.18(10)
∠S2-Ga3-S4	90.82(7)	∠S13-Ga7-S12	109.65(9)
∠S6-Ga3-S2	108.51(8)	∠S13-Ga7-S14	114.71(8)
∠S6-Ga3-S4	119.17(8)	∠S14-Ga7-S8	101.52(7)
∠S6-Ga3-S16	116.47(8)	∠S9-Ga8-S14	109.10(8)
∠S16-Ga3-S2	115.07(8)	∠S9-Ga8-S15	101.26(8)
∠S16-Ga3-S4	104.33(8)	∠S11-Ga8-S9	106.04(9)
∠S5-Ga4-S2	96.30(8)	∠S11-Ga8-S14	119.61(8)

∠Atom-Atom-Atom	Angle	∠Atom-Atom-Atom	Angle
∠S7-Ga4-S2	111.42(9)	∠S11-Ga8-S15	111.26(9)
∠S7-Ga4-S5	107.72(9)	∠S15-Ga8-S14	107.98(8)
∠S7-Ga4-S10	116.85(10)	∠S1-Ga9-S13	115.80(9)
∠S10-Ga4-S2	110.12(8)	∠S1-Ga9-S16	110.44(8)
∠S10-Ga4-S5	112.54(9)	∠S11-Ga9-S1	109.13(9)
∠S3-Ga5-S8	102.42(8)	∠S11-Ga9-S13	108.47(10)
∠S7-Ga5-S3	108.22(9)	∠S11-Ga9-S16	106.54(9)
∠S7-Ga5-S8	117.15(8)	∠S13-Ga9-S16	106.05(8)

Table S5. The laser-induced damage thresholds of $Cs_5Ga_9S_{16}$, $LiGaS_2$, and benchmark $AgGaS_2$.

Compounds	Damage energy (mJ)	Spot area (cm^2)	τ_p (ns)	Damage threshold [$MW \cdot cm^{-2}$]
$Cs_5Ga_9S_{16}$,	15.1	0.028	10	53.3
$LiGaS_2$	13.2	0.028	10	46.6
$AgGaS_2$	3.4	0.028	10	12.0