Supporting Information for

$Pb_5Ga_6ZnS_{15}$: a noncentrosysmmetric framework with chains of T2-supertetrahedra

Rui-Huan Duan,[a,b] Ju-Song Yu,[a,b] Hua Lin,[b] Yu-Jun Zheng,[a,b] Hua-Jun Zhao,[c] Shang-Xiong Huang-Fu,[d] Muhammad Ali Khan,[a,b] Ling Chen[b] and Li-Ming Wu*[b]

a. Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China. E-mail: liming_wu@fjirsm.ac.cn; Tel: +(011)86-591-63173211

b. University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China.

c. Laboratory of Applied Research on the Characteristic Resources in the North of Guizhou Province, School of Chemistry and Chemical Engineering, Zunyi Normal College, Zunyi, Guizhou 563002, China.

d. Physics Institute of the Univeristy of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland.

Corresponding author: Li-Ming Wu; liming_wu@fjirsm.ac.cn

Tel: (+011)86-591-63173211

Experimental Details

Syntheses of the Title Compound. All elements were stored in an Ar-filled glovebox with controlled oxygen and moisture levels below 0.1 ppm, and all operations were carried out in the glovebox. PbS (with purities of 99.999%), Zn (99.99%), Ga (99.999%) and S (99.9%) were purchased from Aladdin China (Shanghai) Co. Ltd. Elements of Pb:Ga:Zn:S in 5:6:1:15 molar ratio with about 300 mg mixtures were heated to 900 °C at 24 °C /h and held at this temperature for 100 h. Then it was cooled to 300 °C through 100 h and closed the furnace. Some earthy yellow crystals of $Pb_5Ga_6ZnS_{15}$ were got with some byproducts of black PbS and yellow $ZnGa_2S_4$.

Single-Crystal X-ray Crystallography. Single-crystal X-ray diffraction data collections were performed on a Rigaku Saturn70 CCD diffractometer equipped with Mo Kα radiation at 293 K. The data were corrected for Lorentz and polarization factors. Absorption corrections were performed by the multiscan method.[1] The structure was solved by the direct methods and refined by the full-matrix least-squares fitting on F^2 by SHELX-97.[2] The assignments of three Pb and nine S atoms were out of events, but the Ga and Zn sites at M1 (4*b*), M2 (8*c*), M3 (4*b*), M4 (8*c*), M5 (4*a*) were difficult to assign with their similar X-ray scattering factors. According to the EDS measurement and valence balance, the ratio of Ga and Zn was close to 6:1. Then with the valence bond sum $V_i = \sum s_{ij}$, where s_{ij} is the bond valenc ($s_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$, where the d_{ij} is bond length between nearest neighboring atoms i–j, R_{ij} is known as the bond-valence parameter and its values are tabulated in the literature).[3,4]

The M1 (4*b*), M2 (8*c*), M3 (4*b*), M4 (8*c*) sites were assigned as Ga with VBS about 3 for the S member and M5 (4*a*) was assigned as Zn with VBS about 2 for the S member with the formula of $Pb_5Ga_6ZnS_{15}$ generated. Such assignments could be found in $Pb_4Ga_4GeS_{12}$, $Li_2Ga_2GeS_6$ and $LiGaGe_2Se_6$.[5-7] The structures were verified using the ADDSYM algorithm from the program PLATON.[8]

Powder X-ray Diffraction. The power XRD pattern was collected on a PANalytical X'Pert Pro diffractometer at 40 kV and 40 mA using Cu Kα radiation (λ = 1.5406 Å) at ambient temperature. Data were collected in the range $2\theta = 10-70°$ with scan steps of 0.02°. The measured X-ray powder diffraction pattern of the sample is shown in Figure S4 with the simulated one calculated from the single crystal data.

Elemental Analysis. Semiquantitative microprobe analyses on the compound were performed with the aid of a field emission scanning electron microscope (FESEM. JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDX, Oxford INCA). It shows that the crystal contains Pb, Ga, Zn and S atom (Figure S2).

UV/Vis Diffuse Reflectance Spectroscopy. The optical diffuse reflectance spectrum was measured using a Perkin-Elmer Lambda 950 UV–Vis spectrophotometer equipped with an integrating sphere attachment and $BaSO_4$ as a reference in the range of 0.2–2.5 μm at room temperature. The absorption spectrum was calculated from the reflection spectrum via the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, in which α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.[9]

Electronic Structure Calculations. Band structure and densities of states (DOS) were calculated by the Vienna *ab initio* simulation package VASP.[10] The generalized

gradient approximation (GGA)[11] was chosen as the exchange-correlation functional and a plane wave basis with the projector augmented wave (PAW) potentials was used.[12] The plane-wave cutoff energy of 400 eV, and the threshold of 10^{-5} eV were set for the self-consistent-field convergence of the total electronic energy. Pseudo atomic calculations were performed for Pb, $5d^{10}6s^26p^2$; Ga, $3d^{10}4s^24p^1$; Zn, $3d^{10}4s^2$ and S, $3s^23p^4$. The k integration over the Brillouin zone was performed by the tetrahedron method using a 10 × 4 × 4 Monkhorst-Pack mesh.

The macroscopic linear optical properties of $Pb_5Ga_6ZnS_{15}$ are drawn with the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, which is closely related to the electronic band structure of the material. Nevertheless, the imaginary part $\varepsilon_2(\omega)$ of the dielectric function which originates from the contribution of the interband transition between the occupied and unoccupied states is only significant in metallic compounds.[13] In Figure S7, the energy dependences of real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$ are projected. On the basis of the equation $\varepsilon_1(0) = 1/3\ [\varepsilon_{1xx}(0) + \varepsilon_{1yy}(0) + \varepsilon_{1zz}(0)]$, the average value of polarized zero-frequency dielectric constant is calculated with the value of 9.05, which is slightly smaller than $Pb_4Ga_4GeSe_{12}$. The main peak of imaginary part $\varepsilon_2(\omega)$ is located about 3.8 eV, which can be mainly regarded as electronic interband transitions from the S-3p to S-3p and Pb-6p states. In Figure S8, the calculated refractive index $n(\omega)$, absorption coefficient $I(\omega)$ and reflectivity $R(\omega)$ are also shown. The function $n(\omega)$ shows its peak value around 3.0 eV and rapidly decrease from 4.0 to 18.0 eV, corresponding mainly to the higher values for $R(\omega)$ in this region. Due to the free carrier adsorptions in semiconductors,[14] the absorption

coefficient $I(\omega)$ is very large (about 10^5 cm^{-1}), and the calculated absorption edge of the compound is 2.32 eV.

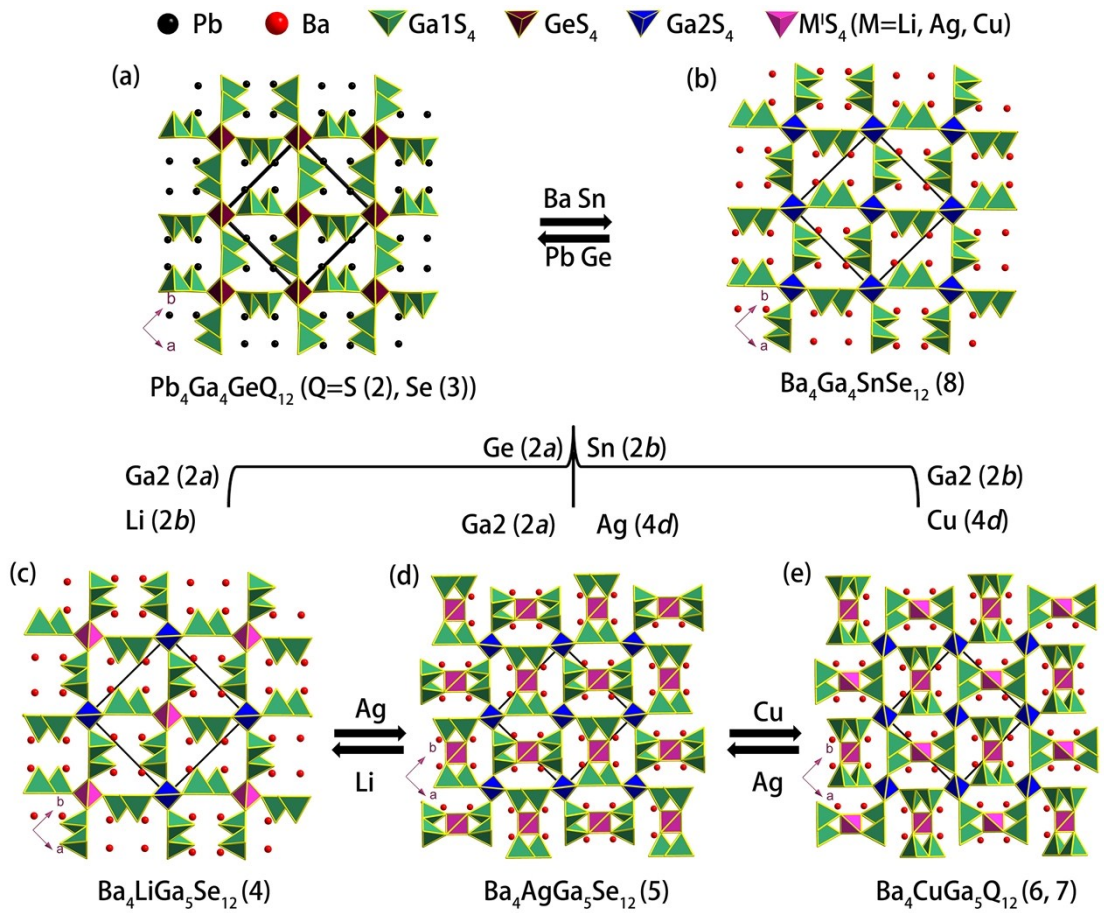


Figure S1. The unite cell structure relationship between (a) $Pb_4Ga_4GeQ_{12}$ (Q = S (**2**), Se (**3**)), (b) $Ba_4Ga_4SnSe_{12}$ (**8**), (c) $Ba_4LiGa_5Se_{12}$ (**4**), (d) $Ba_4AgGa_5Se_{12}$ (**5**) and (e) $Ba_4CuGa_5Q_{12}$ (Q = S (**6**), Se (**7**)).

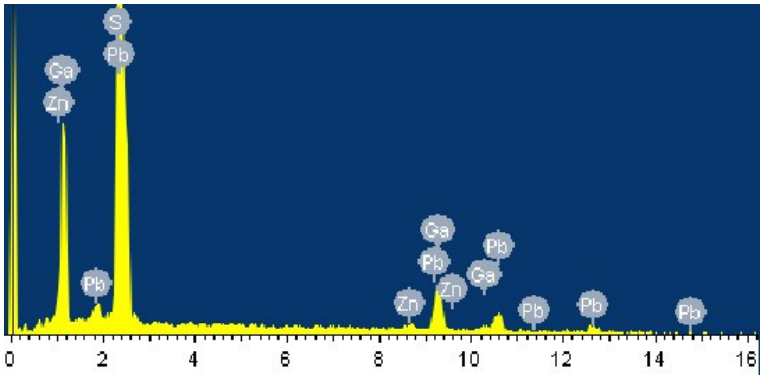


Figure S2. EDS spectrum of $Pb_5Ga_6ZnS_{15}$

Point-1				Point-2			
Element	Weight	Atomic%	Formula	Element	Weight	Atomic%	Formula
S	23.6	54.0	15.0	S	23.5	54.4	14.9
Zn	3.1	3.5	0.9	Zn	3.2	3.7	1.0
Ga	23.5	24.7	6.2	Ga	22.2	23.6	6.5
Pb	49.9	17.7	5.0	Pb	51.1	18.3	5.0
Totla	100.0			Totla	100.0		
Point-3				Point-4			
Element	Weight	Atomic%	Formula	Element	Weight	Atomic%	Formula
S	22.8	53.0	14.6	S	24.1	55.2	14.6
Zn	3.6	3.6	1.0	Zn	4.1	4.6	1.2
Ga	22.9	24.8	6.2	Ga	21.2	22.3	5.8
Pb	51.4	18.7	5.1	Pb	50.6	17.9	4.7
Totla	100.0			Totla	100.0		
Point-5							
Element	Weight	Atomic%	Formula	Average Formula $Pb_5Ga_{6.2}ZnS_{14.8}$			
S	22.6	53.0	14.7				
Zn	3.2	3.6	1.0				
Ga	22.9	24.8	6.2				
Pb	51.4	18.7	4.9				
Totla	100.0						

Table S1. Crystal data and structure refinements for $Pb_5Ga_6ZnS_{15}$[a]

Formula	$Pb_5Ga_6ZnS_{15}$
fw	2000.76
crystal system	Orthorhombic
crystal color	Earthy yellow
space group	*Ama*2 (No.40)
a (Å)	22.232(9)
b (Å)	17.933(7)
c (Å)	6.225(2)
V (Å^3)	2481.9(2)
Z	4
D_c (g.cm^{-3})	5.36
μ (mm^{-1})	42.4
F(000)	3462
GOOF on F^2	0.722
R_1, wR_2 ($I > 2\sigma(I)$) [a]	0.0483, 0.100
R_1, wR_2 (all data)	0.0583, 0.118
Absolute structure parameter	0.04(2)
Largest diff. peak and hole (e Å^{-3})	2.24 and -3.40

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters of $Pb_5Ga_6ZnS_{15}$.

Atom	Wyckoff	x	y	z	U(eq)
Pb1	8*c*	0.88154(4)	0.64043(5)	0.9819 (2)	0.0312(2)
Pb2	8*c*	0.88709(4)	0.85020(5)	0.5744(2)	0.0308(2)
Pb3	4*b*	3/4	0.35470(9)	0.6242(3)	0.0383(4)
Ga1	4*b*	3/4	0.6960(2)	0.5920(6)	0.0121(6)
Ga2	8*c*	0.33815(9)	0.9677(2)	0.9665(4)	0.0139(4)
Ga3	4*b*	0.7500	0.5301(2)	0.9415(6)	0.0167(7)
Ga4	8*c*	0.47267(9)	0.6950(2)	0.5564(4)	0.0112(4)
Zn1	4*a*	0	0	0.0000(5)	0.0073(6)
S1	4*b*	3/4	0.6594(4)	0.951(2)	0.016(2)
S2	8*c*	0.8426(2)	0.6592(2)	0.4740(9)	0.0136(9)
S3	8*c*	0.9188(2)	0.9935(3)	0.7689(8)	0.0128(9)
S4	8*c*	0.4921(2)	0.8077(2)	0.7123(8)	0.0129(2)
S5	8*c*	0.9972(2)	0.5954(2)	0.7413(8)	0.0131(9)
S6	4*b*	3/4	0.8207(3)	0.564(2)	0.0153(2)
S7	8*c*	0.8715(2)	0.7978(2)	0.9940(9)	0.0129(9)
S8	8*c*	0.8334(2)	0.4792(3)	0.7956(8)	0.0135(9)
S9	4*b*	3/4	0.9931(4)	0.796(2)	0.0126(2)

Table S3. Selected bond lengths (Å) and angles (deg) for $Pb_5Ga_6ZnS_{15}$.

Pb1-S7	2.832(4)	Ga2-S2	2.279(5)	S8-Ga3-S8	110.4(3)
Pb1-S1	2.951(2)	Ga2-S3	2.284(5)	S8-Ga3-S9*2	105.6 (2)
Pb1-S4	2.994(5)	Ga2-S9	2.337(4)	S8-Ga3-S1*2	114.5(2)
Pb1-S5	3.083(5)	Ga3-S8*2	2.258(5)	S9-Ga3-S1	105.4(3)
Pb1-S2	3.201(6)	Ga3-S9	2.304(7)	S5-Ga4-S4	111.4 (2)
Pb1-S3	3.289(5)	Ga3-S1	2.319(8)	S5-Ga4-S4	115.6(2)
Pb1-S8	3.294(5)	Ga4-S5	2.227(5)	S4-Ga4-S4	110.6 (2)
Pb1-S2	3.295(6)	Ga4-S4	2.281(5)	S5-Ga4-S7	115.4(2)
Pb2-S7	2.797(6)	Ga4-S4	2.284(5)	S4-Ga4-S7	100.3(2)
Pb2-S4	2.921(5)	Ga4-S7	2.287(5)	S4-Ga4-S7	102.0(2)
Pb2-S3	2.927(5)	Zn1-S5*2	2.278(5)	S5-Zn1-S5	97.5(3)
Pb2-S6	3.094 (2)	Zn1-S3*2	2.311(5)	S5-Zn1-S3*2	113.2(2)
Pb2-S8	3.129(5)	S6-Ga1-S2*2	105.23(2)	S5-Zn1-S3*2	115.3 (2)
Pb2-S5	3.445(5)	S2-Ga1-S2	128.8(3)	S3-Zn1-S3	103.0(3)
Pb3-S7*2	2.999(5)	S6-Ga1-S1	110.8(3)		
Pb3-S8*2	3.092(5)	S2-Ga1-S1*2	103.1(2)		
Pb3-S9	3.214(7)	S8-Ga2-S2	113.8(2)		
Pb3-S6	2.804(9)	S8-Ga2-S3	113.4(2)		
Ga1-S6	2.244(7)	S2-Ga2-S3	106.3(2)		
Ga1-S2*2	2.283(5)	S8-Ga2-S9	104.2(2)		
Ga1-S1	2.327(8)	S2-Ga2-S9	110.3(2)		
Ga2-S8	2.261(5)	S3-Ga2-S9	108.8(2)		

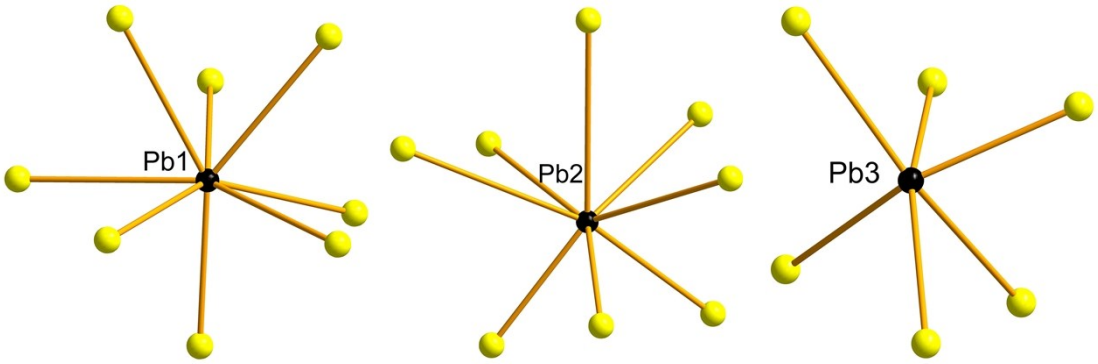


Figure S3. The coordination environment of Pb with S (The black and yellow balls represent Pb and S atoms)

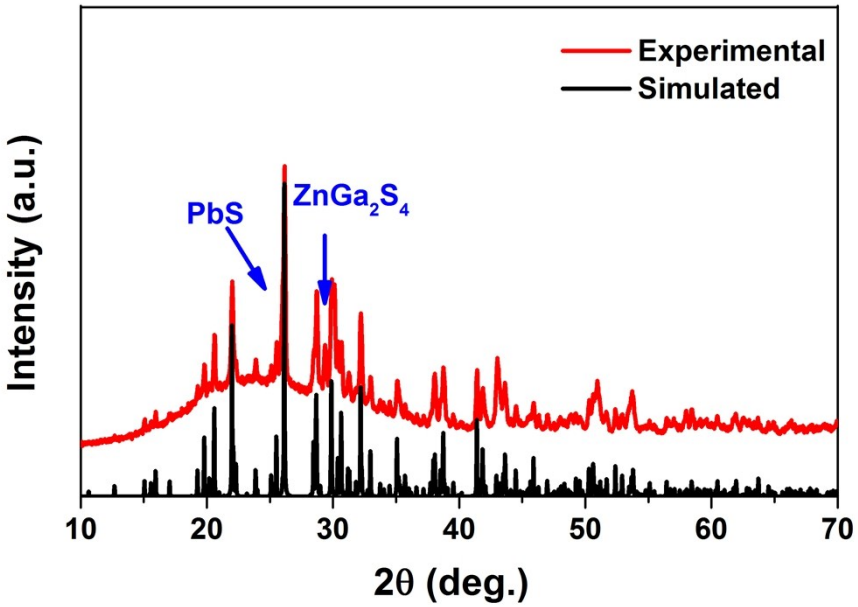


Figure S4. Experimental and simulated powder XRD of $Pb_5Ga_6ZnS_{15}$.

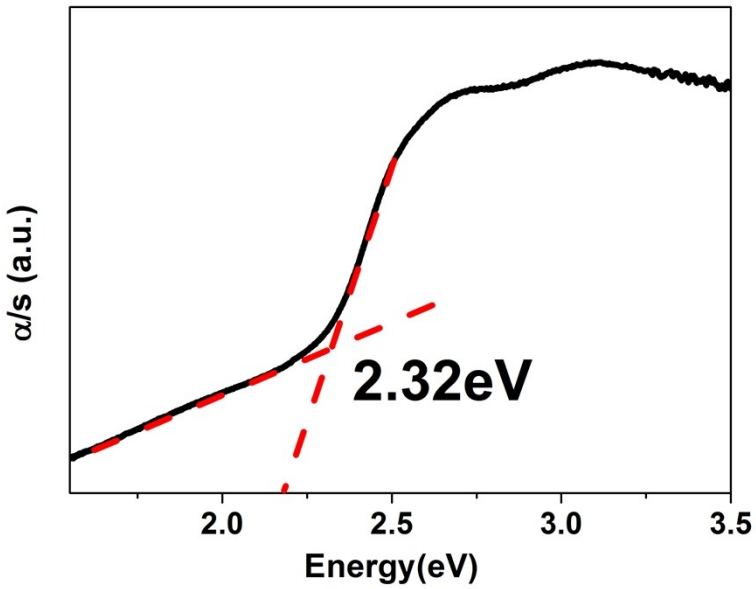
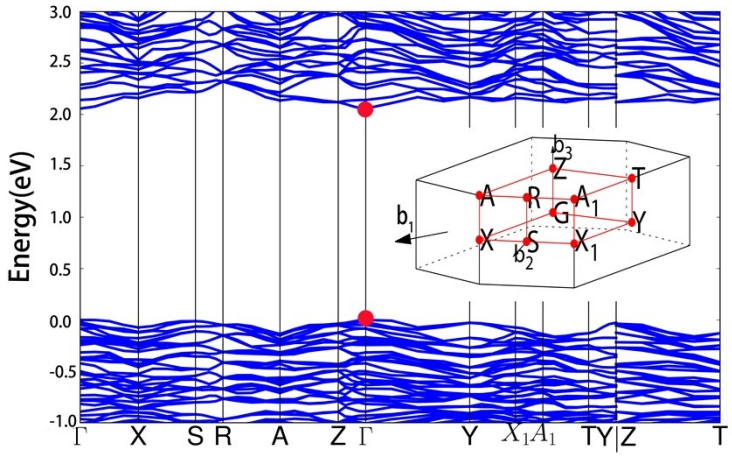


Figure S5. UV-Vis diffuse reflection spectra of $Pb_5Ga_6ZnS_{15}$.



Figrue S6. Caculated band structure of $Pb_5Ga_6ZnS_{15}$ and the Brillouin zones (BZ)

(inset panel).

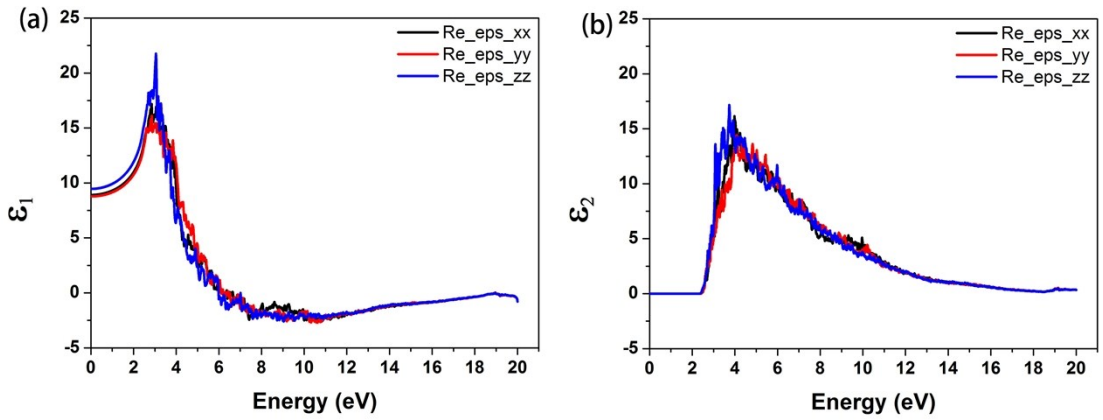


Figure S7. Energy dependences of (a) the real part ε_1 and (b) imaginary part ε_2 in $Pb_5Ga_6ZnS_{15}$.

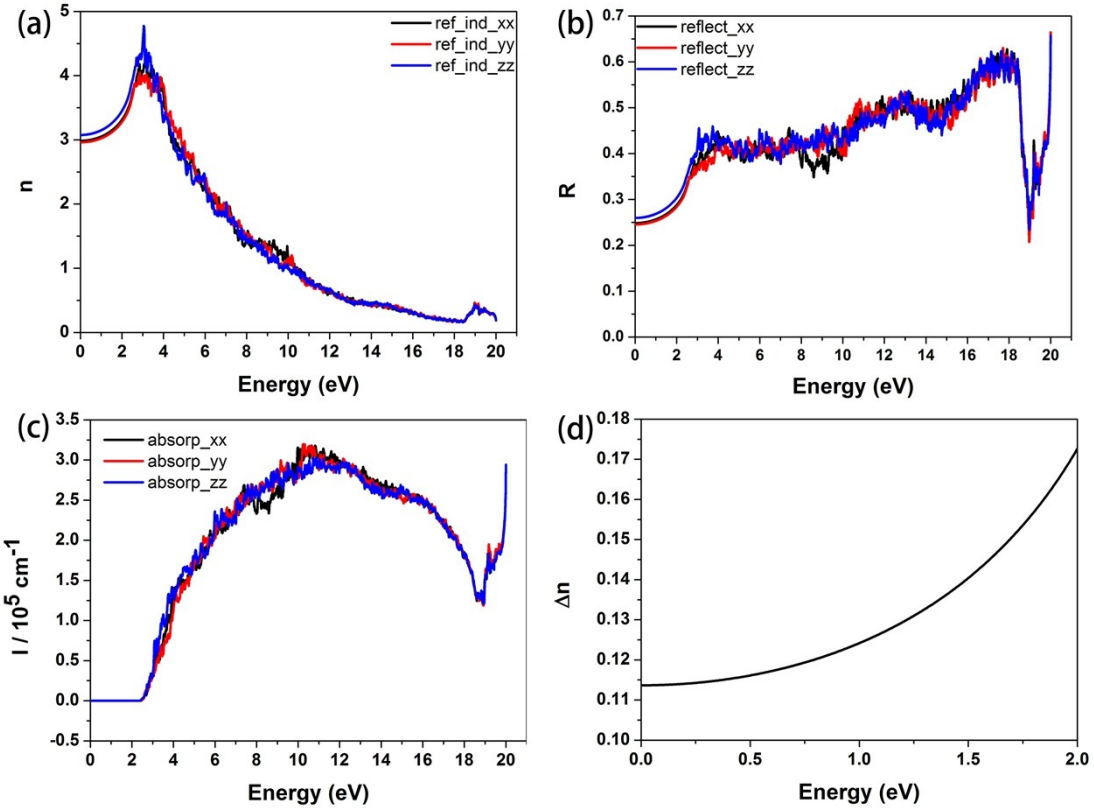


Figure S8. The calculated optical properties of $Pb_5Ga_6ZnS_{15}$ (a) variations of the refractive index n, (b) the reflectivity R, (c) the absorption coefficient α, (d) the birefringence ($\triangle n$).

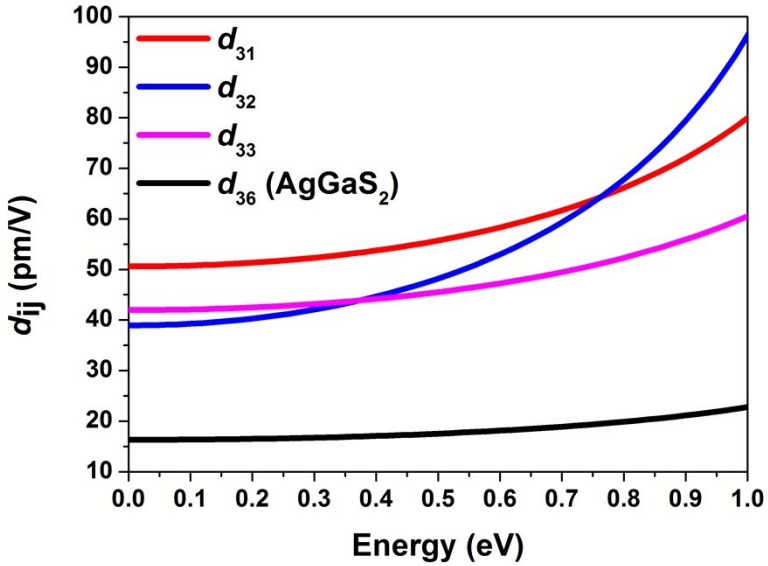


Figure S9. Calculated frequency-dependent second harmonic generation coefficients for $Pb_5Ga_6ZnS_{15}$ and $AgGaS_2$.

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