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Electronic Supplementary Information (ESI)

Quaternary Semiconductor $Ba_8Zn_4Ga_2S_{15}$ Featuring Unique One-dimensional Chains and Exhibiting Desirable Yellow Emission

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1 Experimental Section

1.1 Materials and Instruments

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. 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. Meanwhile, An Ultima-2 inductively coupled plasma emission spectrometer (ICP-OES) was used to quantitatively determine the composition of the polycrystalline powder of the title compound. 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 is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.[1] Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out on a NETZSCH STA 449C thermal analyzer. Photoluminescence spectra were recorded in the range of 300–750 nm by a FLS920 spectrofluorometer at room temperature.

1.2 Synthesis of $Ba_8Zn_4Ga_2S_{15}$.

The homogenous polycrystalline $Ba_8Zn_4Ga_2S_{15}$ was obtained in a preparation based on the precursors BaS (2N), ZnS (4N), and Ga_2S_3 (3N) in the ratio of 8:4:1 ratios by the high-temperature solid-state reaction. The starting materials were loaded into a graphite crucible under 10^{-3} Pa atmosphere, and finally placed in a temperature-controlled tube furnace. The heating profile was heating to 1123 K in 35 h, dwelling for 100 h, and then cooling to 573 K in 110 h. The homogeneity of the product was confirmed by the powder X-ray diffraction (PXRD) patterns. Crystals $Ba_8Zn_4Ga_2S_{15}$ are stable in air for more than half a year so far. The semi-quantitative element constitution was confirmed by EDX using a JSM-6700F SEM on several single crystals and the measurements showed the presence of Ba/Zn/Ga/S at an approximate molar ratio of 8:4:2:15, which agrees well with the formula determined by single-crystal XRD.

1.3 Single crystal X-ray Crystallography. The single-crystal diffraction data collections was taken on a Mercury CCD equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room-temperature. The absorption correction was done using the multiscan method.[2] and the structure was solved by the direct methods and refined by the full-matrix least-square fitting on F^2 using the *SHELX–2014* software.[3] All of the non-hydrogen atoms were refined with anisotropic thermal parameters and the coordinates were standardized using *STRUCTURE TIDY*.[4] The assignments of Ba and S were determined on the basis of the interatomic distances and relative displacement parameters. It is difficult to distinguish Zn and Ga atoms in the assignment of three tetrahedral sites (M1, M2 and M3) 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,[5] $V_i = \Sigma S_{ij}$, 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. The VBS calculation suggests that M3 site is more reasonable to be assigned as Ga (VBS = 2.98), rather than Zn (VBS = 2.45). While for M1 and M2 sites, they are more reasonable to be assigned as Zn (M1: VBS = 1.83; M2: VBS = 2.19) rather than Ga (M1: VBS = 2.23; M2: VBS = 2.67) atoms. Such an assignment generated a formula of $Ba_8Zn_4Ga_2S_{15}$, which satisfied the charge-balance requirement and the ICP and EDX results (Zn/Ga = 2:1). Nevertheless, we had also tried to refine the structure with different mixed occupancies of Zn/Ga in three M sites. However, such treatments generated unreasonable temperature factors, short bond distance, unacceptable R values, or large residual peaks. Therefore, the refinement of the structure was correct. The refinement details are summarized in Table S1. The positional coordinates and isotropic equivalent thermal parameters are given in Table S2, and the selected bond distances are listed in Table S3. CCDC number: 1922207.

2 Electronic Structure Calculations

The electronic structures were calculated using the Vienna *ab initio simulation* package VASP[6] to investigate the structure-property relationship in more detail. The following orbital electrons of Ba: $5s^25p^66s^2$, Zn: $3d^{10}4s^2$, Ga: $3d^{10}4s^24p^1$ and S: $3s^23p^4$ were treated as valence electrons. The exchange-correlation functional was calculated by the local density approximation (LDA).[7] A plane wave basis set energy cut-off of 500 eV with the projector augmented wave (PAW) potentials was used,[8,9] and a 5×5×3 Monkhorst-Pack *k*-point grid was chosen. The Fermi level was set at 0 eV. All structural geometries were fully relaxed until the residual forces on each atom was less than 0.01 eV/Å and the total energy varied by less than 1.0×10^{-5} eV.

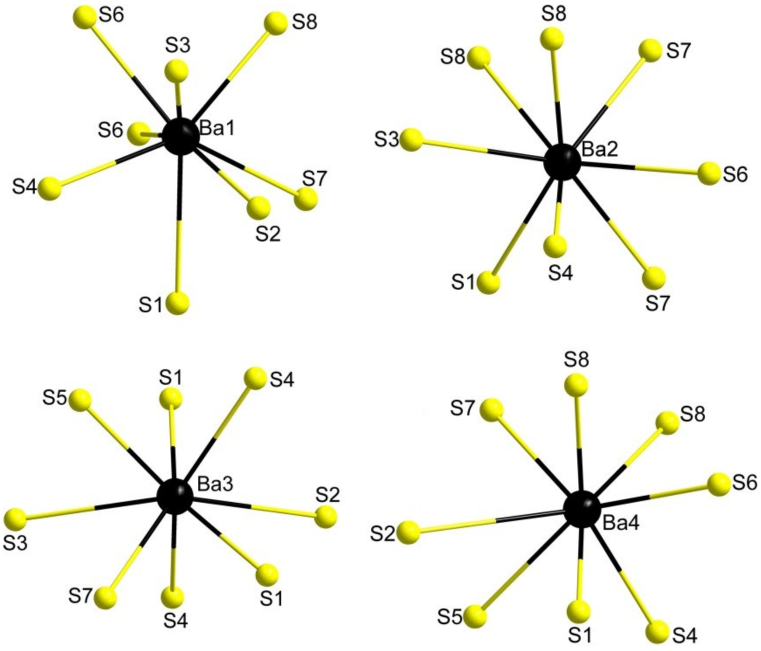


Fig. S1 Coordination geometry of Ba atoms in $Ba_8Zn_4Ga_2S_{15}$.

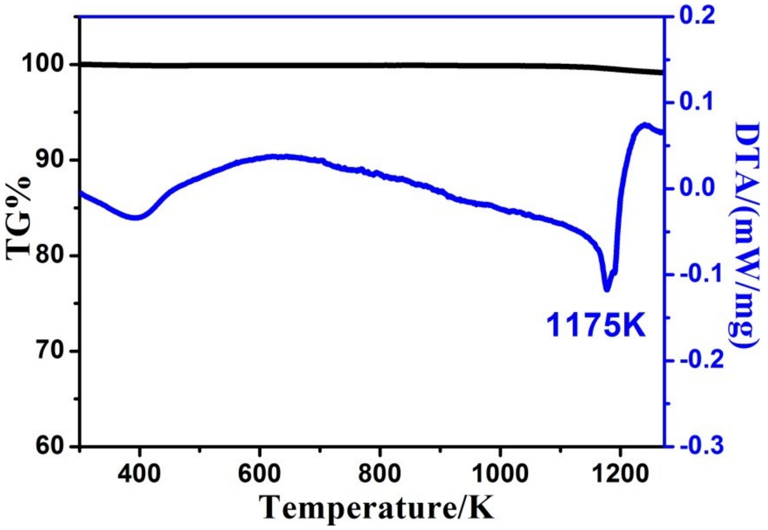
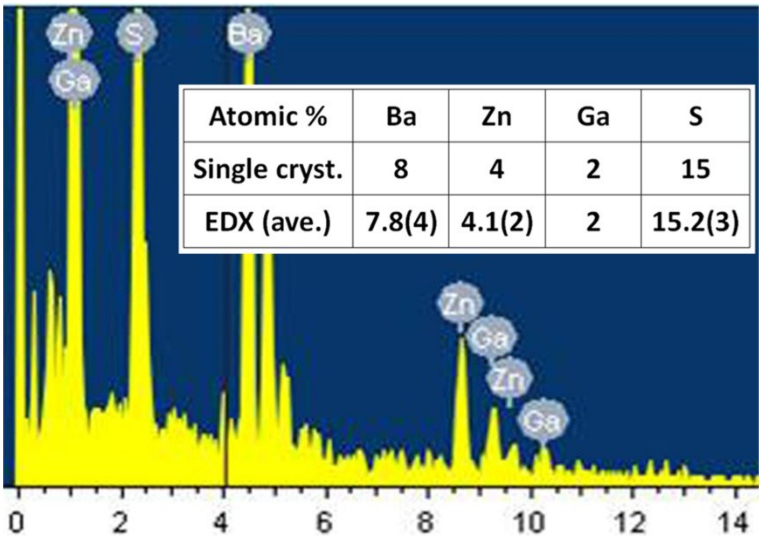


Fig. S2 The TG and DTA curves of $Ba_8Zn_4Ga_2S_{15}$.



Atomic %	Ba	Zn	Ga	S
Single cryst.	8	4	2	15
EDX (ave.)	7.8(4)	4.1(2)	2	15.2(3)

Fig. S3 The EDX results of $Ba_8Zn_4Ga_2S_{15}$.

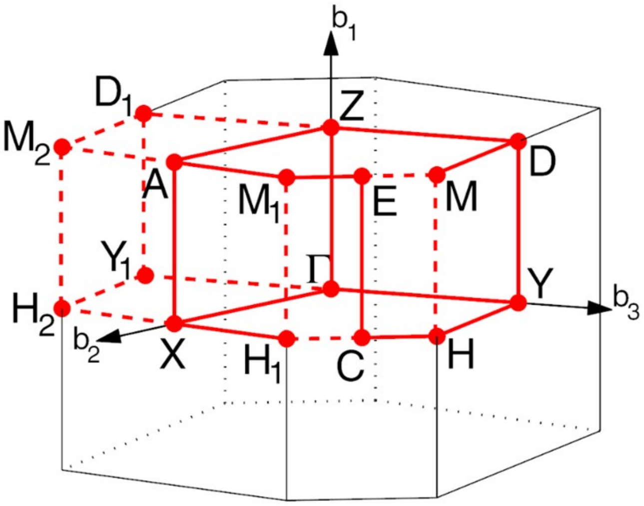


Fig. S4 The Brillouin zone with symmetry points.

Table S1. Crystallographic data and refinement details for $Ba_8Zn_4Ga_2S_{15}$.

Empirical formula	$Ba_8Zn_4Ga_2S_{15}$
Formula weight	1980.54
Temperature(K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$ (No.14)
a (Å)	13.328(2)
b (Å)	9.0097(4)
c (Å)	13.332(2)
α (°)	90
β (°)	109.520(5)
γ (°)	90
V (Å^3)	1508.8(2)
Z	2
D_c (g·cm^{-3})	4.359
μ (mm^{-1})	16.148
GOOF on F^2	1.084
R_1, wR_2 ($I > 2\sigma(I)$) [a]	0.0223, 0.0466
R_1, wR_2 (all data)	0.0260, 0.0481
Largest diff. peak and hole (e·Å^{-3})	1.053, –2.355

[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 $Ba_8Zn_4Ga_2S_{15}$.

Atom	Wyck.	x	y	z	$U_{(eq)}$(Å^2)^a	Occ.
Ba1	4*e*	0.83429(2)	0.07953(3)	0.02051(2)	0.01235(7)	1.0
Ba2	4*e*	0.54567(2)	0.90629(3)	0.66568(2)	0.01465(7)	1.0
Ba3	4*e*	0.77039(2)	0.07886(3)	0.33047(2)	0.01469(7)	1.0
Ba4	4*e*	0.60076(2)	0.38754(3)	0.80504(2)	0.01405(7)	1.0
Zn1	4*e*	0.55801(7)	0.90526(7)	0.08161(5)	0.03544(19)	1.0
Zn2	4*e*	0.01613(5)	0.20061(6)	0.61305(4)	0.01171(12)	1.0
Ga	4*e*	0.78809(4)	0.68233(5)	0.90060(4)	0.00941(11)	1.0
S1	4*e*	0.90374(11)	0.32425(13)	0.25224(9)	0.0170(3)	1.0
S2	4*e*	0.61349(10)	0.13775(13)	0.04784(10)	0.0175(3)	1.0
S3	4*e*	0.65474(10)	0.81267(13)	0.93580(9)	0.0144(2)	1.0
S4	4*e*	0.90331(10)	0.86024(13)	0.21380(9)	0.0131(2)	1.0
S5	2*b*	0	0	0.5	0.0202(4)	1.0
S6	4*e*	0.05753(10)	0.19432(13)	0.05466(9)	0.0142(2)	1.0
S7	4*e*	0.81947(10)	0.46356(12)	0.99037(8)	0.0120(2)	1.0
S8	4*e*	0.76494(10)	0.13602(13)	0.77728(9)	0.0143(2)	1.0

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

Table S3. Selected bond lengths (Å) and angles (°) of $Ba_8Zn_4Ga_2S_{15}$.

Zn1–S1	2.224(2)	Ba2–S7	3.213(2)	∠S1–Zn1–S2	120.60(5)
Zn1–S2	2.315(2)	Ba2–S4	3.255(2)	∠S1–Zn1–S2	120.73(6)
Zn1–S2	2.392(2)	Ba2–S7	3.349(2)	∠S2–Zn1–S2	107.26(5)
Zn1–S3	2.795(2)	Ba2–S6	3.387(2)	∠S1–Zn1–S3	126.12(6)
Zn2–S4	2.264(2)	Ba2–S8	3.406(2)	∠S2–Zn1–S3	83.31(5)
Zn2–S2	2.305(2)	Ba2–S8	3.483(2)	∠S2–Zn1–S3	90.10(5)
Zn2–S5	2.317(5)	Ba2–S1	3.501(2)	∠S4–Zn2–S2	113.74(5)
Zn2–S3	2.375(2)	Ba2–S3	3.507(2)	∠S4–Zn2–S5	112.55(4)
Ga–S6	2.237(2)	Ba3–S7	3.183(2)	∠S2–Zn2–S5	100.89(4)
Ga–S7	2.271(2)	Ba3–S1	3.187(2)	∠S4–Zn2–S3	117.87(5)
Ga–S8	2.275(2)	Ba3–S5	3.218(4)	∠S2–Zn2–S3	103.72(5)
Ga–S3	2.305(2)	Ba3–S1	3.221(2)	∠S5–Zn2–S3	106.33(4)
Ba1–S6	3.037(2)	Ba3–S4	3.350(2)	∠S6–Ga–S7	107.45(5)
Ba1–S8	3.103(2)	Ba3–S4	3.358(2)	∠S6–Ga–S8	107.88(5)
Ba1–S3	3.128(2)	Ba3–S3	3.614(2)	∠S7–Ga–S8	109.17(5)
Ba1–S4	3.131(2)	Ba3–S2	3.686(2)	∠S6–Ga–S3	113.30(5)
Ba1–S6	3.184(2)	Ba4–S1	3.129(2)	∠S7–Ga–S3	110.68(5)
Ba1–S3	3.313(2)	Ba4–S7	3.203(2)	∠S8–Ga–S3	108.28(5)
Ba1–S7	3.482(2)	Ba4–S8	3.256(2)		
Ba1–S1	3.654(2)	Ba4–S8	3.276(2)		
		Ba4–S6	3.276(2)		
		Ba4–S4	3.381(2)		
		Ba4–S5	3.4522(4)		
		Ba4–S5	3.899(4)		

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