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Contribution of Disulfide S_2^{2-} Anions to the Crystal and Electronic Structures in Ternary Sulfides, $Ba_{12}In_4S_{19}$, $Ba_4M_2S_8$ (M = Ga, In)

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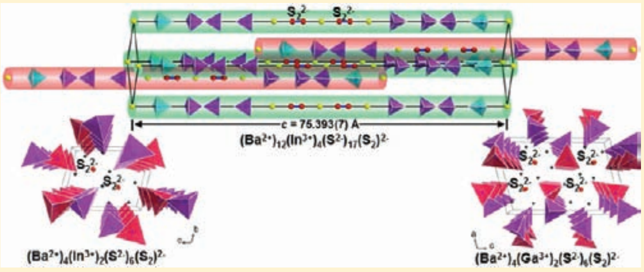
S *Supporting Information*



ABSTRACT: Three semiconducting ternary sulfides have been synthesized from the mixture of elements with about 20% excess of sulfur (to establish oxidant rich conditions) by solid-state reactions at high temperature. $Ba_{12}In_4S_{19} \equiv (Ba^{2+})_{12}(In^{3+})_4(S^{2-})_{17}(S_2)^{2-}$, **1**, crystallizes in the trigonal space group $R\overline{3}$ with $a = 9.6182(5)$ Å, $b = 9.6182(5)$ Å, $c = 75.393(7)$ Å, and $Z = 6$, with a unique long period-stacking structure of a combination of monometallic InS_4 tetrahedra, linear dimeric In_2S_7 tetrahedra, disulfide S_2^{2-} anions, and isolated sulfide S^{2-} anions that is further enveloped by Ba^{2+} cations. $Ba_4In_2S_8 \equiv (Ba^{2+})_4(In^{3+})_2(S^{2-})_6(S_2)^{2-}$, **2**, crystallizes in the triclinic space group $P\overline{1}$ with $a = 6.236(2)$ Å, $b = 10.014(4)$ Å, $c = 13.033(5)$ Å, $\alpha = 104.236(6)°$, $\beta = 90.412(4)°$, $\gamma = 91.052(6)°$, and $Z = 2$. $Ba_4Ga_2S_8 \equiv (Ba^{2+})_4(Ga^{3+})_2(S^{2-})_6(S_2)^{2-}$, **3**, crystallizes in the monoclinic $P2_1/c$ with $a = 12.739(5)$ Å, $b = 6.201(2)$ Å, $c = 19.830(8)$ Å, $\beta = 104.254(6)°$ and $Z = 4$. Compounds **2** and **3** represent the first one-dimensional (1D) chain structure in ternary Ba/M/S (M = In, Ga) systems. The optical band gaps of **1** and **3** are measured to be around 2.55 eV, which agrees with their yellow color and the calculation results. The CASTEP calculations also reveal that the disulfide S_2^{2-} anions in **1**−**3** contribute mainly to the bottom of the conduction bands and the top of valence bands, and thus determine the band gaps.

INTRODUCTION

Ternary and quaternary gallium or indium chalcogenides show rich structural chemistry and interesting physical properties; among them, some are important nonlinear optical (NLO) materials, such as $AgGaQ_2$ (Q = S, Se),[1,2] $LiInQ_2$ (Q = S, Se),[3,4] $LiGaQ_2$ (Q = S, Se, Te),[5,6] $BaGa_4S_7$,[7] $Li_2Ga_2GeS_6$[8] and $Ag_2Ga_2GeS_6$,[9−12] and some show interesting photovoltaic properties, such as $CuInS_2$.[13] The known ternary Ba/M/S (M = In, Ga) compounds include $Ba_2In_2S_5$,[14] $BaIn_2S_4$,[15] $BaGa_4S_7$,[16] $Ba_2Ga_2S_5$,[17] $Ba_3Ga_2S_6$,[18] $Ba_4Ga_2S_7$,[18] $Ba_5Ga_2S_8$,[19] and $BaGa_2S_4$,[20] and each of them shows that its own structure type is constructed from the same primary building unit, a MS_4 tetrahedron, in a corner- or edge-sharing manner. Examples are a three-dimensional (3D) framework in $BaGa_4S_7$;[16] a two-dimensional (2D) network in $Ba_2In_2S_5$;[14] tetranuclear Ga_4S_{10} anions in $Ba_2Ga_2S_5$;[17] dimeric Ga_2S_6 in $Ba_3Ga_2S_6$,[18] or monomeric GaS_4 anion in $Ba_5Ga_2S_8$.[19]

Previous reports show that the involvement of disulfide S_2^{2-} anion can give rise to a new structure type. For example, $BaLaBi_2S_6$ is considered to be stabilized by the disulfide S_2^{2-} anions.[21] $Rb_8[Cd_2(AsS_4)_2(AsS_5)_2]$ contains a building unit of AsS_5 that coordinates the disulfide S_2^{2-} anion.[22] However, in the ternary Ba/M/S (M = Ga, In) systems, a compound containing disulfide S_2^{2-} anion is not known yet.

In this paper, three novel ternaries containing disulfide S_2^{2-} anions $Ba_{12}In_4S_{19}$, **1**, $Ba_4In_2S_8$, **2**, and $Ba_4Ga_2S_8$, **3**, were synthesized with excess sulfur (to establish oxidant rich conditions) by solid-state reactions. Different from the common building unit in Ba/In/S compounds, such as monometallic InS_4,[23] dimeric In_2S_6,[24] and tetranuclear In_4S_{10},[25] the dimeric In_2S_7 tetrahedra in **1** is unique. Compounds **2** and **3** represent the first one-dimensional (1D) chain structure in ternary Ba/M/S (M = In, Ga) systems. The optical band gaps of **1** and **3** were measured, and the band structures were studied with the aid of CASTEP.

EXPERIMENTAL SECTION

Materials and Method. The elements were used as acquired and stored in an Ar-filled glovebox (moisture and oxygen level is less than 0.1 ppm), and all manipulations were performed inside the glovebox. The Ba (99%) was purchased from Alfa Aesar China Co., Ltd. (Tianjin, China). The Ni (99.5%), In (99.999%), Ga (99.999%), and S (99.999%) were purchased from Sinopharm Chemical Reagent Co., Ltd.

*Synthesis of $Ba_{12}In_4S_{19}$, **1**.* The single crystal of $Ba_{12}In_4S_{19}$ was first obtained from the elemental mixture of Ba, Ni, In, and S with a ratio of 2:1:1:6 at 850 °C. The mixture of Ba, Ni, In, and S were weighed

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Table 1. Crystallographic Data and Refinement Details for 1−3

	$Ba_{12}In_4S_{19}$, **1**	$Ba_4In_2S_8$, **2**	$Ba_4Ga_2S_8$, **3**
fw	2716.494	517.744	472.644
crystal system	trigonal	triclinic	monoclinic
Z	6	2	4
space group	$R\bar{3}$ (No. 148)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	9.6182(5)	6.236(2)	12.739(5)
b (Å)	9.6182(5)	10.014(4)	6.201(2)
c (Å)	75.393(7)	13.033(5)	19.830(8)
α (deg.)	90	104.236(6)	90
β (deg.)	90	90.412(4)	104.254(6)
γ (deg.)	120	91.052(6)	90
V (Å^3)	6040.1(7)	788.7(5)	1518(2)
D_c (g cm^{-3})	4.481	4.36	4.135
μ (mm^{-1})	14.744	13.724	14.768
F (000)	7032	900	1656
θ range (deg)	2.43 to 27.48	2.10 to 27.46	2.99 to 27.48
GOF on F^2	1.075	1.125	1.082
$R1$, $wR2$ ($I > 2\sigma(I)$)[a]	0.0485, 0.0830	0.0362, 0.0879	0.0275, 0.0640
$R1$, $wR2$ (all data)	0.0770, 0.0941	0.0426, 0.0929	0.0318, 0.0669
diff peak, hole (e Å^{-3})	3.517, −1.722	1.444, −1.867	1.323, −1.672

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

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Ba_{12}In_4S_{19}$, 1

atom	Wyck.	x	y	z	U(eq)(Å^2) [a]	occu.
Ba1	18*f*	0.07532(8)	0.35177(8)	0.187640(8)	0.0139(2)	1
Ba2	18*f*	0.04967(8)	0.32677(8)	0.104397(9)	0.0145(2)	1
Ba3	18*f*	0.07933(8)	0.34959(8)	0.270798(9)	0.0149(2)	1
Ba4	18*f*	0.07266(8)	0.33335(8)	0.020601(9)	0.0162(2)	1
In1	6*c*	0	0	0.30338(2)	0.0138(3)	1
In2	6*c*	0	0	0.2359(2)	0.013(2)	0.203(3)
In3	6*c*	0	0	0.22183(3)	0.0154(5)	0.797(3)
In4	6*c*	0	0	0.15337(2)	0.0167(3)	1
In5	6*c*	0	0	0.07110(2)	0.0130(3)	1
S1	6*c*	0	0	0.42345(7)	0.015(2)	1
S2	6*c*	0	0	0.45197(7)	0.015(2)	1
S3	18*f*	0.2461(3)	0.0005(4)	0.31271(4)	0.017(2)	1
S4	6*c*	0	0	0.27094(6)	0.014(2)	1
S5	18*f*	0.0105(3)	0.2517(3)	0.22894(4)	0.0140(6)	1
S6	6*c*	0	0	0.18750(7)	0.013(2)	1
S7	18*f*	0.0072(3)	0.2505(3)	0.14624(4)	0.0142(6)	1
S8	6*c*	0	0	0.10360(7)	0.015(2)	1
S9	18*f*	0.0135(3)	0.2512(3)	0.06215(4)	0.0144(6)	1
S10	3*a*	0	0	0	0.020(2)	1
S11	3*b*	0	0	0.5	0.013(2)	1
S12	6*c*	0	0	0.37346(7)	0.016(2)	1

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

accordingly with an overall loading of about 300 mg and loaded into a graphite crucible and then sealed in an evacuated silica tube under vacuum at 10^{-3} Pa. The sealed assembly was placed into a temperature-controlled tube furnace, heated to 850 °C in 36 h, and annealed at this temperature for 144 h, then slowly cooled at 3 °C/h to 200 °C before the furnace was turned off, and finally the sample was cooled radiatively to ambient temperature in the furnace. The energy dispersive X-ray spectroscopy (EDX) results on single crystals of **1** confirm the presence of only Ba, In, and S. The EDX analyses gave an average atomic percentage of 29.5% Ba, 11.4% In, and 59.1% S, which are consistent in principle with the calculated values: 34.3% Ba, 11.4% In, and 54.3% S. Neither Ni nor another element, such as Si or O from the reaction container, was found.

After the establishment of the structure of **1**, the stoichiometric synthesis of the Ba, In, S elemental mixture had been carried out, but none of them had yielded the target compound. After careful re-study of the crystal structure, we noticed that the disulfide S_2^{2-} anions are important to the structure. We therefore considered that extra sulfur may be crucial for the growth of the crystal. Then, different experimental conditions were explored, such as changing the annealing temperature from 850 to 1100, 950, 700, 650, and 600 °C and changing the excess amount of sulfur from 5% to 10−25%. Finally, **1** was synthesized as a major phase (about 85%, Supporting Information, Figure S1) together with a byproduct of $Ba_2In_2S_5$[15] when 20% excess S was loaded and the annealing temperature was 850 °C. Compound **1** and $Ba_2In_2S_5$ are of different color (yellow vs light-yellow); further property measurements on **1** were made on the handpicked crystals.

Syntheses of $Ba_4In_2S_8$, ***2***. In the effort to obtain the single-phased compound **1**, another yellow rod-shaped crystal, **2**, was found. The EDX results on single crystals of **2** confirm the presence of only Ba, In, and S. The EDX analyses gave average atomic percentages of (obs./cal.%) Ba: 24.6/28.6; In: 13.1/14.3; and S: 62.3/57.1. Unfortunately, the pure phased **2** is extremely difficult to synthesize. The stoichiometric reaction did not yield the target compound as well as many other attempts, such as at different anneal temperatures, 850, 950, 1000, or 1050 °C; different amount of the excess of S, 5 to 45%, or different amount of the excess of Ba, 5 to 25%. The best result that can be achieved under the experimental conditions is a mixture of **2** (∼40%) and $Ba_2In_2S_5$[15] (Supporting Information, Figure S2) with excess amount of Ba (5%) and S (19%) annealed at 850 °C.

Synthesis of $Ba_4Ga_2S_8$, ***3***. The synthesis of the Ga analogue of **2** had been attempted with similar conditions. Single phased **3** with yellow rod-shaped crystals were produced (>95%, Supporting Information, Figure S3) when excess Ba (5%) and S (19%) were loaded and annealed at 850 °C for 96 h. The EDX results on single crystals of **3** confirm the presence of only Ba, Ga, and S with an average atomic percentage of (obs./cal.%): Ba: 24.9/28.6; Ga: 9.7/14.3; and S: 65.4/57.1. Although compounds **2** and **3** have the same stoichiometry and similar structural motif, their crystallographic structures are different as detailed below.

Many inorganic solids containing the S_2^{2-} anion, such as $Rb_8[Cd_2(AsS_4)_2(AsS_5)_2]$[22] and $Cs_2Ti_2(P_2S_8)(PS_4)_2$,[26] were synthesized by the reactive flux method because the melting points of As_2S_3, Rb_2S, Cs_2S_3, and P_2S_5 are relatively low, ∼310, ∼650, ∼213, and ∼300 °C, respectively. However, such a method is impractical in the Ba/M/S (M = Ga, In) systems because the melting points of BaS and In_2S_3 are high (BaS: ∼1050 °C, In_2S_3: ∼1090 °C). On the other hand, since sulfur will partially volatilize under the anneal temperature so as to pervade the reaction container, the stoichiometric syntheses all failed to produce the single-phased title compounds. Finally, the optimal experimental conditions were established, which requires the presence of about 20% excess S in the starting reactants. We consider that the sulfur in these reactions acts as reagent as well as flux. More importantly, the excess sulfur establishes an oxidant rich reaction environment, under which the sulfur element cannot be fully reduced to its lowest oxidation state; therefore, the disulfide anions can be formed.

Crystal Structure Determinations. *$Ba_{12}In_4S_{19}$,* ***1***. Single crystal data collections were performed on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K using ω scans. The data were corrected for

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Ba_4In_2S_8$, 2

atom	Wyck.	x	y	z	U(eq) (Å^2)[a]	occu.
Ba1	2i	0.25418(9)	0.62166(5)	0.47760(4)	0.0144(2)	1
Ba2	2i	0.23774(9)	0.07810(5)	0.38171(4)	0.0155(2)	1
Ba3	2i	0.74110(9)	0.10773(5)	0.15078(4)	0.0160(2)	1
Ba4	2i	0.25584(9)	0.42479(6)	0.10794(4)	0.0163(2)	1
In1	2i	0.3207(2)	0.20772(6)	0.69669(5)	0.0149(2)	1
In2	2i	0.1688(2)	0.80323(6)	0.11118(5)	0.0158(2)	1
S1	2i	0.0780(4)	0.3481(2)	0.3126(2)	0.0172(5)	1
S2	2i	0.4174(4)	0.3475(2)	0.3132(2)	0.0178(5)	1
S3	2i	0.2308(4)	0.2208(2)	0.8800(2)	0.0174(5)	1
S4	2i	0.2391(4)	0.3372(2)	0.5706(2)	0.0161(5)	1
S5	2i	0.7357(4)	0.0415(2)	0.3932(2)	0.0163(5)	1
S6	2i	0.2789(4)	0.7442(2)	0.2767(2)	0.0168(5)	1
S7	2i	0.2444(4)	0.0406(2)	0.1133(2)	0.0180(5)	1
S8	2i	0.7519(4)	0.3687(2)	0.0486(2)	0.0156(5)	1

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

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Ba_4Ga_2S_8$, 3

atom	Wyck.	x	y	z	U(eq)(Å^2)[a]	Occu.
Ba1	4e	0.47439(3)	0.23097(4)	0.31256(2)	0.01170(9)	1
Ba2	4e	0.38318(3)	0.23480(4)	0.03681(2)	0.01147(9)	1
Ba3	4e	0.14684(3)	0.74192(4)	0.04930(2)	0.01180(9)	1
Ba4	4e	0.10533(3)	0.23604(4)	0.21312(2)	0.01308(9)	1
Ga1	4e	0.11667(5)	0.31651(9)	0.40122(3)	0.0111(2)	1
Ga2	4e	0.69690(5)	0.31156(9)	0.10111(3)	0.0107(2)	1
S1	4e	0.3136(2)	0.4039(2)	0.17262(6)	0.0136(3)	1
S2	4e	0.3138(2)	0.0628(2)	0.17221(6)	0.0134(3)	1
S3	4e	0.2697(2)	0.1789(2)	0.37349(6)	0.0123(3)	1
S4	4e	0.0386(2)	0.7348(2)	0.17695(7)	0.0122(3)	1
S5	4e	0.1162(2)	0.2451(2)	0.01250(7)	0.0124(3)	1
S6	4e	0.1317(2)	0.6832(2)	0.38393(7)	0.0144(3)	1
S7	4e	0.6114(2)	0.2330(2)	0.48420(7)	0.0118(3)	1
S8	4e	0.5819(2)	0.2247(2)	0.16454(7)	0.0135(3)	1

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

Lorentz and polarization factors. Absorption corrections were performed by the SADABS program.[27,28] All structures were solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[29]

The assignments of Ba, In, and S were determined on the basis of the interatomic distances and relative displacement parameters. All of the atoms were refined with anisotropic thermal parameters and a secondary extinction correction. The final atomic positions were standardized with the Structure Tidy program. The structure was solved and refined successfully in the $R\bar{3}$ space group. After the first refinement, the isotropic temperature factor for In3 was very high (U(eq) = 0.035 in comparison with those of In1 (0.014), In4 (0.017), and In5 (0.013)) and large R values of $R1$ = 0.0727 and $wR2$ = 0.1414. At a distance of 1.062 Å from In3, a high electron density peak that behaved as an Indium atom was found and was assigned as In2. In the following refinement, the occupancies of In2 and In3 were allowed to vary, the refinement was converged to better R values ($R1/wR2$ = 0.0485/0.0941), and comparative temperature factors (0.015 and 0.013) for In3 and In2 atoms with occupancies of 79.96 and 20.57%, respectively, were obtained. To satisfy the charge balance requirements, the sum of the occupancy of In3 and In2 was constrained to be 1.0; after this procedure, the occupancies of In3 and In2 were 79.7 and 20.3%, respectively. Crystallographic data and structural refinement details are presented in Table 1, the positional coordinates and isotropic equivalent thermal parameters are given in Table 2.

*$Ba_4In_2S_8$, **2** and $Ba_4Ga_2S_8$, **3**.* Data collections were performed on a Rigaku Saturn724 CCD equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K using ω scans. The data were corrected for Lorentz and polarization factors. Absorption corrections were performed by the SADABS program.[27,28] All structures were solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[29] All atoms were refined with anisotropic thermal parameters. All positions were fully occupied. Apparently, the unit cell parameters of **2** could be transferred roughly into those of **3** via a matrix of (0 0 1, 1 0 0, 0 2 0). This seemed to suggest that the symmetry of **2** listed in Table 1 was wrong. Then, we attempted to solve the structure of **2** in a monoclinic symmetry. First, a check on **2** with the aid of PLATON[30,31] gave no hint for any higher symmetry. Nevertheless, we had tried to refine the structure in the monoclinic system with an input space group of $P2_1/c$. Note that such treatment generated an unreasonable R_{int} = 0.3504 (vs R_{int} = 0.0408 for **2** in triclinic system; and 0.0321 for **3** in monoclinic system). Subsequently, a raw structure of "$Ba_4In_2S_8$" could be obtained, which was isostructural with **3**. However, the ADP of all the atoms were nonpositive definite; S3 and S6 showed extraordinary large temperature factors (5 times larger than other sulfur atoms); and the residual peak was large, 4.95 e Å^{-3} vs 1.444 in triclinic; R_1/wR_2 ($I > 2\sigma(I)$) values of 0.1537/0.4090 were definitely unreasonable (vs 0.0362/0.0879 in triclinic). All these data indicated that **2** should be solved in the triclinic system as listed in Table 1. The crystallographic difference between **2** and **3** might originate from the different distortion of their building units MS_4 (M = Ga, In) as described below. Despite of the stoichiometry and structural similarities of **2** and **3**, their crystallographic features are different; such a phenomenon has been found in the literature such as in the case of $Ba_2Ga_2S_5$ in $C2/c$[17] vs $Ba_2In_2S_5$ in $Fddd$.[14] Crystallographic data and structural refinement details are summarized in Table 1 as well; the positional coordinates and isotropic equivalent thermal parameters for **2** and **3** are given in Tables 3 and 4.

UV/vis Diffuse Reflectance Spectroscopy. The optical diffuse reflectance spectra of powdery samples of **3** and handpicked crystals of **1** were measured at room temperature using a Perkin-Elmer Lambda 900 UV−vis spectrophotometer equipped with an integrating sphere attachment and $BaSO_4$ as a reference. (Supporting Information, Figures S7, S8) The absorption spectra were calculated from the reflection spectra via the Kubelka−Munk function $\alpha/S = (1 - R)^2/2R$,[32] in which α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.

Powder X-ray Diffraction (XRD). The powder XRD patterns were taken at room temperature on a Rigaku DMAX 2500 diffractometer with monochromatized Cu Kα radiation. Data were collected in the range of 2θ = 5−85°.

Elemental Analysis. Microprobe elemental analysis was performed on some single crystals of **1**−**3**, including those used for X-ray diffraction analyses. Spectra were collected on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (Oxford INCA). The results indicated the presence of all Ba, In, Ga, and S elements.

Electronic Structure Calculations. First principle studies of band structures and density of states (DOS) were performed with the CASTEP code.[33] The Perdew−Burke−Ernzerhof (PBE) functional of the generalized gradient approximations (GGA)[34] was employed as the exchange-correlation function. Ultrasoft pseudopotentials[35,36] were used to treat the core electrons, in which the valence atomic configurations were $5s^25p^66s^2$, $3d^{10}4s^24p^1$, $4d^{10}5s^25p^1$, and $3s^23p^4$ for Ba, Ga, In,

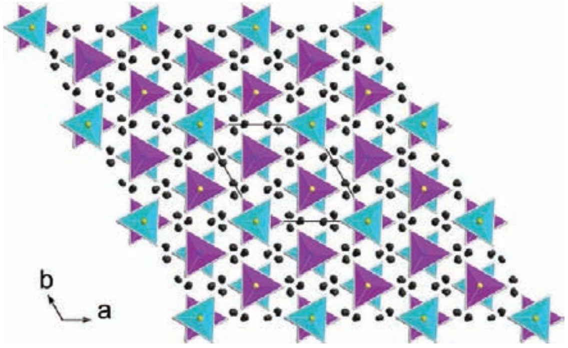

Figure 1. Structure of $Ba_{12}In_4S_{19}$, **1**, viewed approximately along the *c* axis. Black: Ba^{2+}; yellow: S^{2-} anion; light blue tetrahedra: monometallic $In5S_4$; purple tetrahedra: linear dimeric In_2S_7 and monometallic $In1S_4$.

and S, respectively. The number of plane waves was determined using a cutoff energy of 310, 310, and 295 eV along with a Monkhorst−Pack k-mesh of 3 × 3 × 3, 4 × 3 × 2 and 2 × 4 × 1 for **1**, **2** and **3**, respectively.

RESULTS AND DISCUSSION

Crystal Structure. *Structure of $Ba_{12}In_4S_{19}$,* ***1***. Compound **1** crystallizes in the trigonal space group $R\overline{3}$ with $a = 9.6182(5)$ Å, $b = 9.6182(5)$ Å, $c = 75.393(7)$ Å and features a unique long period-stacking structure of a combination of monometallic InS_4 tetrahedra, linear dimeric In_2S_7 tetrahedra, disulfide $S_2{}^{2-}$ anions, and isolated S^{2-} anions, (Figure 2) which are surrounded by Ba^{2+} cations. (Figure 1) Different from the commonly found discrete species in indium sulfides, for example, InS_4,[23] In_2S_6,[24] or In_4S_{10},[25] such a linear dimeric In_2S_7 tetrahedra is observed for the first time.

The long period-stacking of **1** is characterized by the very large *c* parameter of about 75 Å, which is about 8 times larger than the other two unit cell parameters. Such an anionic repeat unit is also described as a "column" as shown in Figure 2 by a green or a pink cylinder. The linear dimeric In_2S_7 tetrahedra are constructed by the central base-sharing In2/In3 bi-tetrahedra that are fused with $In4S_4$ tetrahedra on vertexes of S6, respectively. In3 and In2 are disordered over two crystallographic independent sites with occupancies of 79.7 and 20.3%, respectively. The In2−In3 distance is 1.062(8) Å. (Table 5) Similar positional disorder has been found on two copper atoms in La_2CuInS_5[37] in which the occupancies of Cu1 and Cu2 are 18 and 82%, respectively, and the Cu1−Cu2 distance is 0.61 Å. Note that the coordinates of the principal axial atoms in the linear dimeric In_2S_7 anion and InS_4 anion (namely, In1, S4, In2, In3, S6, and In4 atoms) differ only in *z* as listed in Table 2, which indicate that they are lined up in a straight line. (Figure 3) The isolated $In1S_4$ and $In5S_4$ tetrahedra are common building unit found in related indium sulfides, such as in La_3InS_6.[38] The two disulfide $S_2{}^{2-}$ anions are parallel to the *c* axis with a S−S bond of 2.150(7) Å, which is comparable to 2.14(1) Å in $BaLaBi_2S_6$.[21] Considering the formal oxidation state, the charge balanced formula of **1** can be described as $Ba_{12}In_4S_{19} \equiv (Ba^{2+})_{12}(In^{3+})_4(S^{2-})_{17}(S_2)^{2-}$.

There are three crystallographically independent as well as a pair of positionally disordered In atoms in **1**. Each In atom is coordinated by four S atoms in a slightly distorted tetrahedral geometry with S−In−S bond angles ranging from 102.5(2) to 115.4(2)° and In−S distances varying from 2.430(3) to 2.64(2) Å. These values are comparable to the ranges 97.19(5) to

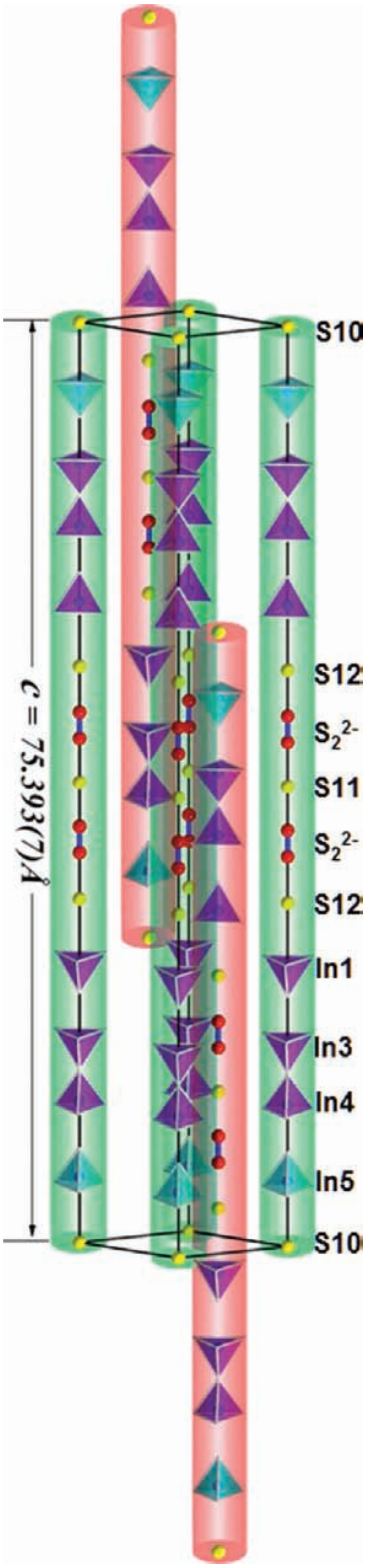

Figure 2. Side view of "column" in **1**. Cylinder confines different "column" starting at different *c*: green: starts at $c = 0$; pink: starts at $c = 1/3$. Red: disulfide $S_2{}^{2-}$ anion with S−S = 2.150(7) Å; yellow: isolated S^{2-} anion; light blue tetrahedra: monometallic $In5S_4$; purple tetrahedra: linear dimeric In_2S_7 and monometallic $In1S_4$.

Table 5. Selected Bond Distances (Å) of $Ba_{12}In_4S_{19}$, $Ba_4In_2S_8$, and $Ba_4Ga_2S_8$

bond	dist. (Å)	bond	dist. (Å)	bond	dist. (Å)
$Ba_{12}In_4S_{19}$					
S1−S2	2.150(7)	In2−S4	2.64(2)	In4−S6	2.574(5)
In2−In3	1.062(8)	In2−S5 × 3	2.430(3)	In4−S7 × 3	2.435(3)
In1−S3 × 3	2.467(3)	In3−S5 × 3	2.432(3)	In5−S8	2.450(5)
In1−S4	2.446(5)	In3−S6	2.588(5)	In5−S9 × 3	2.449(3)
$Ba_4In_2S_8$					
S1−S2	2.117(4)	In1−S5	2.499(2)	In2−S6	2.469(3)
In1−S3	2.430(2)	In1−S6	2.539(3)	In2−S7	2.408(3)
In1−S4	2.388(3)	In2−S3	2.505(3)	In2−S8	2.414(2)
$Ba_4Ga_2S_8$					
S1−S2	2.115(2)	Ga1−S5	2.241(2)	Ga2−S6	2.274(2)
Ga1−S3	2.3144(2)	Ga1−S6	2.315(2)	Ga2−S7	2.322(2)
Ga1−S4	2.250(2)	Ga2−S3	2.349(2)	Ga2−S8	2.219(2)

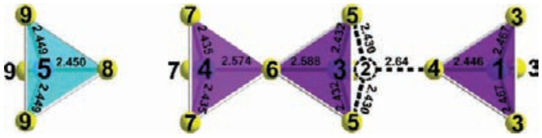

Figure 3. Monometallic InS_4 and linear dimeric In_2S_7 in **1** with atomic numbers and bond lengths (Å) marked. Blue: In; yellow: S; light blue tetrahedra: monometallic $In5S_4$; purple tetrahedra: linear dimeric In_2S_7 and monometallic $In1S_4$. In3 and In2 atoms are disordered over two 6*c* sites with occupancies of 79.7% and 20.3%, respectively.

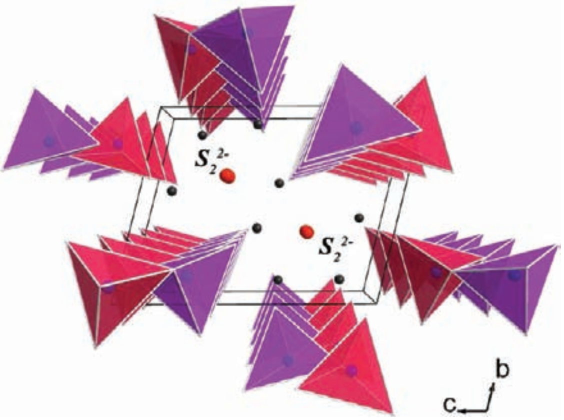

Figure 4. Structure of $Ba_4In_2S_8$, **2** viewed along *a* axis with unit cell outlined. Black, Ba^{2+}; blue, In; red, disulfide S_2^{2-} anion with S−S = 2.117(4) Å; purple and red tetrahedra, $In1S_4$ and $In2S_4$. Ba−S bonds are omitted for clarity.

118.95(5)° in $CaYbInS_4$[39] and 2.401(1) to 2.932(1) Å in $La_4Ag_2In_4S_{13}$.[40]

As shown in Supporting Information, Figure S4, Ba4 is 7-fold coordinated in a monocapped trigonal prism by S^{2-} anions. Atoms Ba1−3 are 8-fold coordinated in bicapped trigonal prisms. The difference is that the disulfide S_2^{2-} anion in $Ba2S_8$ acts as a bidentate ligand, but as a unidentate ligand in $Ba1S_8$ and $Ba3S_8$. The Ba−S distances vary from 2.9340(7) to 3.588(3) Å, which are consistent with those of 2.93(3) to 3.76(2) Å in Ba_3FeS_5.[41]

*Structure of $Ba_4In_2S_8$, **2**, and $Ba_4Ga_2S_8$, **3**.* Compounds **2** and **3** represent the first 1D chain structure type in Ba/In(Ga)/S systems. Although **2** and **3** show the identical stoichiometry, they crystallize in different crystal systems, $P\bar{1}$ vs $P2_1/c$. **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.236(2)$ Å, $b = 10.014(4)$ Å, $c = 13.033(5)$ Å, $\alpha = 104.234(6)°$, $\beta = 90.412(4)°$, $\gamma = 91.052(6)°$, and $Z = 2$ (Figure 4). **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.739(5)$ Å, $b = 6.201(2)$ Å, $c = 19.830(8)$ Å, $\beta = 104.254(6)°$, and $Z = 4$ (Figure 5). Nevertheless, they share similar characteristic 1D wavy chains of MS_4 tetrahedra that differ only in propagation directions (*a* in **2** vs *b* in **3**, Figure 4 vs 5) and wavy M1−M2−M1 angles (101.8° in **2** vs 104.8° in **3**). Also, the distortion of MS_4 in **2** is larger than that of **3** as indicated by the range of the S−M−S angles in the corresponding MS_4 tetrahedron, S−In−S angles from 97.87(8) to 135.84(9)° versus S−Ga−S angles from 101.17(5) to 125.99(6)°. We consider that these structural differences give rise to the different crystallographic features of these two compounds. Similar as the known Ba/M/S (M = Ga, In) compounds which adopt either 3D, 2D, or 0D structures,[14−20] the primary building units in **2** and **3** are also MS_4 tetrahedra; their new 1D chain motif may be owed to the involvement of the disulfide S_2^{2-} anion in the crystal structures. The isolated disulfide S_2^{2-} anions are parallel to the 1D chains with S−S distances of 2.117(4) Å in **2** and 2.115(2) Å in **3**, which are similar to 2.150(7) Å in **1**, 2.14(1) Å in $BaLaBi_2S_6$,[21] or 2.118(6) Å in $K_2La_2Sb_2S_9$.[42] The charge balanced formula of **2** and **3** can be described as $Ba_4In_2S_8 \equiv (Ba^{2+})_4(In^{3+})_2(S^{2-})_6(S_2)^{2-}$ and $Ba_4Ga_2S_8 \equiv (Ba^{2+})_4(Ga^{3+})_2(S^{2-})_6(S_2)^{2-}$, respectively.

There are two crystallographic independent In or Ga atoms in **2** or **3**, both are tetrahedrally coordinated by S^{2-} anions. The MS_4 (M = In, Ga) tetrahedra are distorted with angle variations of S−In−S from 97.87(8) to 135.84(9)° and of S−Ga−S from 101.17(5) to 125.99(6)°, and distance variations of In−S from 2.408(3) to 2.539(3) Å and of Ga−S from 2.219(2) to 2.349(2) Å. These data are comparable to those in $La_4Ag_2In_4S_{13}$[40] and $CsGa_3S_5$.[43] The MS_4 (M = In, Ga) tetrahedra are joined by sharing the apex of S3 and S6. (Figure 6)

As shown in Supporting Information, Figures S5, S6, the coordination motif of the crystallographic independent Ba atoms in **2** and **3** are quite similar as those in **1** described above. The Ba−S distances range from 3.106 (2) to 3.472(2) Å in **2** and from 3.110(2) to 3.532(2) Å in **3**, which are similar as those in **1**.

Optical Properties. The optical band gaps have been measured by the diffuse-reflectance spectra at room temperature. The band gaps are measured to be 2.56 eV for **1** (Supporting Information, Figure S7), and 2.55 eV for **3** (Supporting Information, Figure S8). Such values are in agreement with the yellow color and suggest the semiconductor behavior. The band gaps of **1** and **3** are also comparable to the reported values for some related compounds, such as β-In_2S_3 (∼2.67 eV),[44] Ga_2S_3 (2.7 eV),[45] $Zn_3In_2S_6$ (2.81 eV),[46] $AgGaS_2$ (2.64 eV),[47] and β-$LaGaS_3$(2.5 eV).[48]

Electronic Structures. To understand the distribution of the orbitals near the Fermi level, the DOS of **1** was calculated and is shown in Figure 7. The valence band (VB) is dominated by the S 3p block with the minor contributions from Ba 5d, In 5s, and In 5p whereas the conduction band (CB) are primarily Ba 5d, which are hybridized with S 3p, In 5s, and In 5p. The band structure of **1** indicates that the VB maximum and CB minimum are located at

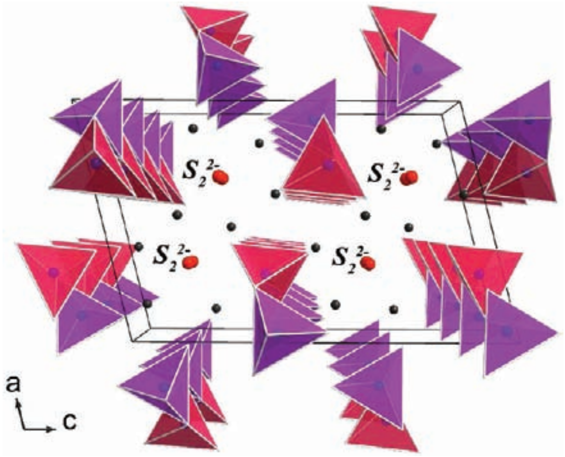

Figure 5. Structure of $Ba_4Ga_2S_8$, **3** viewed along *b* axis with unit cell outlined. Black, Ba^{2+}; blue, Ga; red, disulfide S_2^{2-} anion with S−S = 2.115(2) Å; purple and red tetrahedra: $Ga1S_4$ and $Ga2S_4$. Ba−S bonds are omitted for clarity.

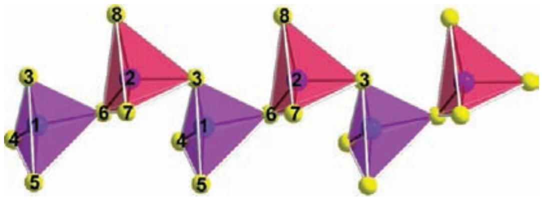

Figure 6. Apex-sharing InS_4 tetrahedra in an 1D wavy chain motif in $Ba_4In_2S_8$, **2**. Blue, In; yellow, S; purple and red tetrahedra, $In1S_4$ and $In2S_4$. Ba−S bonds are omitted for clarity.

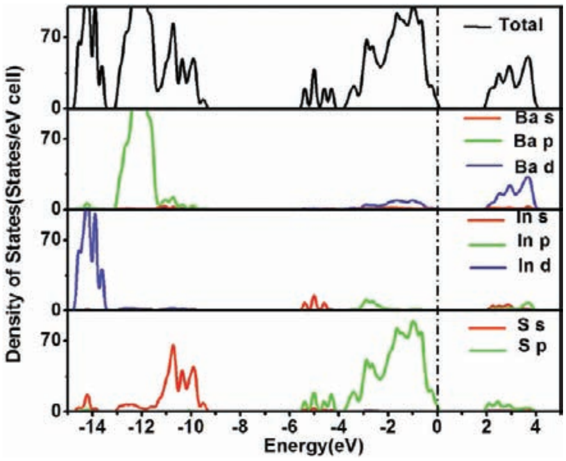

Figure 7. Total and partial DOS of $Ba_{12}In_4S_{19}$, **1**.

the same *k* point (Supporting Information, Figure S9), and the computational direct band gap is about 1.97 eV, which in principle agrees with the experimental result.

The total and partial DOSs of **2** (Figure 8) and **3** (Figure 9) are quite similar because the similarities in crystal structures and electronegativities (Ga vs In). Similar as those in **1**, the VBs of both compounds are constructed by dominating S 3p bands and minor contribution from Ba 5d, whereas the CBs are composed of S 3p and Ba 5d. The VB maximum and CB minimum are located at the same *k* point (Supporting Information, Figures S10, S11); their computational direct band gaps are 1.84 and

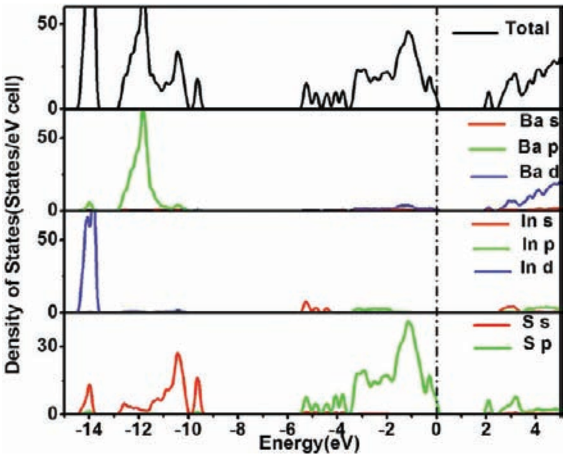

Figure 8. Total and partial DOS of $Ba_4In_2S_8$, **2**.

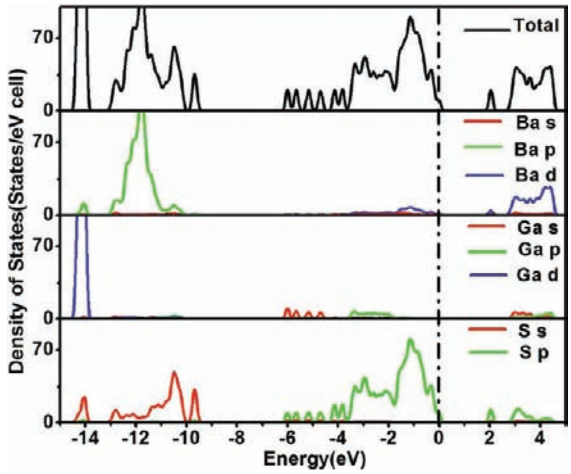

Figure 9. Total and partial DOS of $Ba_4Ga_2S_8$, **3**.

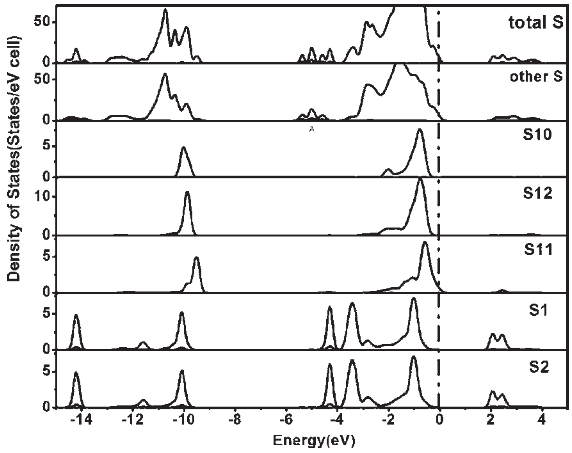

Figure 10. Total and partial DOS of S in $Ba_{12}In_4S_{19}$, **1**. S1 and S2 come from the disulfide S_2^{2-} anion, S10, S11, and S12 are the isolated S^{2-} anions, other S: sulfide S^{2-} anions of S3−S9.

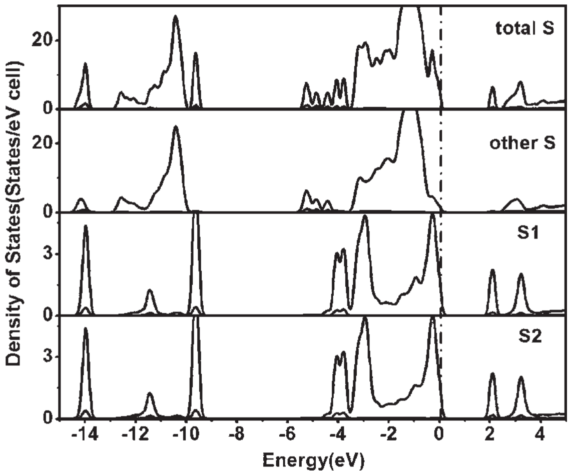

Figure 11. Total and partial DOS of S in $Ba_4In_2S_8$, **2**. S1 and S2 come from the disulfide S_2^{2-} anion, other S: sulfide S^{2-} anions of S3−S8.

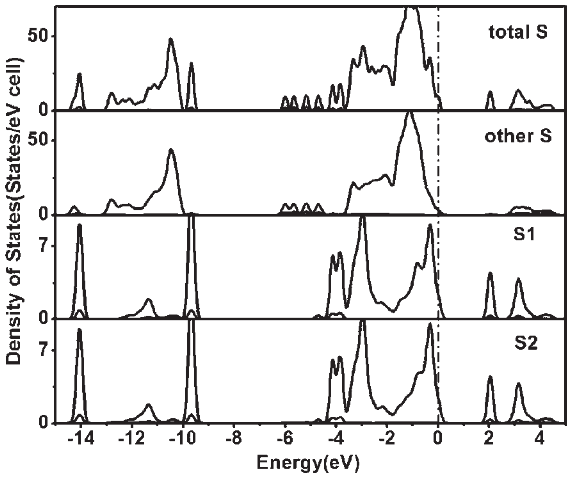

Figure 12. Total and partial DOS of S in $Ba_4Ga_2S_8$, **3**. S1 and S2 come from the disulfide S_2^{2-} anion, other S: sulfide S^{2-} anions of S3−S8.

1.79 eV for **2** and **3**, respectively. The similarity in band gaps agrees with the experimental observation.

To illustrate the different contributions of isolated disulfide S_2^{2-} anions and the sulfide S^{2-} anions in the three title compounds, the corresponding partial DOSs are shown along with the total DOSs of sulfur atoms. (Figure 10−12) Because of the strong covalent S−S bonding nature of the disulfide S_2^{2-} anions, each S1 band or S2 band can be identified with the corresponding intradimer molecular orbitals.[49−51] The two S1 peaks at −14.2 and −10.1 eV are the bonding and antibonding bands of 3sσ; those at about −4.2, −3.4, and −1.0 eV are the bonding pσ, bonding pπ and antibonding pπ^* bands, respectively. The antibonding pσ^* band is located at 1.9 to 2.7 eV above E_F.

The total DOSs shown in Figures 8 and 9 indicate that the band gap transitions for **2** and **3** are determined by the sulfur species. Detailed partial DOS analyses of different sulfur atoms regarding their different chemical environments are studied and shown in Figure 10−12. The results reveal that in **2** and **3** (Figure 11 and 12), the S_2^{2-} anion contributes to both the top of the VB and the bottom of the CB, that is, the band gaps are determined by the electron transition from 3pσ^* to 3pπ^* orbitals of the S_2^{2-} anion. As for **1** (Figure 10), the band of isolated S^{2-} anions (S10, S11, and S12) is slightly higher in energy than those of S_2^{2-} anions, the top of the VB and the bottom of the CB of **1** comes from the 3p orbitals of S11 and the 3pπ^* of the S_2^{2-} anion, respectively. In brief, the band gaps of both compounds are determined mainly by the disulfide S_2^{2-} anions.

■ CONCLUSION

In summary, three new yellow ternary sulfides, $Ba_{12}In_4S_{19}$, **1**, $Ba_4In_2S_8$, **2**, and $Ba_4Ga_2S_8$, **3**, have been synthesized by solid-state reaction from the mixture of elements with about 20% excess of sulfur. Compound **1** features a unique long period-stacking structure of a combination of monometallic InS_4 tetrahedron, linear dimeric In_2S_7 tetrahedra, disulfide S_2^{2-} anions, and isolated sulfide S^{2-} anions. The wavy 1D chains of vertex-sharing MS_4 tetrahedra (M = In or Ga) in **2** and **3** are reported for the first time in the ternary Ba/M/S (M = In, Ga) system. Interestingly, the disulfide S_2^{2-} anions are found to mainly determine the band gaps of the title compounds according to the CASTEP calculations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. The cif data, additional XRD patterns, band gap measurements, and band structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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