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Ba_3GeS_5 and Ba_3InS_4Cl: Interesting size effects originated from the tetrahedral anions

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ABSTRACT

Two new barium chalcogenides, Ba_3GeS_5 and Ba_3InS_4Cl, were synthesized by using high temperature solid-state reactions and their structures were determined by single-crystal X-ray diffraction technique. Despite the similar chemical formula, the structures of Ba_3GeS_5 and Ba_3InS_4Cl are subtly different due to the size effects originated from the tetrahedral anions. Ba_3GeS_5 crystallizes in the orthorhombic space group *Pnma* (no. 62) with cell parameters of $a=12.0528(9)$ Å, $b=9.5497(7)$ Å and $c=8.5979(6)$ Å, while Ba_3InS_4Cl adopts a different tetragonal system (space group: *I*4/*mcm*, no. 140, $a=b=8.3613(6)$ Å, $c=14.3806(18)$ Å). The measured optical band gap of Ba_3GeS_5 is 3.0 eV, a little smaller than the value of 3.42 eV in Ba_3InS_4Cl. Theoretical calculations by Wien2k are provided as well in order to better understand these results.

1. Introduction

Chalcogenides condensed with triels or tetrels have already exhibited diverse structure units and featured rich information on crystallographic chemistry. For example, in $Ba_5Ga_2S_8$ [1] isolated $[GaS_4]$ tetrahedra intersperse among the ion ocean regularly, while in $Ba_{12}In_4S_{19}$ [2] the structure contains monometallic $[InS_4]$ tetrahedra, linear dimeric $[In_2S_7]$ groups, disulfide S_2^{2-} and isolated S^{2-} anions. Especially, some novel anion structures such as supertetrahedral clusters can also be frequently resulted and these examples can be found in $NaInSe_2 \cdot xH_2O$ [3] and $Ba_3CsGa_5Se_{10}Cl_2$ [4]. Among these cases, compounds with discrete tetrahedral $[MQ_4]$ anions (M=triels or tetrels; Q=chalcogens) form a large family with dozens of structure types reported which benefits from the flexibility of the distortion on the tetrahedral units [5–8]. Besides, the rich structures in chalcogenide compounds are often related to interesting physical properties, which have drawn intensive attention recently, especially for the applications involving nonlinear optics (NLO) [9] and thermoelectrics. For Example, strong second harmonic generation (SHG) effect has been frequently reported for $Li_2Ga_2GeS_6$, [10] $LiInQ_2$ (Q=S, Se), [11,12] and $Ba_{23}Ga_8Sb_2S_{38}$. [13] $CsBi_4Te_6$ [14], PbTe [15] and Cu_2Se [16] are novel thermoelectric materials with high figure of merits.

Our previous work on the Ba_4MTrQ_6 (*M*=Cu, Ag; Tr=triels; Q=chalcogens) system has demonstrated interesting structural variation in the complex chalcogenide compounds, which is closely related to the flexible arrangement between the transition metals and triels [17]. In this paper, two new chalcogenide compounds, Ba_3InS_4Cl and Ba_3GeS_5, were synthesized from the $BaCl_2$-flux reactions and their structure feature discrete $[InS_4]$ and $[GeS_4]$ tetrahedral anions. In spite of the very similar chemical compositions, the packing structures of these two compounds are subtly different, which show very interesting relationship originated from the tetrahedral anions. The optical band gaps were measured as well and the results are in good agreement with theoretical predictions.

2. Experimental

2.1. Synthesis

All synthesis processes were conducted in an argon-filled glovebox or under vacuum. Starting materials were commercial grade and used as received: Ba (Alfa, 99%), In (Alfa, 99.99%), Ge (Alfa, 99.999%), S (Alfa, 99.999%), $BaCl_2$ (Alfa, 99.998%).

Ba_3InS_4Cl was obtained from a reaction of $BaCl_2$, BaS and In_2S_3 in a molar ratio of 3:5:1 and a slight excess of $BaCl_2$ was used as the flux. The reactants were loaded into a graphite crucible and sealed in fused silica tube under vacuum. The mixture was firstly heated to 1000 °C at a rate of 30 °C/h and homogenized at this temperature for 30 h, followed by a slowly cooling process down to 400 °C at a rate of 5 °C/h, then the furnace was powered off and the sample was cooled naturally down to ambient temperature.

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The product of the reaction contains mainly light red crystals of the title compound which can be easily purified by dissolving the excessive $BaCl_2$ flux into the deionized water. The synthesis of Ba_3GeS_5 adopts the similar procedure as described for Ba_3InS_4Cl, except that a different loading ratio of $BaS:BaCl_2:GeS = 4:3:1$ was used instead. The resulted product is composed of yellow crystals of the targeted compound in excellent crystal quality.

2.2. Single-crystal X-ray diffraction and structure determination

Single crystal data collections were performed on a *Bruker SMART APEX-II CCD* area detector with graphite-monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å) at 296 K using ω scans. Data reduction and integration, together with global unit cell refinements were done by the *INTEGRATE* program incorporated in *APEX2* software [18]. Semi-empirical absorption corrections were applied using the *SCALE* program for area detector [18]. The structures were solved by direct methods and refined by full matrix least-squares methods on F^2 using *SHELX* [19]. In the last refinement cycles, the atomic positions for the three compounds were standardized using the program *Structure TIDY* [20,21]. All structures were refined to converge with anisotropic displacement parameters.

Crystallographic data and structural refinements are summarized in Table 1. Atomic positions and anisotropic displacement parameters are provided in Table 2. Selected bond lengths are given in Table 3. Further information in the form of CIF has been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de)—depository CSD-number 427795 and 427796 for Ba_3GeS_5 and Ba_3InS_4Cl, respectively.

2.3. Powder X-ray diffraction

Powder X-ray diffraction patterns were taken at room temperature by a *Bruker AXS X-ray* powder diffractometer using Cu*K*α radiation. The data were recorded in a 2θ mode with a step size of 0.02° and the counting time of 10 s.

2.4. Elemental analysis

Energy dispersive X-ray spectroscopy was taken on picked single crystals of Ba_3GeS_5 and Ba_3InS_4Cl with a Hitachi FESEM-4800 field emission microscopy equipped with a Horiba EX-450 EDS. The energy dispersive spectra (*EDS*) taken on visibly clean surfaces of the measurement proved the identical results as the crystallographic data.

Table 1
Selected crystal data and structure refinement parameters for Ba_3InS_4Cl and Ba_3GeS_5.

Empirical formula	Ba_3InS_4Cl	Ba_3GeS_5
Formula weight	690.53 g/mol	644.91 g/mol
Temperature	296(2) K	
Radiation, wavelength	Mo*K*α, 0.71073 Å	
Crystal system	Tetragonal	Othorhombic
Space group unit cell dimensions	$I4/mcm$ (no. 140) $a = b = 8.3613(6)$ Å $c = 14.3806(18)$ Å	$Pnma$(no. 62) $a = 12.0528(9)$ Å $b = 9.5497(7)$ Å $c = 8.5979(6)$ Å
Unit cell volume (Z)	1005.37(16) Å^3, 4	989.62(12) Å^3, 4
Density (calc.)	4.562 g/cm^3	4.329 g/cm^3
Goof	1.077	0.997
Final R indices[a]$[I > 2\sigma_{(I)}]$	$R_1 = 0.0205$ $wR_2 = 0.0403$	$R_1 = 0.0204$ $wR_2 = 0.0463$
Final R indices[a][all data]	$R_1 = 0.0272$ $wR_2 = 0.0421$	$R_1 = 0.0249$ $wR_2 = 0.0480$

[a] $R_1 = \sum 00F_o| - |F_c||/47F_o|$; $wR_2 = [R \quad w(F_o^2 - F_c^2)^2]/ \quad 4w(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2 F_o^2 + (A \times P)^2 + B \times P]$, $P = (F_o^2 + 2F_c^2)/3$; A and B are weight coefficients.

Table 2
Refined atomic coordinates and isotropic displacement parameters for Ba_3InS_4Cl and Ba_3GeS_5.

Atoms	*Wyckoff*	x	y	z	U_{eq} (Å^2)
			Ba_3InS_4Cl		
Ba1	8*h*	0.65435(4)	0.15435(4)	0	0.01169(15)
Ba2	4*a*	0	0	0.25	0.02048(22)
In1	4*b*	0	0.5	0.25	0.01098(21)
S1	16*l*	0.15788(13)	0.65788(13)	0.14221(11)	0.01649(34)
Cl1	4*c*	0	0	0	0.02175(75)
			Ba_3GeS_5		
Ba1	8*d*	0.31916(2)	0.01817(3)	0.07708(3)	0.01884(10)
Ba2	4*c*	0.47850(3)	0.25	0.61141 (4)	0.01583(12)
Ge1	4*c*	0.09917(5)	0.25	0.30502(7)	0.01234(15)
S1	8*d*	0.05705(10)	0.05917(11)	0.18060(14)	0.01834(24)
S2	4*c*	0.00282(12)	0.25	0.52145(18)	0.01636(32)
S3	4*c*	0.23356(13)	0.25	0.81856(19)	0.01796(33)
S4	4*c*	0.28037(13)	0.25	0.35097(18)	0.01613(31)

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3
Important interatomic distances (Å) in Ba_3InS_4Cl and Ba_3GeS_5.

Atom pairs	Distances (Å)	Atom pairs	Distances (Å)
	Ba_3InS_4Cl		
Ba1–S1 × 2	3.0186(16)	Ba2–S1 × 8	3.5112(9)
S1 × 4	3.3164(14)	Cl1 × 2	3.5951(5)
Cl1 × 2	3.1651(3)		
In1–S1 × 4	2.4265(15)		
	Ba_3GeS_5		
Ba1–S1	3.3054(12)	Ba2–S1 × 2	3.0421(11)
S1	3.5658(12)	S1 × 2	3.2436(12)
S2	3.2433(11)	S2	3.1702(16)
S2	3.3750(10)	S3	3.2737(16)
S3	3.2659(12)	S4	3.1325(16)
S3	3.4317(11)	S4	3.4479(16)
S4	3.3025(12)		
S4	3.3575(11)		
Ge1–S1 × 2	2.1733(11)		
S2	2.1935(16)		
S3	2.2194(17)		

2.5. Differential thermal analysis and thermogravimetry measurements (DTA/TG)

The thermal stability was tested on the polycrystalline samples of Ba_3InS_4Cl (mass: 9.97 mg) and Ba_3GeS_5 (mass: 5.88 mg) with a *Mettler-Toledo TGA/DSC/1600HT* instrument under the protection of high-purity argon gas. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were performed as well and the measured temperature range is from 300 K to 1073 K with a heating rate of 10 K/min applied.

2.6. UV–vis–NIR diffuse reflectance spectrum

The optical diffuse reflectance spectra were measured using a *Shimadzu UV-2550 PC* spectrometer equipped with an integrating sphere attachment and $BaSO_4$ is used as a reference 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 [22].