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Disconnection Enhances the Second Harmonic Generation Response: Synthesis and Characterization of $Ba_{23}Ga_8Sb_2S_{38}$

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Supporting Information

ABSTRACT: An unusual zero-dimensional quaternary sulfide, $Ba_{23}Ga_8Sb_2S_{38}$, that crystallizes in the noncentrosymmetric polar space group $Cmc2_1$ was discovered by solid-state reaction of an elemental mixture. The involvement of a second building unit consisting of SbS_3 pyramid and constituting 20% of the structure helped to realize the disconnection of the asymmetric GaS_4 tetrahedra. Such a disconnection leads to the strongest powder second harmonic generation intensity in the IR region among sulfides to date, ~22 times that of commercial $AgGaS_2$ at an incident laser wavelength of 2.05 μm with the same particle size of 46−74 μm.

Infrared nonlinear optical (NLO) crystals are of great importance in laser technology and are facing increased need in military and civil applications.[1] However, it is of particular difficulty to have suitable materials working in the IR region that possess a high NLO coefficient and high laser damage threshold simultaneously. To date, only a few are commercially available, such as $AgGaS_2$,[1c,2] $AgGaSe_2$,[1c,3] and $ZnGeP_2$,[1c,4] but unfortunately, each of them still has its own drawbacks. Thus, the development of IR NLO materials is of broad scientific and technological interest. Main-group thiometalates, such as thiogalliumates,[5] thioarsenates,[6] thiotellurates,[7] and thioantimonates,[8] are suitable in the IR region and are therefore of great importance in fundamental and applications research.

The presence of strong dipoles and polarizable asymmetric units in a structure can give rise to an intense second harmonic generation (SHG) response if they are packed in-phase and do not generate centrosymmetric symmetry operations.[5−9] However, the majority of main-group thiometalates are centrosymmetric structures because the interaction between the cations (usually an alkali metal, alkaline-earth metal, or rare-earth metal) and the anions (i.e., asymmetric building units) is a directionless ionic bonding interaction, causing the asymmetric building units to pack centrosymmetrically. For instance, all of the known ternary Ba/Sb/S compounds are centrosymmetric, even though their primary building units are asymmetric; examples included $Ba_8Sb_6S_{17}$,[10] $BaSb_2S_4$,[11] and $Ba_3Sb_{4.7}S_{10}$,[12] in which the inversion center invariably is located between the anionic moieties. Similarly, among the eight known Ba/Ga/S compounds, only two, $BaGa_4S_7$[5] and $BaGa_2GeS_6$,[13] are noncentrosymmetric (NCS) compounds, in which the anionic moieties form acentric, rigid 3D networks themselves to ensure the NCS structures. They have moderate SHG intensities roughly equal to that of $AgGaS_2$ at an incident laser wavelength of 2.05 μm.

Because diversity of the asymmetric anionic unit would enhance the difficulty of spontaneously producing a mirror plane or inversion center during the packing process, we considered that an approach involving two or more types of asymmetric building units in a structure would have a high possibility to form an NCS structure. Guided by such a strategy, we discovered an unusual zero-dimensional (0D) quaternary sulfide, $Ba_{23}Ga_8Sb_2S_{38}$ $[(Ba^{2+})_{23}(GaS_4{}^{5-})_8(SbS_3{}^{3-})_2]$, that exhibits the strongest SHG response in the IR region among sulfides to date, ~22 times that of commercial $AgGaS_2$ at an incident laser wavelength of 2.05 μm with a particle size of 46−74 μm. Structural analyses revealed that the second building unit, SbS_3 (constituting 20% of the structure according to the 4:1 Ga:Sb stoichiometry ratio), contributes negligibly to the SHG intensity but nevertheless helps to realize the disconnection of the asymmetric GaS_4 building units (Figure 1), which remarkably leads to a strong powder SHG intensity.

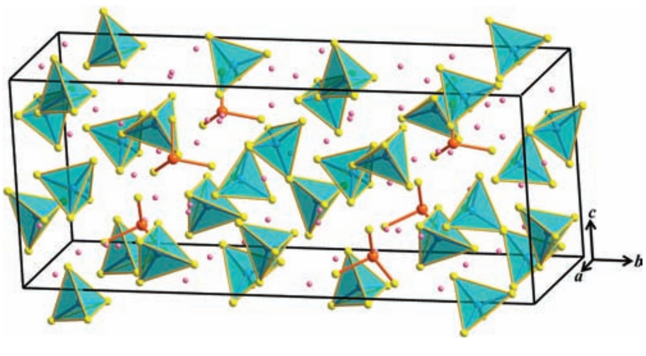

Figure 1. Structure of orthorhombic $Ba_{23}Ga_8Sb_2S_{38}$ with the unit cell marked. Sb is coordinated above or below the S_3 triangle; only half of the Sb atoms are shown because of the 50% occupancy. The Ba−S bonds have been omitted for the sake of clarity. Pink, Ba; dark-cyan, Ga; orange, Sb; yellow, S; light-blue tetrahedra: GaS_4.

Light-yellow $Ba_{23}Ga_8Sb_2S_{38}$ was synthesized via a solid-state reaction by heating of a mixture of the elements Ba, Ga, Sb, and S in an evacuated silica tube [see the Supporting Information

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(SI)]. This compound was stable in air. The purity of hand-picked crystals was confirmed by X-ray diffraction (XRD) analyses. Semiquantitative energy-dispersive X-ray (EDX) analyses of several crystals confirmed the presence of Ba, Ga, Sb, and S with average mass percentages of 60.8(35), 9.4(4), 5.4(6), and 24.4(36)%, respectively. Quantitative inductively coupled plasma (ICP) emission spectra gave consistent values of 58.57, 10.51, and 4.77% for Ba, Ga, and Sb, respectively (calcd: 61.00, 10.77, and 4.70%) (Figure 2 and Figure S1 in the SI).

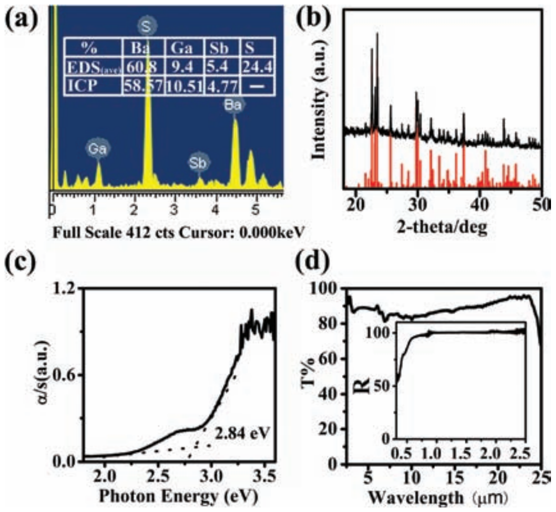

Figure 2. Property measurements on $Ba_{23}Ga_8Sb_2S_{38}$: (a) EDX and ICP results; (b) experimental and simulated powder XRD patterns; (c) UV−vis diffuse-reflectance spectrum; (d) reflection (inset) and FT-IR spectra.

The title compound features an extraordinary acentric 0D structure containing totally isolated GaS_4 tetrahedra and discrete SbS_3 pyramids with Ba^{2+} cations located between them (Figure 1). The S atoms of an SbS_3 pyramid serve as the triangle base, and the Sb atom is disordered above and below such a plane, as shown in Figure S2. Such an NCS structural motif containing a matrix of isolated GaS_4 tetrahedra has never been seen before in A/Ga/S compounds (A = alkali or alkaline-earth metal). The only compound containing isolated GaS_4 tetrahedra is the centrosymmetric $Ba_5Ga_2S_8$,[14] whereas the majority of thiogalliumates and thioantimonates are high-dimensional structures or centrosymmetric 0D clusters, such as 3D networks [i.e., $AgGaS_2$,[2] $BaGa_4S_7$,[5] $BaGa_2GeS_6$,[13] $BaGa_2S_4$[15]]; 2D layers (i.e., $BaSb_2S_4$,[11] $Ba_3Sb_{4.7}S_{10}$[12]); 1D chains (i.e., Ba_2BiGaS_5,[16] Ln_4GaSbS_9,[8b] $Ba_4Ga_2S_8$[17]); or centrosymmetric dimers ($Ba_4Ga_2S_7$, $Ba_3Ga_2S_6$[18]), trimers ($Ba_8Sb_6S_{17}$[10]), or tetramers ($Ba_2Ga_2S_5$[19]).

Fractional occupancies of the Wyckoff sites 8*b* (Ba8), 4*a* (Ba9), and 8*b* (Sb) are observed. Such occupancies converge better *R* values, reasonable temperature factors, and a charge-balanced formula (see the SI). The distortion of the SbS_3 pyramid is evidenced by deviations of both the Sb−S bonds (2.42−2.47 Å) and the S−Sb−S angles (95−99°), which are attributable to the stereoactive lone pairs on Sb. Such a pyramidal geometry is commonly observed in thioantimonates, such as $Ba_3Sb_{4.7}S_{10}$ (in which Sb5 is ~60% occupied),[12] $CsAgSb_4S_7$,[20] and $Cs_3Ag_2Sb_3S_8$.[21] In spite of its local asymmetry, the sum polarization of SbS_3 units coming from the lone pairs is zero because the *c* glide plane at (x, 0, z) correlates the SbS_3 units and the lone pairs of neighboring SbS_3 units are restricted to be oppositely oriented (Figure S3)

In contrast, all of the distorted GaS_4 tetrahedra on which the twofold screw axis operates generate a net dipole moment along the *c* axis, as expected from the *Cmc*2$_1$ space-group symmetry (Figure S3). Such an alignment leads to a macroscopic polar nature that eventually gives rise to the strong SHG response. Each GaS_4 tetrahedron is slightly distorted, with S−Ga−S angles varying from 105 to 120° and Ga−S bonds ranging from 2.21 to 2.32 Å. These agree well with the values for related compounds, such as 105−113° and 2.27−2.31 Å in Sm_4GaSbS_9.[8b] Although the SbS_3 pyramid is a minor component in quantity and hardly contributes to the overall polarity, it helps to disconnect the GaS_4 building units, breaking the symmetry and leading to the NCS packing.

The Ba^{2+} cations are six- to eight-fold-coordinated, with Ba−S bond distances varying from 2.89 to 3.67 Å (Figure S2), which are comparable to the distances of 3.24−3.35 Å in Ba_2BiGaS_5.[16]

The SHG intensity was measured with a modified Kurtz NLO system using a 2.05 μm laser.[22] $Ba_{23}Ga_8Sb_2S_{38}$ exhibits the strongest SHG response in the IR region reported for sulfides to date (~22 times that of commercial $AgGaS_2$ at the same particle size of 46−74 μm; Figure 3a) and non-type-I phase-matchable behavior (Figure 3b). Several other key parameters are also comparable with those of commercial $AgGaS_2$, such as a larger band gap (2.84 vs 2.56 eV) and a similar transparent range (0.7−23.5 μm vs 0.6−23 μm) (Figure 2 and Figure S4) The SHG response of $Ba_{23}Ga_8Sb_2S_{38}$ is significantly stronger than those of reported compounds such as Sm_4GaSbS_9 (3.8 × $AgGaS_2$),[8b] $Eu_2Ga_2GeS_7$ (1.6 × $AgGaS_2$),[23] $BaGa_4S_7$ (1.4 × $LiGaS_2$),[5] and Ba_2BiInS_5 (0.8 × $KTiOPO_4$).[16] It is clear that the constructive alignment of the dipole moments of the isolated GaS_4 distorted tetrahedra gives rise to such a strong SHG response.[24] More deeply, the isolated GaS_4 units have four terminal S atoms (i.e., μ_t-S, each of which has only one covalent bond with Ga), and thus, the title compound has a higher sulfur ionic bonding component than any known Ga/S species that contains bridging μ_b-S, such as polynuclear Ga/S clusters and polymeric Ga/S 1D chains, 2D layers, and 3D networks. Moreover, the isolated GaS_4^{5-} tetrahedra, as anionic species, contact with the neighboring species via ionic bonding interactions. Such a characteristic allows more nonbonding S 3p orbitals in the electronic structure than does any μ_b-S-containing Ga/S species. These features make the title compound easily polarizable; as a result, a very strong SHG intensity has been realized. In fact, we consider this not to be accidental, as the well-known β-BaB_2O_4

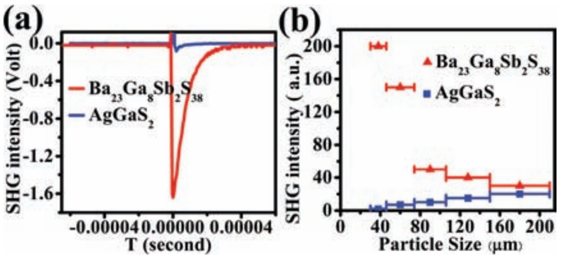

Figure 3. SHG intensities of $Ba_{23}Ga_8Sb_2S_{38}$ with commercial $AgGaS_2$ as a reference: (a) oscilloscope traces of SHG signals; (b) phase-matching curves (i.e., particle size vs SHG response).

(BBO) is also a structure constructed from isolated B_3O_6 building units.[25]

The electronic structure was studied. Because of the fractional occupancies at the Sb, Ba8, and Ba9 sites, a 2×1×1 supercell was constructed as described in Figure S5. The band structure (Figure S6a) reveals that the valence band (VB) maximum and conduction band (CB) minimum are located at the same point (Γ), giving a direct band gap of ~2.52 eV, which is comparable to the experimental value (2.84 eV). Figure S6b shows the total density of states (TDOS) and partial densities of states (PDOS). The VB between −4 and −2 eV mainly originates from S 3p, Ga 4p, and Sb 5p states mixed with a small portion of Ba 5d states. The top of the VB comes predominantly from S 3p states and minor Ba 5d states. The bottom of the CB arises from Sb 5p, Ba 5d, and S 3p states. The CB ranging from 3 to 5 eV is composed of Ba 5d states with small amounts of S 3p, S 3s, Ga 4s and Ga 4p states. Thus, the optical absorption can be assigned mainly to the charge transfer transitions from S 3p to Sb 5p and Ba 5d states. Further studies of the SHG mechanism are ongoing.

In summary, an unusual 0D quaternary sulfide, $Ba_{23}Ga_8Sb_2S_{38}$ $[(Ba^{2+})_{23}(GaS_4^{5-})_8(SbS_3^{3-})_2]$, was discovered and characterized by single-crystal XRD. This compound showed the strongest SHG response in the IR region reported to date (~22 times that of commercial $AgGaS_2$ at an incident laser wavelength of 2.05 μm), a non-type-I phase-matchable behavior, comparable transparent range, and adequate band gap. Analyses revealed for the first time that the SHG effect is directly attributable to the disconnection of the asymmetric GaS_4 tetrahedra. Consequently, we considered that the in-phase alignment of the discrete polar units (such as GaS_4 with four terminal S atoms) would enhance the SHG response to the greatest extent, yet known compounds had proven that it was extremely difficult to obtain disconnected GaS_4 in the crystal structure. Here we discovered that a small amount (20%) of a second building unit, SbS_3 pyramids, in spite of its negligible contribution to the polarity, helped to disconnect the isolated GaS_4 tetrahedron array, breaking the symmetry of the inversion center and leading to an NCS compound. This was a new idea for the predesign of an NLO material and will definitely shed useful insight on the further exploration in such a field.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data (CIF), experimental and theoretical methods, and additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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