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Synthesis and Crystal Structure of Barium Thioborate $Ba_7(BS_3)_4S$

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The thioborate phase $Ba_7(BS_3)_4S$ was synthesized from solid state reaction and its crystal structure determined by single crystal X-ray diffraction analysis. It crystallizes in the monoclinic space group $C2/c$ (No. 15) with $a = 10.1750(15)$ Å, $b = 23.970(4)$ Å, $c = 10.1692(15)$ Å, $\beta = 90.095(2)°$, and $Z = 4$. The structure consists of isolated trigonal planar $(BS_3)^{3-}$ anions, and isolated S^{2-} anions and Ba^{2+} cations. The additional sulfur anions have five-fold barium coordination, while the barium cations are coordinated by eight or nine sulfur atoms. Powder X-ray diffraction patterns from a bulk sample are compared to the calculated diffraction pattern from the single crystal structural analysis, and there is excellent agreement in general. The vibrational modes of the isolated $(BS_3)^{3-}$ units were measured from Raman scattering and IR absorption spectra, and the frequencies agree very well with those found for similar orthothioborate phases.

The synthesis of suitable thioborate single crystals for single crystal X-ray diffraction is difficult due to the high chemical reactivity of boron sulfide. Thus far, the structure has only been determined for a relatively small number of thioborates (~35); surprisingly these thioborates show various structural types and units.[1,2] The boron atom coordinates with either three or four sulfur atoms to form $(BS_3)^{3-}$ or $(BS_4)^{5-}$ groups. These $(BS_3)^{3-}$ and $(BS_4)^{5-}$ units may be either isolated or connected to form planar structural $(BS_3)^{3-}$, $(B_3S_6)^{3-}$, $(B_2S_4)^{2-}$, and $(B_2S_5)^{2-}$ units or polymeric units in chains, layers, or three-dimensional units such as $(B_{10}S_{18}S_{2/2})^{8-}$, $(B_{10}S_{16}S_{4/2})^{6-}$, and $(B_{19}S_{30}S_{6/2})^{9-}$.[1,2] The thioborates containing polymeric anionic groups such as $Ag_6B_{10}S_{18}$ [3] and $Li_{6+2x}(B_{10}S_{18})S_x$ ($x = 2$)[4] have been considered as ion conduction materials because they possess three-dimensional networks with large open channels.[4] Recently, thioborates have also been investigated as new nonlinear optical materials for infrared applications because of the variety of structural units and large polarizability of planar structural units.[5] Here we report the synthesis and structure of the new thioborate $Ba_7(BS_3)_4S$.

A small yellowish prismatic crystal with approximate dimensions 0.15 × 0.15 × 0.08 mm^3 was obtained among many other smaller crystal phases from a solid state reaction compositionally batched to yield the orthothioborate phase $Ba_2Zn(BS_3)_2$. After preliminary X-ray diffraction experiments suggested that the new $Ba_7(BS_3)_4S$ phase was proposed instead, the polycrystalline compound $Ba_7(BS_3)_4S$ was prepared from a stoichiometric mixture of B_2S_3 and BaS (Cerac, 99.9%). High purity glassy B_2S_3 was prepared from amorphous boron (99.9% metal basis, Cerac) and sulfur (99.999%, Cerac) using a modified literature procedure.[6] The BaS and B_2S_3 stoichiometric mixture was transferred into a vitreous carbon crucible using a He glovebox (<5 ppm O_2 and < 5 ppm H_2O), and then placed inside a dried quartz tube sealed under vacuum. The sealed tube was heated at a rate of 1 °C/min to 1000 °C, held for 24 h, cooled to 400 °C at a rate of 1 °C/min, and then quenched to room temperature. A yellowish-white powder was obtained after grinding. The corresponding powder X-ray diffraction pattern[7] agreed well with the calculated peak locations from the single crystal data as shown Figure 1. The X-ray single crystal data were collected at 298 K using the full sphere routine with a Bruker CCD-1000 diffractometer and Mo Kα ($\lambda = 0.71073$ Å) radiation.[8]

The structural data of $Ba_7(BS_3)_4S$ indicate the presence of isolated planar trigonal $(BS_3)^{3-}$ anions, barium metal cations Ba^{2+}, and additional S^{2-} anions configured in a monoclinic unit cell with an adopted space group of $C2/c$. Isotypic crystal structures were found for $Sr_{4.2}Ba_{2.8}(BS_3)_4S$

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(7) The powder X-ray diffraction data were collected at 298 K on a Scintag XDS2000 diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). It was operated at 40 kV and 30 mA in the 2θ range 5−70° with step size 0.02°.
(8) The data were collected at 298 K using the full sphere routine with a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation. The structural refinement method was based on full-matrix least-squares on F^2. Crystal data for $Ba_7(BS_3)_4S$: monoclinic $C2/c$; $a = 10.1750(15)$ Å, $b = 23.970(4)$ Å, $c = 10.1692(15)$ Å, $\beta = 90.095(2)°$; $V = 2480.2(7)$ Å^3; $Z = 4$; $D = 3.807$ g/cm^3; $\mu = 12.014$ mm^{-1}; R1 = 0.0297, wR2 = 0.0739; GOF on F^2 is 1.153.

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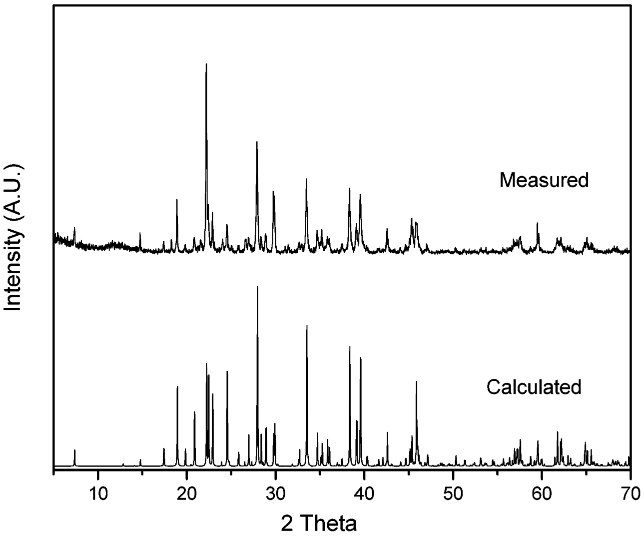

Figure 1. Observed (top) and calculated (bottom) X-ray diffraction powder patterns for $Ba_7(BS_3)_4S$ with $5° < 2\theta < 70°$.

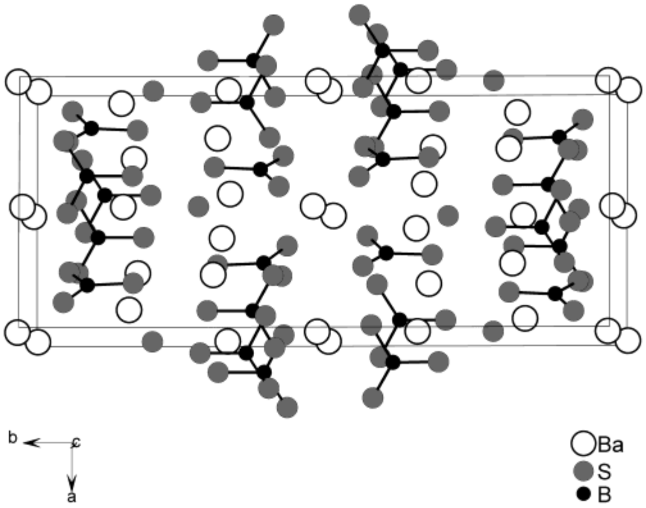

Figure 2. Unit cell representation of the $Ba_7(BS_3)_4S$ phase.

and $Ba_7(BSe_3)_4Se$,[9] but $Ba_7(BS_3)_4S$ has slightly different unit cell dimensions compared to those of $Sr_{4.2}Ba_{2.8}(BS_3)_4S$ (a = 9.902 Å, b = 23.504 Å, c = 9.884 Å, and β = 90.01°) and $Ba_7(BSe_3)_4Se$ (a = 10.513 Å, b = 25.021 Å, c = 10.513 Å, and β = 90.10°). Figure 2 shows planar $(BS_3)^{3-}$ anions arranged in layers parallel to the a-axis and perpendicular to each other within these layers in the structure of $Ba_7(BS_3)_4S$. The mean B−S bond length (1.823 Å) of the $(BS_3)^{3-}$ unit is very similar to that found in $Sr_{4.2}Ba_{2.8}(BS_3)_4S$ (1.822 Å). Figure 3 presents a structural representation of the two unique $(BS_3)^{3-}$ anions in their first cation coordination sphere for the $Ba_7(BS_3)_4S$ phase, and Table 1 presents corresponding bond lengths and angles. The additional sulfur anions are coordinated by five barium cations to form square pyramids. Ba−S distances range from 3.058 to 3.137 Å, within range of those reported for $Sr_{4.2}Ba_{2.8}(BS_3)_4S$ (3.0−4.5 Å).[9]

Four of the five unique barium cation positions exhibit an eight-fold sulfur coordination, while the Ba(1) position is nine-fold coordinated by sulfur atoms to form an irregular coordination polyhedron. All five different barium cation coordination spheres are presented in Figure 4. The mean Ba−S bond length is 3.272 Å; specific Ba−S bond lengths in the $Ba_7(BS_3)_4S$ phase are presented in Table 2.

Figure 5 presents the IR absorption and Raman scattering spectra for polycrystalline samples.[10,11] The strong absorption bands in the IR spectra and the weak absorption bands in

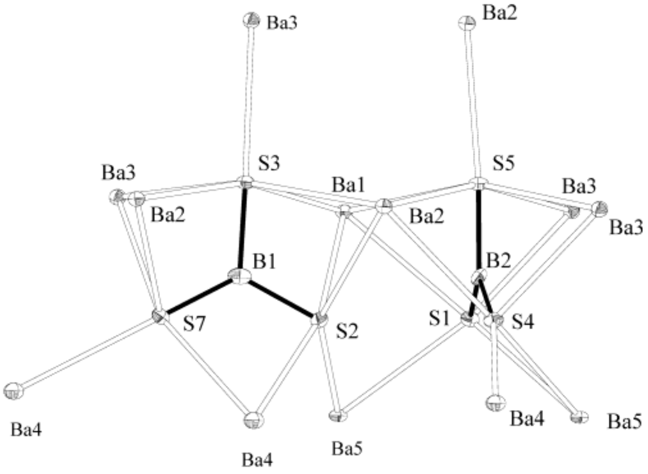

Figure 3. The two unique $(BS_3)^{3-}$ anions for $Ba_7(BS_3)_4S$. Thermal ellipsoids are drawn at the 50% probability level.

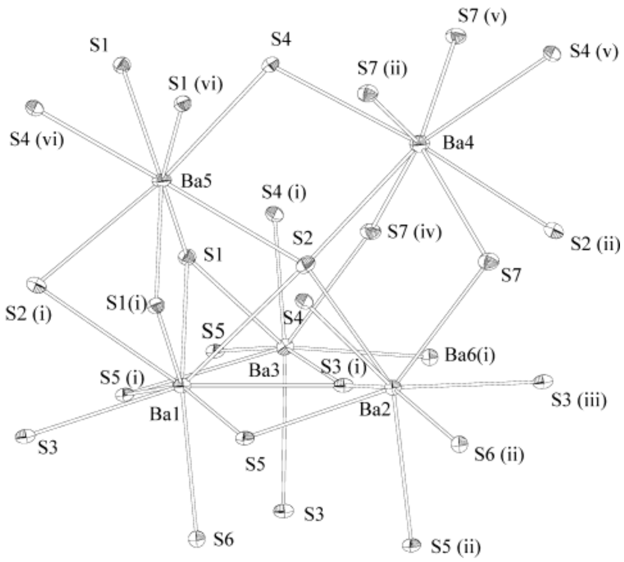

Figure 4. Barium cation environments for $Ba_7(BS_3)_4S$. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Bond Lengths (Å) and Angles (deg) for the $(BS_3)^{3-}$ Anions Present in $Ba_7(BS_3)_4S$

bond lengths		bond angles	
B(1)−S(2)	1.817(6)	S(2)−B(1)−S(3)	115.2(3)
B(1)−S(3)	1.879(6)	S(2)−B(1)−S(7)	124.0(3)
B(1)−S(7)	1.796(6)	S(3)−B(1)−S(7)	120.7(3)
B(2)−S(4)	1.818(6)	S(4)−B(2)−S(5)	119.9(3)
B(2)−S(5)	1.859(6)	S(4)−B(2)−S(1)	123.6(3)
B(2)−S(1)	1.808(6)	S(5)−B(2)−S(1)	116.4(3)

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(10) The mid-IR and far-IR absorption spectra were recorded with a Bruker IFS 66v/S spectrometer using 32 scans at 4 cm^{-1} resolution. Samples (2 mg) were grounded with 100 mg of CsI and pressed into pellets for transmission.

Table 2. Barium−Sulfur Bond Lengths (Å) for $Ba_7(BS_3)_4S^a$

Ba1−S6	3.058(2)	Ba3−S3^{i}	3.263(2)
Ba1−S1^{i}	3.325(1)	Ba3−S5^{i}	3.276(1)
Ba1−S1	3.325(1)	Ba3−S5	3.382(1)
Ba1−S3^{i}	3.370(1)	Ba3−S7^{iv}	3.408(1)
Ba1−S3	3.370(1)		
Ba1−S5	3.373(1)	Ba4−S2^{ii}	3.256(1)
Ba1−S5^{i}	3.373(1)	Ba4−S2	3.256(1)
Ba1−S2^{i}	3.452(1)	Ba4−S7	3.290(1)
Ba1−S2	3.452(1)	Ba4−S7^{v}	3.290(1)
		Ba4−S7^{ii}	3.290(1)
Ba2−S7	3.130(1)	Ba4−S4	3.357(1)
Ba2−S6^{ii}	3.137(1)	Ba4−S4^{v}	3.357(1)
Ba2−S5	3.198(1)	Ba4−S7^{iv}	3.306(1)
Ba2−S2	3.216(1)		
Ba2−S5^{ii}	3.218(1)	Ba5−S1	3.205(1)
Ba2−S3^{iii}	3.261(1)	Ba5−S1^{vi}	3.205(1)
Ba2−S4	3.286(1)	Ba5−S4^{vi}	3.207(1)
Ba2−S3^{i}	3.355(1)	Ba5−S4	3.207(1)
		Ba5−S2	3.258(1)
Ba3−S4^{i}	3.108(1)	Ba5−S2^{i}	3.258(1)
Ba3−S6^{i}	3.121(1)	Ba5−S1^{xi}	3.286(1)
Ba3−S3	3.178(1)	Ba5−S1^{i}	3.286(1)
Ba3−S1	3.207(1)		

[a] Symmetry transformations used to generate equivalent atoms: (i) $-x$, $2 + y$, $0.5 - z$; (ii) $-x$, $1 + y$, $0.5 - z$; (iii) x, $-1 + y$, z; (iv) x, $1 + y$, z; (v) $-x$, $1 + y$, $1.5 - z$; (vi) $-x$, $2 + y$, $1.5 - z$; (vii) x, $-1 + y$, $-1 + z$; (viii) x, y, $-1 + z$; (ix) $-1 + x$, y, z; (x) $1 + x$, y, z; (xi) $2 - x$, y, $0.5 - z$; (xii) $2.5 - x$, $0.5 - y$, $-z$.

the Raman spectra around 850 cm^{-1} are assigned to the E asymmetrical stretching modes of the $(BS_3)^{3-}$ units with point symmetry group of D_{3h}. Around 450 cm^{-1}, the weak absorption bands in the IR spectra and the strong absorption bands in the Raman spectra are assigned to the A_1' symmetrical stretching modes of the $(BS_3)^{3-}$ units. These two absorption bands in both the IR and Raman spectra are also observed in the Na_3BS_3 crystal.[12] Many orthothioborates consisting of $(BS_3)^{3-}$ units, such as $SrLiBS_3$,[13] $BaLiBS_3$,[14] and alkali orthothioborate M_3BS_3 (M = Li, Na, K, Rb and Cs) crystals,[15] show these two absorption bands in their IR spectra. The absorption bands below 300 cm^{-1} may be assigned to the low-frequency bond bending modes and/or transitional modes.

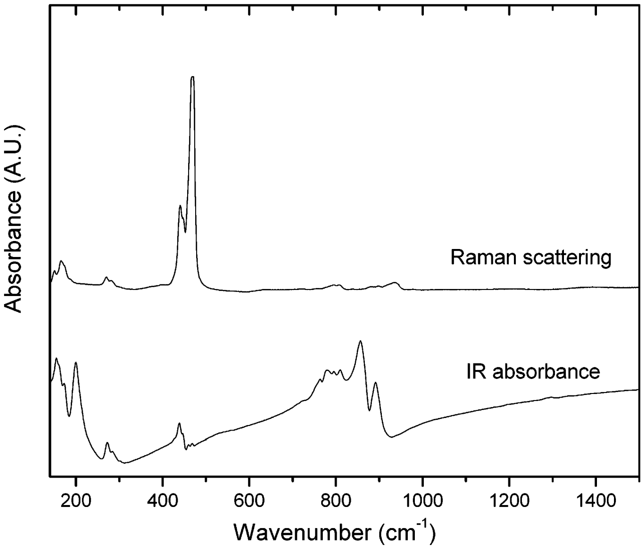

Figure 5. Raman and IR absorption spectra of polycrystalline $Ba_7(BS_3)_4S$.

In summary, the crystal structure of $Ba_7(BS_3)_4S$ has been determined by single crystal X-ray diffraction analysis. This structure is based on the isolated planar trigonal $(BS_3)^{3-}$ anions, additional S^{2-} anions, and eight- and nine-fold coordinated Ba^{2+} cations in a monoclinic unit cell with space group $C2/c$. The vibrational modes of the isolated $(BS_3)^{3-}$ structural units are observable in both Raman scattering and IR absorption spectra of polycrystalline samples.

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Supporting Information Available: Crystallographic file in CIF format for $Ba_7(BS_3)_4S$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The Raman scattering spectrum was collected at 298 K with a Renishaw inVia spectrometer using a 488 nm Ar laser, 2 cm^{-1} resolution, and 25 mW of power. The sample was grounded and packed into a small aluminum cuplike sample holder.

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