Synthesis and structure of BaSc$_3$AgS$_6$

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Abstract

The new quaternary compound BaSc$_3$AgS$_6$ has been synthesized at 1000 °C. The compound crystallizes in the space group D_{2h}^{16}-*Pnma* of the orthorhombic system with eight formula units in a cell of dimensions $a = 16.154(3)$ Å, $b = 11.108(2)$ Å, $c = 10.914(3)$ Å ($T = 115$ K), $V = 1958.4(7)$ Å^3. The structure of the compound was determined from single-crystal X-ray methods. Agreement indices are $R_w(F^2) = 0.123$ for 2022 unique data and 54 variables, $R(F) = 0.056$ for 1201 observations having $F_o^2 > 2\sigma(F_o^2)$. BaSc$_3$AgS$_6$ has a three-dimensional framework structure with single channels that accommodate Ba^{2+} cations. Sc^{3+} cations are octahedrally coordinated whereas Ag$^+$ cations exhibit both square-pyramidal and trigonal-pyramidal coordination.

1. Introduction

The chemistry of quaternary chalcogenides containing an alkaline-earth element, a rare-earth element, and Cu, Ag, or Au has recently been an active area of research [1–4]. It has been found that crystallographically distinct metal coordination can be achieved by judicious selection of reactants, and that by variation of metal size marked changes in structure type can be realized. This rare-earth chemistry has now been extended to scandium. The structure of the new compound BaSc$_3$AgS$_6$ presented here contains some familiar and some unusual metal coordination, further demonstrating the subtlety of these systems.

2. Experimental details

Single crystals of BaSc$_3$AgS$_6$ were prepared from the reaction of BaS (Johnson Matthey, 99.9%) with powders of the elements Sc (Johnson Matthey, 99.9%), Ag (Johnson Matthey, 99.9995%), and S (Alfa, 99.9995%) in a 1:1:1:2 ratio. The starting materials were mixed together, placed in a fused silica tube, evacuated to 10^{-5} Torr, and sealed. In a furnace the tube was heated with the following temperature profile: 400 °C for 12 h, 500 °C for 24 h, 700 °C for 24 h, and 1000 °C for 6 days. The temperature gradient between isotherms

was 100 °C h^{-1}. The tube was cooled from 1000 °C to 280 °C at 3.5 °C h^{-1}. The furnace was then turned off, allowing the tube to cool to room temperature. Light orange, needle-shaped crystals were manually extracted from the melt. The presence of all four elements in a 1:3:1:7 ratio was confirmed with an energy dispersive X-ray analysis (EDX) equipped Hitachi S-570 scanning electron microscope. The compound is stable in air and water.

Preliminary unit cell constants and Laue symmetry *mmm* were determined from Weissenberg photographs obtained at room temperature. The systematic absences ($0kl$, $k+l = 2n+1$; $hk0$, $h = 2n+1$) are consistent with the orthorhombic space groups D_{2h}^{16}-*Pnma* and C_{2v}^9-*Pn2$_1$a*. A crystal of approximate dimensions 0.014 mm $\times$ 0.032 mm $\times$ 0.29 mm was selected for data collection on an Enraf-Nonius CAD4 automatic diffractometer. The final lattice constants were determined from 25 automatically centered reflections in the range $36° < 2\theta$(Mo Kα_1) $< 38°$ at 115 K. The reflections $h, \pm k, l$ were collected in the ω-scan mode. Six standard reflections monitored every 3 h showed no significant change in intensity during data collection. The data were processed and corrected for absorption with the use of programs standard for this laboratory [5].

Intensity statistics and agreement among Friedel pairs favored the centrosymmetric space group *Pnma*. The structure was solved in this space group with the direct methods program SHELXS [6]. The program STRUCTURE TIDY [7] was used to standardize the positional pa-

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Table 1
Crystal data and experimental details for $BaSc_3AgS_6$

Compound	$BaSc_3AgS_6$
Formula weight	572.45
Space group	D_{2h}^{16}-$Pnma$
a (Å)	16.154(3) [a]
b (Å)	11.108(2)
c (Å)	10.914(3)
V (Å^3)	1958.4(7)
Z	8
ρ_c (g cm^{-3})	3.88
T of data collection (K) [b]	115
Crystal vol. (mm^3)	3.0×10^{-5}
Crystal shape	Needle, bounded by {100}, {010}, {001}
Radiation	Graphite monochromated Mo Kα ($\lambda(K\alpha_1) = 0.7093$ Å)
Linear abs. coefficient (cm^{-1})	91.0
Transmission factors [c]	0.840–0.949
Data collected	$4.5 \leqslant 2\theta$(Mo Kα_1) $\leqslant 52°$, $+h$, $\pm k$, $+l$
No. of unique data including $F_o^2 < 0$	2022
No. of variables	54
R_w (F^2) [d]	0.1227
R (on F for $F_o^2 > 2\sigma(F_o^2)$)	0.0563 (1201 reflections)
Error in observation of unit weight	0.959

[a] Obtained from a refinement with the constraint $\alpha = \beta = \gamma = 90°$.
[b] The low-temperature system for the Nonius CAD4 diffractometer is from a design by Prof. J.J. Bonnet and S. Askenazy and is commercially available from Soterem, Z.T. de Vic, 31320 Castanet-Tolosan, France.
[c] The analytical method was used for the absorption correction [5].
[d] $w^{-1} = \sigma^2(F_o^2) + (0.04 \times F_o^2)^2$ for $F_o^2 \geqslant 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2
Atomic coordinates and isotropic displacement parameters for $BaSc_3AgS_6$

Atom	x	y	z	U (Å^2)
Ba	0.29645(5)	0.05647(8)	0.23482(8)	0.0063(2)
Sc(1)	0.0931(3)	$\frac{1}{4}$	0.4300(4)	0.0034(9)
Sc(2)	0.0868(2)	0.5856(3)	0.4219(2)	0.0026(6)
Sc(3)	0.0344(2)	0.0832(3)	0.1410(3)	0.0047(6)
Sc(4)	0.4753(3)	$\frac{1}{4}$	0.6391(4)	0.0051(9)
Ag(1)	0.28814(12)	$\frac{1}{4}$	0.5443(2)	0.0138(4)
Ag(2)	0.67854(12)	$\frac{1}{4}$	0.5514(2)	0.0128(4)
S(1)	0.1898(2)	0.0772(3)	0.4791(3)	0.0057(8)
S(2)	0.0207(4)	$\frac{1}{4}$	0.6376(5)	0.0052(11)
S(3)	0.5757(2)	0.0790(4)	0.5862(3)	0.0040(8)
S(4)	0.1379(4)	$\frac{1}{4}$	0.2028(5)	0.0051(11)
S(5)	0.4266(4)	$\frac{1}{4}$	0.4089(5)	0.0072(12)
S(6)	0.4854(2)	0.0835(4)	0.1355(3)	0.0059(8)
S(7)	0.1322(2)	0.5881(3)	0.1988(3)	0.0042(8)
S(8)	0.3214(4)	$\frac{1}{4}$	0.0111(5)	0.0082(12)

rameters. The structure was refined isotropically with the program SHELXL-93 [8] by full-matrix least-squares techniques, the function $\Sigma w(F_o^2 - F_c^2)^2$ being minimized. The final refinement led to a value of 0.123 for $R_w(F^2)$. The conventional R index (on F for $F_o^2 > 2\sigma(F_o^2)$) is 0.056. The highest residual electron density peak has a height which is 1.8% that of a barium atom.
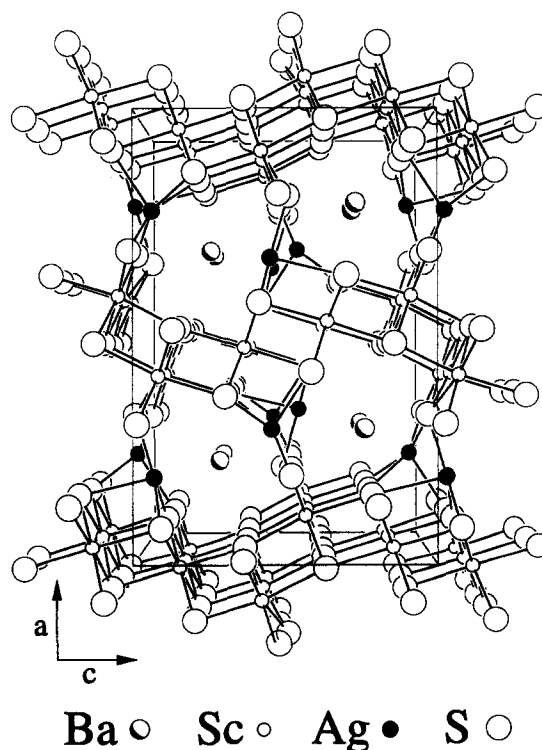

Ba ○   Sc ○   Ag ●   S ○

Fig. 1. View down the [010] direction of the structure of $BaSc_3AgS_6$. Here and in the next figure the atoms are shown as circles of arbitrary size.

Table 3
Selected distances (Å) and angles (deg) for BaSc₃AgS₆

Distances

Ag(1)-S(1)	2.591(4)	Sc(2)-S(7)	2.543(4)
Ag(1)-S(1)#1	2.591(4)	Sc(2)-S(6)#9	2.569(5)
Ag(1)-S(5)	2.681(6)	Sc(2)-S(2)#10	2.602(5)
Ag(1)-S(7)#6	2.781(4)	Sc(2)-S(6)#11	2.607(5)
Ag(1)-S(7)#7	2.781(4)	Sc(3)-S(7)#1	2.552(5)
Ag(2)-S(8)#5	2.406(6)	Sc(3)-S(6)#8	2.564(5)
Ag(2)-S(3)	2.552(4)	Sc(3)-S(3)#8	2.568(4)
Ag(2)-S(3)#1	2.552(4)	Sc(3)-S(4)	2.586(5)
Ag(2)-S(4)#5	2.851(6)	Sc(3)-S(5)#8	2.600(5)
Sc(1)-S(1)#1	2.533(5)	Sc(3)-S(3)#2	2.601(5)
Sc(1)-S(1)	2.533(5)	Sc(4)-S(2)#13	2.545(7)
Sc(1)-S(2)	2.550(7)	Sc(4)-S(3)#1	2.564(5)
Sc(1)-S(4)	2.583(7)	Sc(4)-S(3)	2.564(5)
Sc(1)-S(6)#8	2.637(5)	Sc(4)-S(7)#7	2.584(5)
Sc(1)-S(6)#9	2.637(5)	Sc(4)-S(7)#6	2.584(5)
Sc(2)-S(1)#1	2.535(5)	Sc(4)-S(5)	2.632(7)
Sc(2)-S(8)#6	2.546(5)		

Angles

S(1)-Ag(1)-S(1)#1	95.6(2)	S(5)-Ag(1)-S(7)#7	87.04(13)
S(1)-Ag(1)-S(5)	111.12(12)	S(7)#6-Ag(1)-S(7)#7	80.6(2)
S(1)#1-Ag(1)-S(5)	111.12(12)	S(8)#5-Ag(2)-S(3)	131.79(9)
S(1)-Ag(1)-S(7)#6	158.29(13)	S(8)#5-Ag(2)-S(3)#1	131.79(9)
S(1)#1-Ag(1)-S(7)#6	88.32(11)	S(3)-Ag(2)-S(3)#1	96.2(2)
S(5)-Ag(1)-S(7)#6	87.04(13)	S(8)#5-Ag(2)-S(4)#5	86.8(2)
S(1)-Ag(1)-S(7)#7	88.32(11)	S(3)-Ag(2)-S(4)#5	89.71(12)
S(1)#1-Ag(1)-S(7)#7	158.29(13)	S(3)#1-Ag(2)-S(4)#5	89.71(12)

Symmetry transformations used to generate equivalent atoms: #1, x, $-y+1/2$, z; #2, $-x+1/2$, $-y$, $z-1/2$; #3, $-x+1$, $-y$, $-z+1$; #4, $-x+1/2$, $y-1/2$, $z-1/2$; #5, $x+1/2$, y, $-z+1/2$, #6, $-x+1/2$, $-y+1$, $z+1/2$; #7, $-x+1/2$, $y-1/2$, $z+1/2$; #8, $x-1/2$, y, $-z+1/2$; #9, $x-1/2$, $-y+1/2$, $-z+1/2$; #10, $-x$, $-y+1$, $-z+1$; #11, $-x+1/2$, $y+1/2$, $z+1/2$; #12, x, $-y+3/2$, z; #13, $x+1/2$, y, $-z+3/2$; #14, $x+1/2$, $-y+1/2$, $-z+1/2$; #15, $-x+1/2$, $-y$, $z+1/2$; #16, $x-1/2$, y, $-z+3/2$; #17, $-x$, $y-1/2$, $-z+1$; #18, $-x+1/2$, $-y+1$, $z-1/2$.
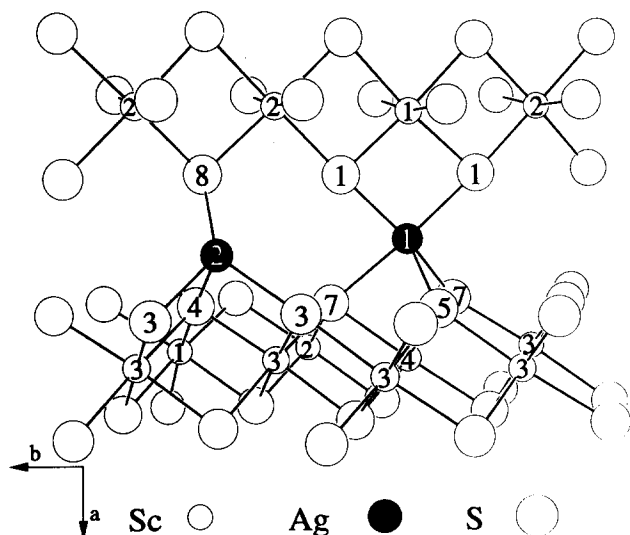

Fig. 2. The connection of layers in the structure of BaSc₃AgS₆ by Ag polyhedra.

Further crystallographic details are given in Table 1, final values of the atomic parameters and isotropic displacement parameters are given in Table 2, and selected distances and angles are given in Table 3.

3. Results and discussion

The structure of BaSc₃AgS₆ consists of a three-dimensional framework of Sc-S and Ag-S polyhedra housing single, one-dimensional channels occupied by Ba²⁺ ions (Fig. 1). Sc³⁺ cations are coordinated to S centers in slightly distorted octahedra, where Sc-S distances range from 2.533(5) Å to 2.637(5) Å and S-Sc-S bond angles range from 85.7(2)° to 98.6(2)°. These distances are reasonable when compared with those found in the Sc₂S₃ [9] structure, which has Sc-S distances ranging from 2.570 Å to 2.610 Å. There are two distinct coordination geometries of the Ag⁺ cations (Fig. 2). Atom Ag(1) is coordinated in a distorted square pyramid with Ag-S distances ranging from 2.591(4) Å to 2.781(4) Å. The Ag(1) atom resides 0.47 Å above the plane described by two S(1) atoms and two S(7) atoms; the Ag(1)-S(5) vector deviates by 7.5° from the normal to the plane. Distorted square-pyramidal coordination of Ag is found in AgYbS₂ [10], where Ag-S distances range from 2.71 Å to 2.81 Å. In BaErAgS₃ [4] Ag-S distances range from 2.543(1)

Å to 3.167(1) Å, but the geometry about the Ag center is closer to trigonal bipyramidal. In the present structure atom Ag(2) has a trigonal-pyramidal geometry with Ag–S distances between 2.406(6) Å and 2.851(6) Å. Trigonal pyramidal geometry about an Ag center is found in the structures of β-Ag$_9$GaSe$_6$ [11] and β'-Ag$_8$GeSe$_6$ [12]. In the present structure Ba^{2+} cations are centered in bicapped trigonal prisms that share triangular faces in the [010] direction. Ba–S distances range from 3.125(4) Å to 3.557(5) Å; compare these with those of 3.208(4)–3.422(6) Å in the bicapped trigonal prism in the BaSm$_2$S$_4$ structure [13].

The three-dimensional structure (Fig. 1) of BaSc$_3$AgS$_6$ is constructed from layers of ScS$_6$ octahedra edge-shared in the [001] direction that are connected by Ag polyhedra in the [100] direction. The step-like appearance along the [001] direction of the layers arises from a shift in the direction of edge sharing every four octahedra. It is necessary to include two such layers when describing the unit cell as these layers, which alternate in direction along [100], cannot be superimposed by translation. This arrangement has similarities to that in the BaErAgS$_3$ structure [4] where a step-like arrangement of the layers is achieved through pairs of edge-sharing octahedra joined together by corner sharing. There the steps of octahedra stack without alternation, and the unit cell therefore contains only one layer.

There is no S–S bonding in BaSc$_3$AgS$_6$; the shortest S–S interactions of about 3.5 Å occur between atoms S(6) and S(8) and are significantly longer than the 2.0 Å separation expected for a S–S single bond [14,15]. It is therefore reasonable to assign the oxidation states Ba(II), Sc(III), Ag(I) and S(−II).

Acknowledgments

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