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Si Extraction from Silica in a Basic Polychalcogenide Flux. Stabilization of $Ba_4SiSb_2Se_{11}$, a Novel Mixed Selenosilicate/Selenoantimonate with a Polar Structure

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An unusual compound, $Ba_4SiSb_2Se_{11}$, was discovered from a reaction of Ba/Th/Sb/Se. It is assumed that Si was extracted from the silica reaction tube. It forms as silver needlelike crystals in the polar space group $Cmc2_1$ with $a = 9.3981(3)$ Å, $b = 25.7192(7)$ Å, $c = 8.7748\ (3)$ Å, and $Z = 4$. A rational synthesis has been devised at 600 °C. The compound is composed of Ba^{2+} ions stabilized between infinite one-dimensional $[SiSb_2Se_{11}]^{8-}$ chains running parallel to the *a* axis. Each chain is composed of a $[SbSe_2]^{-}{}_{\infty}$ backbone with $[SiSe_4]^{4-}$ tetrahedra chelating every other Sb atom from the same side of the backbone. The V-shaped triselenide groups, $(Se_3)^{2-}$, are attached to the rest of the Sb atoms in the chain through one of their terminal Se atoms. The compound has a band gap of 1.43 eV. The Raman spectrum shows a broad shift at 247 cm^{-1} and a shoulder around 234 cm^{-1}, which are related to the Se−Se vibration of the triselenide groups and/or the Si−Se vibrations of the $[SiSe_4]^{4-}$ groups. The compound decomposes at 522 °C.

1. Introduction

Over the past several years, many novel chalcoantimonate compounds have been prepared by the molten flux method, such as $KThSb_2Se_6$,[1] $K_2Ln_2Sb_2Q_9$ (Ln = Gd, La; Q = Se, S),[2] AU_2SbQ_8 (A = K, Rb; Q = Se, S),[3] $RbUSb_{0.33}Te_6$,[4] $K_{2.5}Sb_{8.5}Se_{14}$,[5] A_2AgSbS_4 (A = K, Rb, Cs),[6] $Cs_3Ag_2Sb_3Q_8$ (Q = S, Se),[6] $Rb_2Au_6Sb_4S_{10}$,[7] A_2AuSbS_4 (A = Rb, Cs),[8] $A_2Ag_{20}Sb_4S_{19}$ (A = Rb, Cs),[9] $K_2(RE)_{2-x}Sb_xSb_4Se_{12}$ (RE = La, Ce, Pr, Gd),[10] and $EuSbSe_3$.[11] This class of compounds possesses interesting and diverse structural features partly due to the stereochemically active lone pair of the Sb^{3+} ion. The lone pair can express itself in many different ways, creating various asymmetric local environments around the Sb^{3+} ion such as a trigonal pyramid (CN = 3),[4] a seesaw (CN = 4),[3] a square pyramid (CN = 5),[5] and a distorted octahedron (CN = 6).[1,2,5] This property makes the Sb compounds quite distinctive from other group 15 analogues. For example, the lone pair of the lighter congener, As^{3+}, invariably adopts trigonal pyramidal geometry whereas the lone pair of Bi^{3+} does not have as strong a tendency to localize in a specific direction and usually produces smaller distortions. It is the "in-between" nature of antimony that generates a larger variety in its local environments and enriches the structural chemistry of antimony chalcogenides.

Recently, during our attempts to prepare quaternary Ba/Th/Sb/Se compounds we serendipitously discovered that the reaction mixture had captured Si atoms from the silica tube, used as a container, and produced an unusual new quaternary compound, $Ba_4SiSb_2Se_{11}$. The incorporation of Si atoms to form $SiSe_4$ tetrahedra under the conditions of our experiments is surprising given the strong oxophilicity of Si and the very thermodynamically stable source (i.e., SiO_2) from which it came. For example, accidental extraction of Si has been observed before, but in most cases the Si is extracted as a $[SiO_4]$ unit.[12] A rational way to synthesize bulk samples of this compound has been devised. Compared with the extensively studied silicon oxide compounds, silicon chalcogenides are still sparse. Regarding the selenides, only a handful of ternary systems (e.g., ZrSiSe,[13] Tl_4SiSe_4,[14] $Na_6Si_2Se_8$,[15] $Na_4Si_4Se_{10}$,[16] $Na_6Si_2Se_7$,[17] Pb_2SiSe_4,[18] Ba_2SiSe_4,[19] Mn_2SiSe_4[20]) have been reported. Here we describe $Ba_4SiSb_2Se_{11}$, an exceptional compound that also happens to be a new member of the silicon chalcogenide class.

2. Experimental Section

2.1. Synthesis. Single crystals of $Ba_4SiSb_2Se_{11}$ were initially discovered from a mixture of Ba (0.2 mmol), Th (0.2 mmol), Sb (0.2 mmol), and Se (2 mmol), which was sealed under vacuum in a silica

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tube and heated to 720 °C for 5 days followed by cooling to 150 °C at 2 °C/h. The excess $Ba_xSb_ySe_z$ flux was removed with degassed water to reveal silver needlelike crystals of $Ba_4SiSb_2Se_{11}$ (yield, ~5% based on Sb). The main products were $BaSbSe_3$[21] and $BaTh_7Se_{18}$.[22] The crystals of $Ba_4SiSb_2Se_{11}$ are air- and water-stable. For physicochemical characterization, bulk material was prepared rationally from a near-stoichiometric mixture of Ba (0.8 mmol), Si (0.2 mmol), Sb (0.4 mmol), and Se (2.4 mmol). The mixture was sealed under vacuum in a silica tube and heated to 600 °C for 2 days followed by cooling to 150 °C at 2 °C/h. The homogeneity of the product was confirmed by comparing the powder X-ray diffraction pattern of the product against one calculated using the crystal atom coordinates.

2.2. Physical Measurements. 2.2.1. Solid-State UV/Vis and Raman Spectroscopy. Optical diffuse reflectance measurements were performed at room temperature with a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer operating in the 200−2500 nm region. The material's band gap was determined as described previously.[23] Raman spectra were recorded on a Holoprobe Raman spectrograph equipped with a CCD camera detector using 633 nm radiation from a HeNe laser for excitation. Laser power at the sample was estimated to be about 1 mW, and the focused laser beam diameter was ca.10 μm. A total of 5 scans were needed to obtain good quality spectra. The accumulation time of each scan was 5 s.

2.2.2. Differential Thermal Analysis (DTA). DTA experiments were performed with a Shimadzu DTA-50 thermal analyzer as described elsewhere.[2]

2.3. X-ray Crystallography. A single crystal with dimensions 0.18 mm × 0.05 mm × 0.03 mm was mounted on the tip of a glass fiber, and intensity data were collected on a Bruker SMART Platform CCD diffractometer using graphite monochromatized Mo Kα radiation. The data were collected at 170(2) K over a full sphere of reciprocal space, up to 28.27° in θ. The individual frames were measured with an omega rotation of 0.3° and an acquisition time of 45 s. The SMART[24] software was used for the data acquisition and the SAINT[25] program for the data extraction and reduction. The absorption correction was performed using SADABS.[26] The structure solution and refinement were performed with the SHELXTL package of crystallographic programs.[27] The systematic absence conditions of the data set suggested three possible space groups, $Cmc2_1$ (No. 36), $Cmcm$ (No. 63), and $C2cm$ (No. 40). The structure was solved and refined successfully in the polar space group $Cmc2_1$. The structure of $Ba_4SiSb_2Se_{11}$ is clearly polar with no additional mirror planes perpendicular to the *c* axis and could not be solved in the centrosymmetric space group $Cmcm$. The crystals used for the structure solution were racemically twinned, and the Flack parameter was refined to 0.41(2).

The complete data collection parameters and details of the structure solution and refinement are given in Table 1. The coordinates of all atoms, isotropic temperature factors, and their estimated standard deviations (esd's) are given in Table 2. The selected bond distances and angles are given in Table 3. A full table of crystallographic details, ADP's, and a full table of interatomic distances and angles are deposited with Supporting Information.

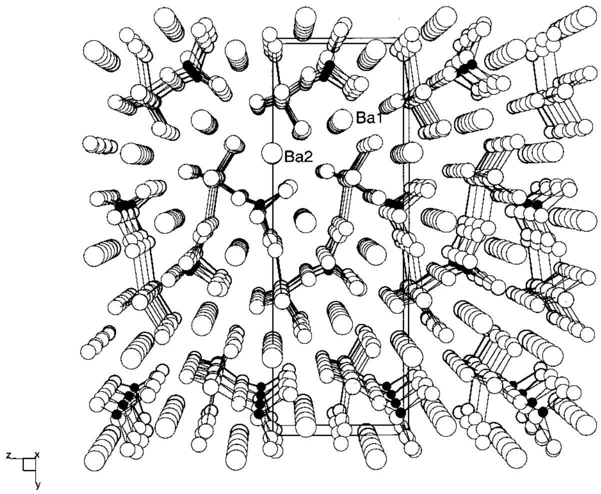

Figure 1. Structure of $Ba_4SiSb_2Se_{11}$ viewed down the *a* axis. Small black-filled circles are Si atoms, open circles are Se atoms, and gray circles are Sb atoms.

Table 1. Summary of Crystallographic Data and Structural Analysis for $Ba_4SiSb_2Se_{11}$

formula	$Ba_4SiSb_2Se_{11}$
fw	1689.51
cryst habit	silver needles
space group	$Cmc2_1$
a, Å	9.3981(3)
b, Å	25.7192(7)
c, Å	8.7748(3)
Z	4
V, Å^3	2120.97(11)
D_{calc}, g/cm^3	5.291
temp, K	170(2)
λ(Mo Kα), Å	0.710 69
μ(Mo Kα), cm^{-1}	287.34
θ_{max}, deg	28.27
goodness of fit on F^2	1.129
R1^a [$I > 2\sigma$]	0.0261
wR2^b [$I > 2\sigma$]	0.0592
R1 (all data)	0.0280
WR2 (all data)	0.0599
Flack param	0.41(2)

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

Table 2. Fractional Atomic Coordinates and Equivalent Atomic Displacement Parameter (U_{eq}) Values for $Ba_4SiSb_2Se_{11}$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq},^{a} Å^2
Ba(1)	0.2474(1)	0.2098(1)	0.5007(1)	0.010(1)
Ba(2)	0.2529(1)	0.0400(1)	0.2610(1)	0.012(1)
Sb(1)	0	0.3510(1)	0.4294(1)	0.011(1)
Sb(2)	0.5	0.3557(1)	0.4331(1)	0.015(1)
Si	0.5	0.4205(1)	−0.9062(4)	0.010(1)
Se(1)	0.5	0.2338(1)	0.7732(1)	0.010(1)
Se(2)	0.2836(1)	0.1647(1)	0.1062(1)	0.013(1)
Se(3)	0.5	0.2692(1)	0.2918(1)	0.010(1)
Se(4)	0.1927(1)	0.0993(1)	0.7402(1)	0.015(1)
Se(5)	0	−0.1253(1)	0.8728(1)	0.011(1)
Se(6)	0	0.0059(1)	0.0165(1)	0.011(1)
Se(7)	0.5	0.1173(1)	0.4046(1)	0.013(1)
Se(8)	0.5	0.0555(1)	0.6053(2)	0.043(1)
Se(9)	0	0.5257(1)	0.9797(1)	0.017(1)

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

3. Results and Discussion

The structure of $Ba_4SiSb_2Se_{11}$ presents infinite $[SiSb_2Se_{11}]^{8-}$ chains running parallel to the *a* axis and separated by Ba atoms (see Figure 1). Each chain consists of tetrahedral $[SiSe_4]^{4-}$ units and triselenide $(Se_3)^{2-}$ groups attached to a $[SbSe_2]^{-}_{\infty}$ "wire", which forms the backbone of the structure. Therefore, the compound is better expressed as $(Ba^{2+})_4[(SbSe_2)_2(SiSe_4)(Se_3)]^{8-}$, projecting an unusual combination of *three* different seleno anions in the structure.

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Table 3. Selected Distances (Å) and Bond Angles (deg) for $Ba_4SiSb_2Se_{11}$

	Bond Distances		
Ba(1)−Se(3)	3.367(1)	Ba(2)−Se(7)	3.308(1)
Ba(1)−Se(2)	3.371(1)	Ba(2)−Se(6)	3.320(1)
Ba(1)−Se(5)	3.373(1)	Ba(2)−Se(5)	3.381(1)
Ba(1)−Se(1)	3.391(1)	Ba(2)−Se(9)	3.409(1)
Ba(1)−Se(1)	3.426(1)	Ba(2)−Se(9)	3.453(1)
Ba(1)−Se(7)	3.465(1)	Ba(2)−Se(6)	3.473(1)
Ba(1)−Se(3)	3.496(1)	Ba(2)−Se(2)	3.496(1)
Ba(1)−Se(4)	3.571(1)	Ba(2)−Se(4)	3.630(1)
Ba(1)−Se(2)	3.666(1)	Ba(2)−Se(8)	3.645(1)
		Ba(2)−Se(8)	3.832(1)
Sb(1)−Se(1)	2.575(1)	Sb(2)−Se(3)	2.547(1)
Sb(1)−Se(2) × 2	2.589(1)	Sb(2)−Se(4) × 2	2.736(1)
Sb(1)−Se(9)	3.202(1)	Sb(2)−Se(2) × 2	3.113(1)
Sb(1)−Se(4) × 2	3.568(1)		
Si−Se(5)	2.270(3)	Se(7)−Se(8)	2.373(2)
Si−Se(4) × 2	2.278(2)	Se(8)−Se(9)	2.361(2)
Si−Se(6)	2.297(3)		
	Bond Angles		
Se(3)−Ba(1)−Se(2)	77.03(3)	Se(6)−Ba(2)−Se(5)	81.71(2)
Se(3)−Ba(1)−Se(5)	126.66(3)	Se(7)−Ba(2)−Se(9)	82.08(2)
Se(2)−Ba(1)−Se(5)	130.42(2)	Se(6)−Ba(2)−Se(9)	89.49(2)
Se(3)−Ba(1)−Se(1)	88.19(2)	Se(5)−Ba(2)−Se(9)	139.36(4)
Se(2)−Ba(1)−Se(1)	72.08(3)	Se(7)−Ba(2)−Se(2)	62.47(3)
Se(5)−Ba(1)−Se(1)	145.67(3)	Se(6)−Ba(2)−Se(2)	92.90(3)
Se(1)−Ba(1)−Se(1)	143.99(2)	Se(5)−Ba(2)−Se(2)	64.84(2)
Se(7)−Ba(1)−Se(3)	137.72(3)	Se(9)−Ba(2)−Se(2)	76.18(3)
Se(1)−Sb(1)−Se(2)	100.76(3)	Se(3)−Sb(2)−Se(4)	93.91(3)
Se(2)−Sb(1)−Se(2)	103.49	Se(3)−Sb(2)−Se(2)	95.17(3)
Se(2)−Sb(1)−Se(9)	94.14(3)	Se(2)−Sb(2)−Se(4)	160.08(3)
Se(2)−Sb(1)−Se(4)	166.02(4)	Se(2)−Sb(2)−Se(4)	78.85(2)
Se(2)−Sb(1)−Se(4)	72.49(2)	Se(2)−Sb(2)−Se(2)	117.82(4)
Se(4)−Si−Se(4)	105.30(13)	Se(7)−Se(8)−Se(9)	104.23(7)
Se(5)−Si−Se(4)	111.45(9)		
Se(5)−Si−Se(6)	104.13(13)		
Se(4)−Si−Se(6)	112.34(9)		

There are two crystallographically unique Sb atoms alternating along the chain (see Figure 2a). The Sb(1) makes three short bonds with Se(1), Se(2), and Se(2′), forming a trigonal pyramid. However, there also exists a moderate interaction (3.202(1) Å) between Sb(1) and Se(9), which belongs to the triselenide group. Inclusion of this interaction makes the local coordination of Sb(1) a distorted seesaw (see Figure 2b).[28] The Sb(2) atom is stabilized in a five-coordinate distorted square pyramidal site, where Sb(2) sits slightly above the square plane (see Figure 2c). The axial bond of the $Sb(2)Se_4$ pyramid is much shorter (2.547(1) Å) than equatorial bonds, the average distance of which is 2.924(1) Å. The Sb^{3+} ions in this coordination mode express their $5s^2$ lone pairs below the pyramid's square plane. The Sb(1) and Sb(2) polyhedra are joined together by sharing Se(2) atoms to form a one-dimensional chain (see Figure 2a).

The Si atom is stabilized in a regular tetrahedral site with Si−Se distances ranging from 2.270(3) to 2.297(3) Å and Se−Si−Se angles varying from 104.13(13)° to 112.34(9)°. The $[SiSe_4]^{4-}$ tetrahedra chelate the Sb(2) atoms through two Se(4) atoms, forming a four-membered ring (see Figure 2c). This binding of $[SiSe_4]^{4-}$ occurs only from the same side of the $[SbSe_2]^-{}_\infty$ chain, which becomes one of the factors that make the structure polar.

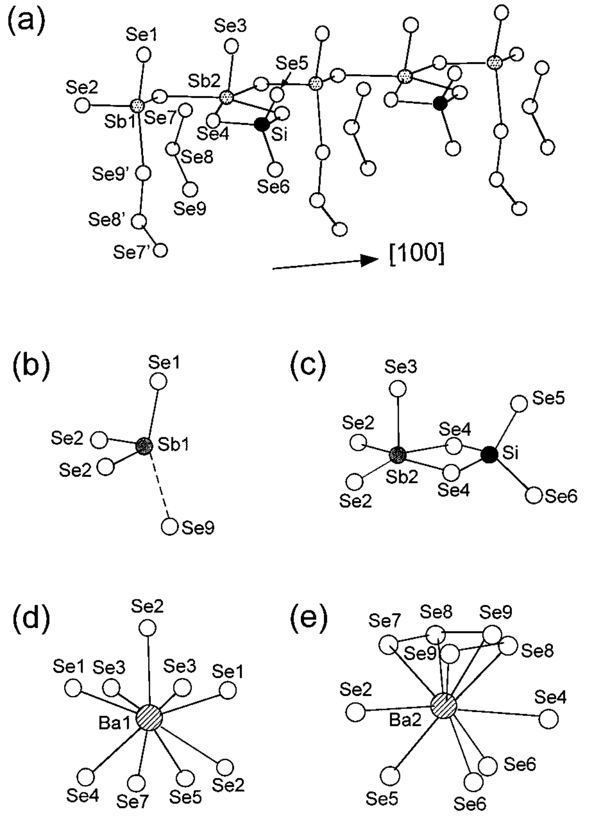

Figure 2. (a) Section of the one-dimensional chain in $Ba_4SiSb_2Se_{11}$. The local coordination environment of (b) Sb(1), (c) Sb(2) and Si, (d) Ba(1), and (e) Ba(2).

The triselenide groups alternate with the $[SiSe_4]^{4-}$ tetrahedra along the $[SbSe_2]^-{}_\infty$ wire as shown in Figure 2a. The V-shaped triselenide group is almost staggered, with the $[SiSe_4]^{4-}$ tetrahedron of another chain giving the illusion of infinite chains along the *c* axis. The terminal Se(9) is loosely attached to the Sb(1) atom of the neighboring chain in the same manner as the Se(9′) shown in Figure 2a. The bond distances and angles of the triselenide group are normal and similar to those found in A_2Se_3 (A = K, Rb, Cs).[29,30] Therefore, this group is reasonably assigned as $(Se_3)^{2-}$ with two terminal Se^{1-} and one central Se^0 atoms. The anisotropic displacement parameter $U_{11}$of the central Se(8) atom is 9 times larger than other values (for example, the U_{11} and U_{22} parameters for Se(8) are 0.105(2) and 0.014(1) Å^2, respectively). This indicates that the triselenide groups are somewhat mobile, performing a "swinging" motion of the Se(8) atom along the *a* axis while Se(7) and Se(9) are fixed.

There are two crystallographically unique Ba atoms in the structure. Ba(1) is nine-coordinate in a distorted monocapped square antiprismatic site (see Figure 2d). Ba(2) is 10-coordinate, and its coordination environment cannot be described in terms of usual polyhedra. Five of the 10 Se atoms form a distorted planar pentagonal face at one end, and three more form a planar triangular face at the other end. The remaining two Se atoms are used to cap two of the faces between the pentagonal and the triangular faces (Figure 2e).

The compound is valence-precise and is expected to be a semiconductor. The UV−vis absorption spectrum of $Ba_4SiSb_2Se_{11}$ shows a gap at 1.43 eV (see Figure 3a). The Raman spectrum of $Ba_4SiSb_2Se_{11}$ (Figure 3b) shows its highest energy shift at 247 cm^{-1} (strong) with a shoulder around 234 cm^{-1}.

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(28) Another way to describe the local coordination of Sb(1) is a distorted trigonal bipyramid, if we consider the lone pair electrons of the Sb^{3+} ion as one of the equatorial ligands. Similarly, the local environment of Sb(2) can be described as a distorted octahedron with its lone pair regarded as the 6th ligand.

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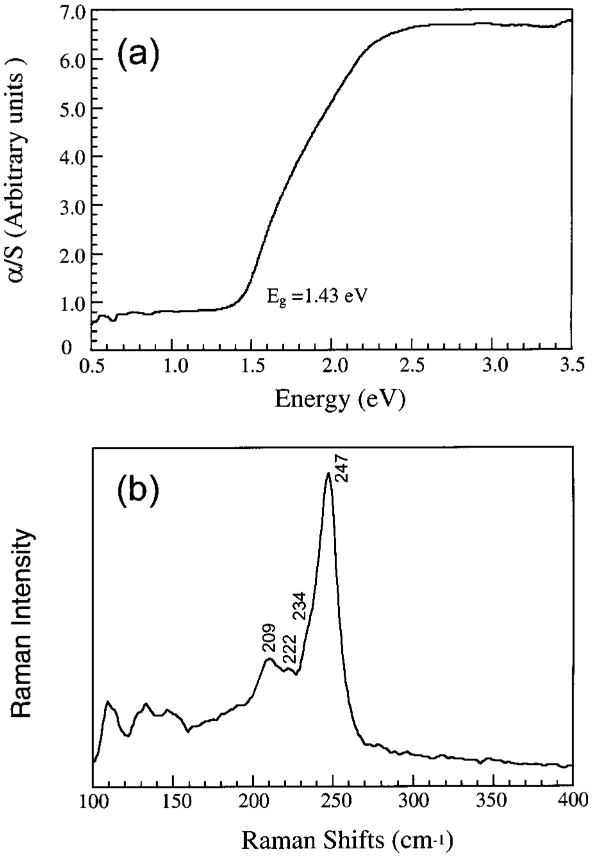

Figure 3. (a) Optical absorption spectrum and (b) Raman spectrum of $Ba_4SiSb_2Se_{11}$.

These shifts seems to be associated with Se−Se stretching vibrations of the triselenide, judging from the Se−Se stretching frequencies reported for other compounds such as elemental Se (234−253 cm^{-1} depending on the structure type of Se)[31] and K_2Se_2 (253 cm^{-1}).[32] It is difficult, however, to unequivocally assign the shifts because the Si−Se vibrations of the $SiSe_4$ tetrahedron also occur in the same region.[33] From differential thermal analysis (DTA) and subsequent XRD studies we observed that the compound decomposes at 522 °C.

Clearly, the complex composition of this unusual quaternary compound suggests that it could not have been anticipated a priori. It was also surprising that $Ba_4SiSb_2Se_{11}$ was stable under ambient conditions because there is the general perception that chalcosilicate chemistry with $[SiS_4]^{4-}$ and $[SiSe_4]^{4-}$ species tends to be air- and moisture-sensitive. The unexpected discovery of $Ba_4SiSb_2Se_{11}$ brings forth several interesting realizations. First, many chalcosilicate compounds may be quite environmentally stable, and second, novel structures may be expected from experiments incorporating simultaneously different anions such as $[SiSe_4]^{4-}$ and $[Sb_xSe_y]^{n-}$.

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Supporting Information Available: Tables of crystallographic details and anisotropic displacement parameters for all atoms and of interatomic distances and angles for $Ba_4SiSb_2Se_{11}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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