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New Quaternary Bismuth Sulfides: Syntheses, Structures, and Band Structures of $AMBiS_4$ (A = Rb, Cs; M = Si, Ge)

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Four new compounds, $RbSiBiS_4$, $RbGeBiS_4$, $CsSiBiS_4$, and $CsGeBiS_4$, have been synthesized by means of the reactive flux method. The isostructural compounds $RbSiBiS_4$, $RbGeBiS_4$, and $CsGeBiS_4$ crystallize in space group $P2_1/c$ of the monoclinic system with four formula units in cells of dimensions at 153 K of $a = 6.4714(4)$ Å, $b = 6.7999(4)$ Å, $c = 17.9058(11)$ Å, and $\beta = 108.856(1)°$ for $RbSiBiS_4$, $a = 6.5864(4)$ Å, $b = 6.8559(4)$ Å, $c = 17.9810(12)$ Å, and $\beta = 109.075(1)°$ for $RbGeBiS_4$, and $a = 6.5474(4)$ Å, $b = 6.9282(4)$ Å, $c = 18.8875(11)$ Å, and $\beta = 110.173(1)°$ for $CsGeBiS_4$. $CsSiBiS_4$ crystallizes in a different structure type in space group $P2_1/c$ of the monoclinic system with four formula units in a cell of dimensions at 153 K of $a = 9.3351(7)$ Å, $b = 6.9313(5)$ Å, $c = 12.8115(10)$ Å, and $\beta = 109.096(1)°$. The two structure types are closely related and consist of ${}^2_\infty[MBiS_4{}^-]$ (M = Si, Ge) layers separated by bicapped trigonal-prismatically coordinated alkali-metal atoms. In each, the M atom is coordinated to a tetrahedron of four S atoms and the Bi atom is coordinated to seven S atoms comprising five close S atoms at the corners of a square pyramid with Bi near the center of the basal plane and the sixth and seventh S atoms further away to complete a distorted monocapped trigonal prism. The optical band gaps of 2.23 eV for $RbGeBiS_4$ and 2.28 eV for $CsGeBiS_4$ were deduced from their diffuse reflectance spectra. From a band structure calculation, the optical absorption for $RbGeBiS_4$ originates from the ${}^2_\infty[GeBiS_4{}^-]$ layer. The Ge 4p orbitals, Bi 6p orbitals, and S 3p orbitals are highly hybridized.

Introduction

Bismuth chalcogenides are an interesting class of compounds with amazing structural and compositional complexity.[1] The stereochemical activity of the $6s^2$ lone pair of electrons of Bi influences the structures, and thus the properties of the compounds. During the past decade exploratory investigations have led to the discoveries of many new bismuth chalcogenides. Some compounds show interesting properties.[2,3] A number of ternary and quaternary group XIV bismuth chalcogenides have been synthesized recently, including $Sn_4Bi_2Se_7$,[4] $SnBi_4Se_7$,[5] $CsPbBi_3Se_6$,[6] $APbBi_3Se_6$ (A = K, Rb),[6] $APbBi_3S_6$ (A = Rb, Cs),[6] $A_{1-x}M_{3-x}Bi_{11+x}Se_{20}$ and $A_{1+x}M_{3-2x}Bi_{7+x}Se_{14}$ (A = K, Rb, Cs; M = Sn, Pb),[7] $Ba_3Bi_6MSe_{13}$ (M = Pb, Sn),[8] $CsMBi_3Te_6$ (M = Pb, Sn),[9] and $CsM_2Bi_3Te_7$ (M = Pb, Sn).[9] In all these structures the group XIV atoms (Sn or Pb), which are in the 2+ oxidation state, show disorder with the Bi or A atoms. The lighter congeners of Sn or Pb, namely, Si and Ge, have a propensity to be in the 4+ oxidation state and as such have far smaller radii than A^+ or Bi^{3+} ions. Thus, incorporation of Si^{4+} or Ge^{4+} ions into bismuth sulfides is likely to lead to ordered structures. We illustrate this by reporting here the syntheses and ordered structures of four new quaternary group XIV bismuth sulfides, namely, $RbSiBiS_4$, $RbGeBiS_4$, $CsSiBiS_4$,

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[†] Department of Chemistry.
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(1) Makovicky, E. *Neues Jahrb. Mineral., Abh.* **1989**, *160*, 269−297.
(2) Chung, D.-Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science* **2000**, *287*, 1024−1027.
(3) Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. *Chem. Mater.* **1996**, *8*, 1465−1474.
(4) Adouby, K.; Pérez-Vicente, C.; Jumas, J. C.; Fourcade, R.; Touré, A. A. *Z. Kristallogr.* **1998**, *213*, 343−349.
(5) Pérez Vicente, C.; Tirado, J. L.; Adouby, K.; Jumas, J. C.; Touré, A. A.; Kra, G. *Inorg. Chem.* **1999**, *38*, 2131−2135.
(6) Chung, D.-Y.; Iordanidis, L.; Rangan, K. K.; Brazis, P. W.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1999**, *11*, 1352−1362.
(7) Mrotzek, A.; Iordanidis, L.; Kanatzidis, M. G. *Inorg. Chem.* **2001**, *40*, 6204−6211.
(8) Wang, Y. C.; DiSalvo, F. J. *Chem. Mater.* **2000**, *12*, 1011−1017.
(9) Hsu, K.-F.; Chung, D.-Y.; Lal, S.; Mrotzek, A.; Kyratsi, T.; Hogan, T.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2002**, *124*, 2410−2411.

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and $CsGeBiS_4$. In addition, we report the optical properties of $RbGeBiS_4$ and $CsGeBiS_4$ and the band structure of $RbGeBiS_4$.

Experimental Section

Syntheses. The following reagents were used as obtained: Rb (Aldrich, 98+%), Cs (Aldrich, 99.5%), Si (Alfa, 99.5%), Ge (Strem, 99.999%), Bi (Johnson Matthey, 99.999%), Bi_2S_3 (Aldrich, 99.5%), S (Aldrich, 99.5%). The compounds A_2S_3 (A = Rb, Cs), the reactive fluxes[10] employed in the syntheses, were prepared by stoichiometric reactions of the elements in liquid NH_3. For the syntheses of the isostructural compounds $RbSiBiS_4$, $RbGeBiS_4$, and $CsGeBiS_4$ reaction mixtures of 0.5 mmol of A_2S_3, 1.0 mmol of M (M = Si, Ge), 0.5 mmol of Bi, and 2.5 mmol of S were loaded into fused-silica tubes under an Ar atmosphere in a glovebox. These tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The samples were heated to 893 K for $RbMBiS_4$ and 873 K for $CsGeBiS_4$ in 15 h, kept at those temperatures for 84 h, and slowly cooled at 6 K/h to 373 K, and then the furnace was turned off.

The compound $CsSiBiS_4$ was prepared by the reaction of 0.5 mmol of Cs_2S_3, 1.0 mmol of Si, 0.5 mmol of Bi_2S_3, and 2.0 mmol of S. The sample was heated to 1073 K in 20 h, kept at 1073 K for 84 h, and cooled at 6 K/h to 373 K, and then the furnace was turned off.

The reaction mixtures were washed free of flux with *N*,*N*-dimethylformamide and then dried with acetone. The products consisted of orange-red plates of $RbSiBiS_4$, $RbGeBiS_4$, and $CsGeBiS_4$ or yellow plates of $CsSiBiS_4$. Unoptimized yields (based on Bi) for $RbGeBiS_4$ and $CsGeBiS_4$ were approximately 70%, whereas those for $RbSiBiS_4$ and $CsSiBiS_4$ were about 20%. Analyses of these compounds with an EDX-equipped Hitachi S-3500 scanning electron microscope showed the presence of A, M, Bi, and S. The compounds are moderately stable in air. The other products of the reactions were black noncrystalline melts consisting of ternary A/Bi/S compounds, as deduced from EDX measurements.

Structure Determinations. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer.[11] The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of the data collection. Data were collected by a scan of 0.3° in ω in groups of 606, 606, 606, and 606 frames at ϕ settings of 0°, 90°, 180°, and 270° for $RbSiBiS_4$, $RbGeBiS_4$, and $CsGeBiS_4$, and in groups of 606, 606, and 606 frames at ϕ settings of 0°, 120°, and 240° for $CsSiBiS_4$. The exposure time was 10 or 15 s/frame. The collection of the intensity data was carried out with the program SMART.[11] Cell refinement and data reduction were carried out with the use of the program SAINT,[11] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[12] Then the program SADABS[11] was employed to make incident beam and decay corrections.

The structures were solved with the direct methods program SHELXS and refined with the least-squares program SHELXL of the SHELXTL.PC suite of programs.[12] Each final refinement included anisotropic displacement parameters. A secondary extinction correction was included for $CsGeBiS_4$. The program TIDY[13] was then employed to standardize the atomic coordinates in each structure. Additional experimental details are given in Table 1. Selected metrical data are given in Table 2. Additional information may be found in the Supporting Information.

Table 1. Crystal Data and Structure Refinements for $RbSiBiS_4$, $RbGeBiS_4$, $CsGeBiS_4$, and $CsSiBiS_4$[a]

	$RbSiBiS_4$	$RbGeBiS_4$	$CsGeBiS_4$	$CsSiBiS_4$
fw	450.78	495.28	542.72	498.22
a (Å)	6.4714(4)	6.5864(4)	6.5474(4)	9.3351(7)
b (Å)	6.7999(4)	6.8559(4)	6.9282(4)	6.9313(5)
c (Å)	17.9058(11)	17.9810(12)	18.8875(11)	12.8115(10)
β (deg)	108.856(1)	109.075(1)	110.173(1)	109.096(1)
V (Å^3)	745.66(8)	767.36(8)	804.21(8)	783.34(10)
ρ_c (g/cm^3)	4.015	4.287	4.482	4.225
μ (cm^{-1})	312.95	340.95	309.81	281.96
$R(F)$[b]	0.0204	0.0252	0.0264	0.0293
$R_w(F_o^2)$[c]	0.0469	0.0611	0.0794	0.0688

[a] For all structures $Z = 4$, space group = $P2_1/c$, $T = 153(2)$ K, and $\lambda = 0.71073$ Å. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (zP)^2$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$ and z = 0.02 for $CsGeBiS_4$ and $RbSiBiS_4$ and 0.03 for $RbGeBiS_4$ and $CsSiBiS_4$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $RbSiBiS_4$, $RbGeBiS_4$, $CsGeBiS_4$, and $CsSiBiS_4$

	$RbSiBiS_4$	$RbGeBiS_4$	$CsGeBiS_4$	$CsSiBiS_4$
M−S1	2.153(2)	2.236(2)	2.236(2)	2.161(3)
M−S2	2.132(2)	2.219(1)	2.222(2)	2.116(2)
M−S3	2.099(2)	2.185(1)	2.190(2)	2.105(3)
M−S4	2.114(2)	2.198(1)	2.199(2)	2.098(2)
Bi−S1	2.686(1)	2.673(1)	2.664(2)	2.664(2)
Bi−S1	3.048(1)	3.098(1)	3.090(2)	3.004(2)
Bi−S2	2.658(1)	2.645(1)	2.639(2)	2.676(2)
Bi−S2	3.316(1)	3.334(1)	3.332(2)	3.462(2)
Bi−S3	2.875(1)	2.889(1)	2.865(2)	2.805(2)
Bi−S3	3.324(1)	3.370(1)	3.414(2)	3.331(2)
Bi−S4	2.779(1)	2.779(1)	2.807(2)	2.799(2)
S1−Bi−S1	86.12(2)	85.67(2)	86.55(3)	78.42(5)
S1−Bi−S2	83.92(3)	84.49(4)	84.63(5)	84.34(5)
S1−Bi−S2	134.95(3)	135.08(4)	136.50(5)	136.85(5)
S1−Bi−S2	164.47(3)	166.09(4)	165.84(5)	158.90(5)
S1−Bi−S2	76.41(3)	75.27(3)	74.78(4)	81.79(4)
S1−Bi−S3	74.18(3)	76.62(4)	76.95(5)	75.69(5)
S1−Bi−S3	147.97(3)	149.68(4)	149.25(5)	148.96(5)
S1−Bi−S3	95.18(3)	94.07(4)	94.89(5)	93.33(5)
S1−Bi−S3	117.43(3)	115.80(3)	114.14(4)	123.80(4)
S1−Bi−S4	86.17(3)	84.00(4)	84.13(5)	89.49(5)
S1−Bi−S4	73.14(3)	75.31(4)	75.22(5)	73.86(5)
S2−Bi−S2	118.95(2)	118.60(2)	119.04(3)	119.28(3)
S2−Bi−S3	93.53(3)	93.20(4)	93.88(5)	94.10(5)
S2−Bi−S3	68.03(3)	70.16(3)	70.17(4)	68.43(5)
S2−Bi−S3	66.65(3)	64.91(3)	66.23(4)	67.60(5)
S2−Bi−S3	74.84(3)	73.77(3)	73.23(4)	72.38(4)
S2−Bi−S4	94.29(3)	93.88(4)	92.85(5)	94.09(5)
S2−Bi−S4	125.87(3)	127.58(3)	126.24(4)	121.01(5)
S3−Bi−S3	120.02(2)	119.88(2)	120.83(3)	119.40(3)
S3−Bi−S4	157.92(3)	158.61(4)	159.21(5)	162.25(5)
S3−Bi−S4	81.03(3)	81.49(3)	79.94(4)	78.30(5)

Diffuse Reflectance Spectroscopy. A Cary 1E UV−vis spectrophotometer with a diffuse reflectance accessory was used to measure the spectra of the compounds $RbGeBiS_4$ and $CsGeBiS_4$ over the range 350 nm (3.54 eV) to 850 nm (1.46 eV).

TB-LMTO Calculation. The electronic structure of $RbGeBiS_4$ was calculated by means of the self-consistent, scalar relativistic linearized muffin-tin orbital program of Andersen and coworkers[14−16] within the atomic sphere approximation. This method

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(10) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202−6204.

(11) Bruker. *SMART Version 5.054 Data Collection*; *SAINT-Plus Version 6.22 Data Processing Software for the SMART System*; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2000.

(12) Sheldrick, G. M. *SHELXTL DOS/Windows/NT Version 6.12*; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2000.

(13) Gelato, L. M.; Parthé, E. *J. Appl. Crystallogr.* **1987**, *20*, 139−143.

(14) Andersen, O. K. *Phys. Rev. B* **1975**, *12*, 3060−3083.

splits the crystal space into overlapping atomic spheres (Wigner−Seitz spheres) whose radii are chosen to fill completely the crystal volume. In the calculation presented here, the von Barth−Hedin exchange-correlation potential was used within the local density approximation.[17] All *k*-space integrations were performed with the tetrahedron method.[18,19] The basis sets consisted of the valence 5s electrons for Rb, the 6s and 6p electrons for Bi, the 4s and 4p electrons for Ge, the 3s and 3p electrons for S, and the 1s electrons for empty spheres. The 5p and 5d electrons for Rb, 6d for Bi, 4d for Ge, 3d for S, and p−d states for empty spheres were downfolded by means of the technique of Löwdin.[20] The crystal orbital Hamiltonian population (COHP),[21] which is the density of states weighted by the corresponding Hamiltonian matrix element, was calculated to analyze the strength and nature of the bonding. Within the irreducible Brillouin zone, 90 *k* points were used.

Results and Discussion

Syntheses. The compounds $\mathrm{RbSiBiS_4}$, $\mathrm{RbGeBiS_4}$, and $\mathrm{CsGeBiS_4}$ were relatively easy to synthesize, although the yield of $\mathrm{RbSiBiS_4}$ was low. On the other hand, the synthesis of $\mathrm{CsSiBiS_4}$ proved to be difficult. Although the reaction of $\mathrm{Cs_2S_3}$, Si, Bi, and S at various temperatures led to the formation of yellow polycrystals that contained all four elements, as determined by EDX measurements, no crystals suitable for X-ray structure analysis were obtained. However, single crystals of good quality were obtained when $\mathrm{Bi_2S_3}$ was used in place of Bi at a reaction temperature of 1073 K.

Structures. The isostructural compounds $\mathrm{RbSiBiS_4}$, $\mathrm{RbGeBiS_4}$, and $\mathrm{CsGeBiS_4}$ crystallize in one structure type, whereas $\mathrm{CsSiBiS_4}$ crystallizes in a different one. In neither structure is there any detectable disorder among M, Bi, or A atoms. Since there are no S−S bonds in the structures, the formal oxidation states of 1+, 4+, 3+, and 2− can be assigned to A, M, Bi, and S, respectively.

The structure of the isostructural compounds $\mathrm{RbSiBiS_4}$, $\mathrm{RbGeBiS_4}$, and $\mathrm{CsGeBiS_4}$ is illustrated in Figure 1. It consists of $^2_\infty[\mathrm{MBiS_4}^-]$ (M = Si, Ge) layers separated by A (A = Rb, Cs) atoms. Each A atom is coordinated to a bicapped trigonal prism of eight S atoms. The A−S bond lengths (Table 2) range from 3.323(1) to 3.577(1) Å in $\mathrm{RbSiBiS_4}$, from 3.309(1) to 3.641(1) Å in $\mathrm{RbGeBiS_4}$, and from 3.432(2) to 3.890(2) Å in $\mathrm{CsGeBiS_4}$. Each bicapped trigonal prism has four edge-sharing neighbors and two corner-sharing ones to form a two-dimensional $^2_\infty[\mathrm{AS_4}^{7-}]$ layer (Figure 2). Each M atom is coordinated to a slightly distorted tetrahedron of four S atoms. The M−S bond lengths range from 2.099(2) to 2.153(2) Å in $\mathrm{RbSiBiS_4}$, from 2.185(1) to 2.236(2) Å in $\mathrm{RbGeBiS_4}$, and from 2.190(2) to 2.236(2) Å in $\mathrm{CsGeBiS_4}$ (Table 2). Each Bi atom is coordinated by seven S atoms. The coordination geometry may, with some arbitrariness, be described as a distorted monocapped trigonal prism comprising five close S atoms at the corners of a square pyramid with Bi near the center of the basal plane and the sixth and seventh S atoms further away (Figure 3). The S atom at the apex of the square pyramid is the cap of the prism. The largest differences in Bi−S bond lengths within these $\mathrm{BiS_7}$

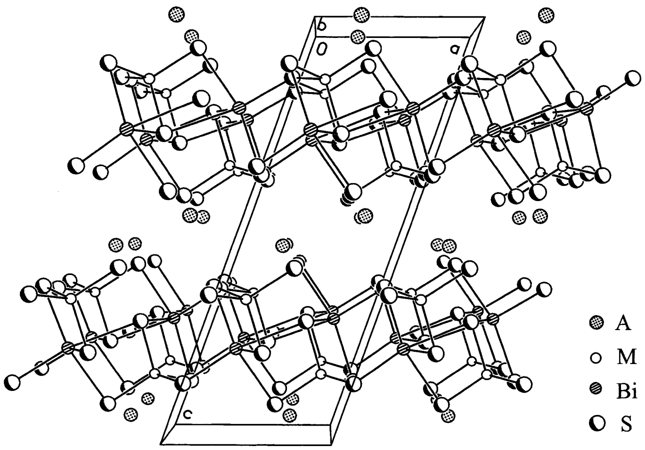

Figure 1. Unit cell of the $\mathrm{RbSiBiS_4}$ structure type viewed along [010].

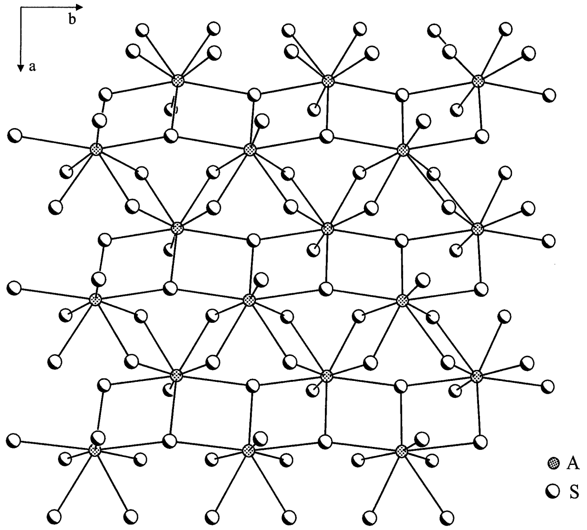

Figure 2. $^2_\infty[\mathrm{AS_4}^{7-}]$ layer in the $\mathrm{RbSiBiS_4}$ structure type.

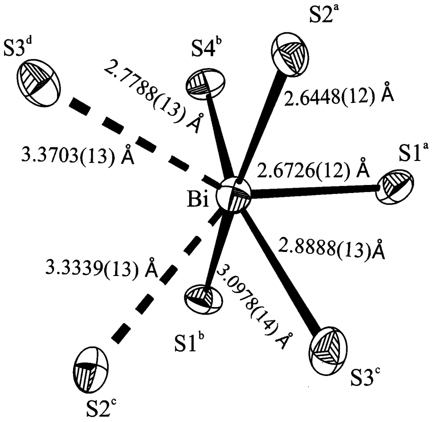

Figure 3. Coordination geometry of Bi in $\mathrm{RbGeBiS_4}$. (The displacement ellipsoids are shown at the 90% level.) Symmetry codes: (a) *x*, *y*, *z*; (b) 1 − *x*, $^1/_2$ + *y*, $^1/_2$ − *z*; (c) −*x*, $^1/_2$ + *y*, $^1/_2$ − *z*; (d) *x*, *y* + 1, *z*.

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(15) Andersen, O. K.; Jepsen, O. *Phys. Rev. Lett.* **1984**, *53*, 2571−2574.

(16) Jepsen, O.; Andersen, O. K. *Z. Phys. B* **1995**, *97*, 35−47.

(17) Hedin, L.; Lundqvist, B. I. *J. Phys. Chem. Solids* **1971**, *4*, 2064−2083.

(18) Lambrecht, W. R. L.; Andersen, O. K. *Phys. Rev. B* **1986**, *34*, 2439−2449.

(19) Jepsen, O.; Andersen, O. K. *Solid State Commun.* **1971**, *9*, 1763−1767.

(20) Löwdin, P.-O. *J. Chem. Phys.* **1951**, *19*, 1396−1401.

(21) Dronskowski, R.; Blöchl, P. E. *J. Phys. Chem.* **1993**, *97*, 8617−8624.

(22) Mumme, W. G.; Watts, J. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 1300−1304.

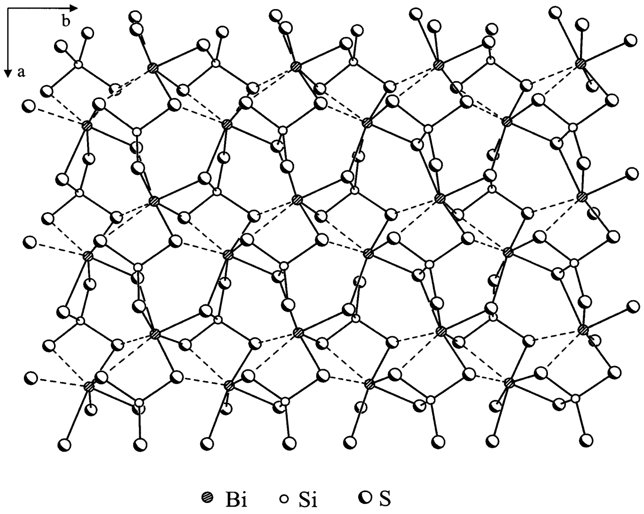

Figure 4. Structure of the $^{2}_{\infty}[SiBiS_4^-]$ layer in $RbSiBiS_4$. Here and in Figure 6 the dashed lines represent the two longest Bi−S bonds; these are mainly ionic in character.

polyhedra are 0.665(1) Å in $RbSiBiS_4$, 0.726(2) Å in $RbGeBiS_4$, and 0.775(2) Å in $CsGeBiS_4$. This kind of coordination geometry is common for the Bi atom, for example, in $HgBi_2S_4$,[22] where the Bi−S bond lengths range from 2.63(3) to 3.34(4) Å. Although the Bi^{3+} cation contains a stereoactive lone pair of electrons, in none of the present structures is the position of this lone pair apparent, either from the distortion of the Bi coordination sphere or from the X-ray diffraction data. The structure of the $^{2}_{\infty}[SiBiS_4^-]$ layer in $RbSiBiS_4$ is shown in Figure 4. The neighboring BiS_7 polyhedra share opposite edges of the rectangular planes of the prisms to form zigzag chains along the *b* direction. Two parallel polyhedral chains are connected by the sharing of opposite edges of the SiS_4 tetrahedra. Each SiS_4 tetrahedron is arranged in such a way that one of the S atoms becomes the cap of an adjacent BiS_7 polyhedron. Although the caps in a single layer point in the same direction along the *b* axis, the caps of neighboring layers point in alternating directions.

The structure of $CsSiBiS_4$, a different structure type, is displayed in Figure 5. It is also a layered structure composed of $^{2}_{\infty}[SiBiS_4^-]$ layers separated by Cs atoms. The coordination environments of the Cs, Si, and Bi atoms are similar to those of the Rb, Si, and Bi atoms in $RbSiBiS_4$, respectively. Each Cs atom is coordinated to a bicapped trigonal prism of eight S atoms, with Cs−S bond lengths ranging from 3.429(2) to 3.758(2) Å. The structure of the $^{2}_{\infty}[CsS_4^{7-}]$ layer formed by these bicapped trigonal prisms is the same as the structure of the $^{2}_{\infty}[RbS_4^{7-}]$ layer in $RbSiBiS_4$. As in $RbSiBiS_4$, the Si atoms are tetrahedrally coordinated to four S atoms, with Si−S bond lengths ranging from 2.098(2) to 2.161(3) Å. The Bi atoms are also coordinated to a distorted monocapped trigonal prism of seven S atoms. The largest difference in Bi−S bond lengths within the BiS_7 polyhedron is 0.798(2) Å.

The $^{2}_{\infty}[SiBiS_4^-]$ layer in $CsSiBiS_4$ is related to but different from the $^{2}_{\infty}[SiBiS_4^-]$ layer in $RbSiBiS_4$. Figure 6 shows the structure of this layer in $CsSiBiS_4$. As in the $RbSiBiS_4$ structure, the BiS_7 distorted monocapped trigonal prisms form zigzag chains along the *b* direction. The chains are connected by SiS_4 tetrahedra. However, there are two obvious differences between the structures of these two layers (Figure 4 vs Figure 6). One is in the disposition of the capping S atoms. In the $CsSiBiS_4$ structure, (Figure 6) the caps on two sides of a chain point in the same direction along the *b* axis but the caps on neighboring chains in the same layer point in alternating directions; in the $RbSiBiS_4$ structure (Figure 4), all the caps within the layer point in the same direction. Another difference lies in the connectivity between Bi atoms. In the $CsSiBiS_4$ structure each BiS_7 polyhedron in one chain is connected to another BiS_7 polyhedron in a neighboring chain by edge sharing, whereas in $RbSiBiS_4$ the connection is by corner sharing.

The structure of the $^{2}_{\infty}[MBiS_4^-]$ (M = Si, Ge) layer in the $RbSiBiS_4$ structure type is similar to the structures of the $^{2}_{\infty}[LaGeS_4^-]$ layer in $KLaGeS_4$ (space group $P2_1$)[23] shown in Figure 7 and the $^{2}_{\infty}[SmGeS_4^-]$ layer in $CsSmGeS_4$ (space group $P2_12_12_1$)[24] shown in Figure 8. However, in $KLaGeS_4$, the length of the *c* axis is about half that in $RbGeBiS_4$ and there is only one $[LaGeS_4^-]$ slab in the unit cell. Thus, the caps of neighboring layers point in the same direction along the polar *b* axis. In $CsSmGeS_4$ there are two $[SmGeS_4^-]$ slabs in the unit cell, but these slabs are related by a 2_1 screw axis

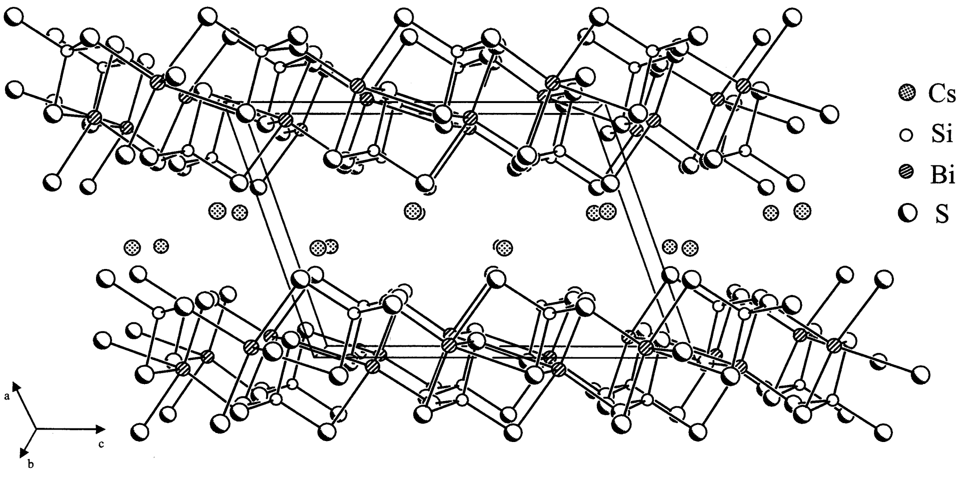

Figure 5. Unit cell of $CsSiBiS_4$ viewed along [010].

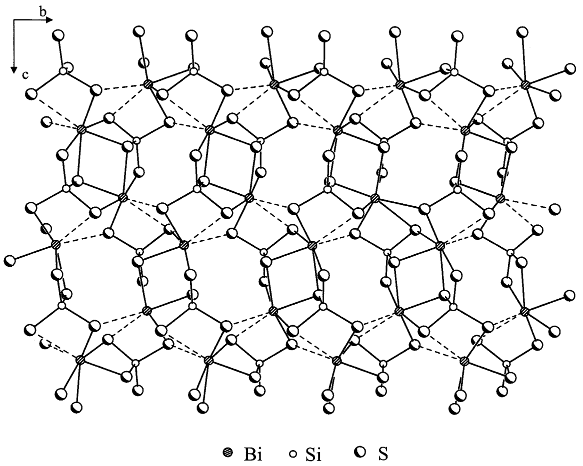

Figure 6. Structure of the $^{2}_{\infty}[\mathrm{SiBiS_4}^-]$ layer in $CsSiBiS_4$.

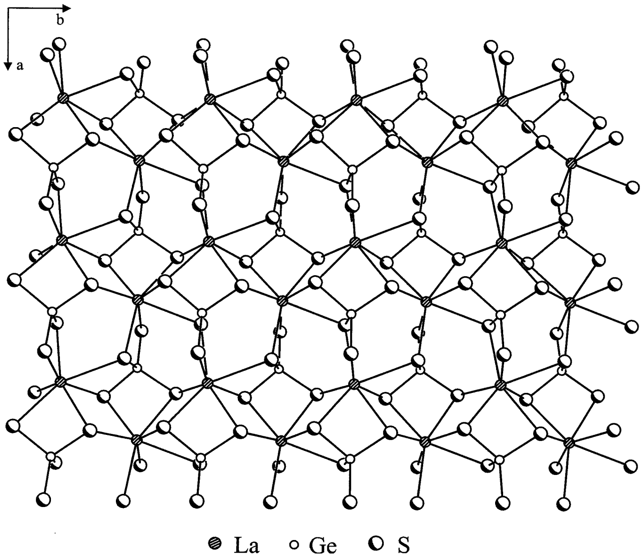

Figure 7. Structure of the $^{2}_{\infty}[\mathrm{LaGeS_4}^-]$ layer in $KLaGeS_4$.

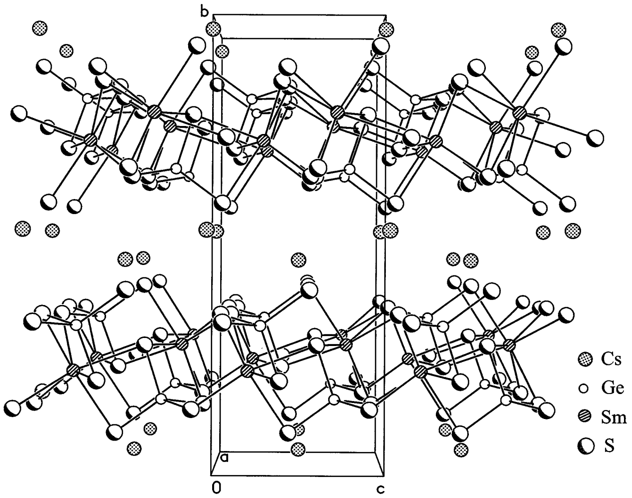

Figure 8. Unit cell of $CsSmGeS_4$ viewed along [100].

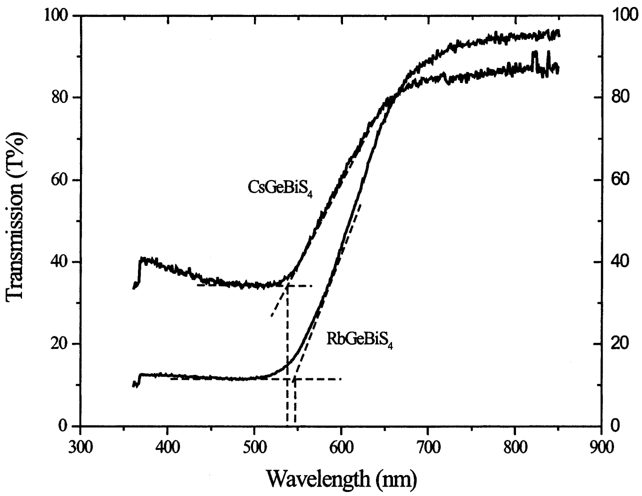

Figure 9. Diffuse reflectance spectra of $RbGeBiS_4$ and $CsGeBiS_4$.

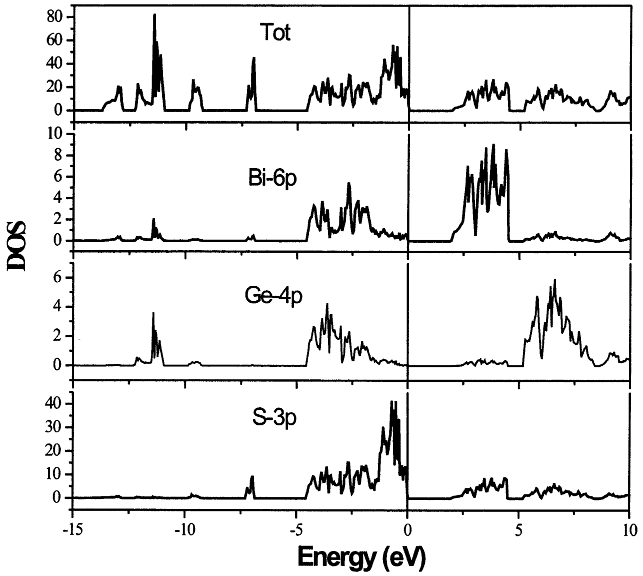

Figure 10. Density of states of $RbGeBiS_4$.

along *c*, not by a center of inversion (Figure 8). The largest differences in the Ln−S (Ln = La, Sm) bond lengths within the LnS_7 distorted monocapped trigonal prisms are 0.225(1) Å in $KLaGeS_4$ and 0.185(1) Å in $CsSmGeS_4$, much smaller than those in the Bi−S bond lengths in the $AMBiS_4$ compounds.

Experimental Band Gaps. The diffuse reflectance spectra of $RbGeBiS_4$ and $CsGeBiS_4$ are shown in Figure 9. Band gaps of 2.23(1) eV for $RbGeBiS_4$ and 2.28(1) eV for $CsGeBiS_4$ were deduced by the straightforward extrapolation method.[25]

Band Structure Calculation. Figure 10 shows the density of states of $RbGeBiS_4$. Most of the contributions around the Fermi level are from the 4p electrons of Ge, the 6p electrons of Bi, and the 3p electrons of S; the Rb 5s electrons contribute minimally. The calculated band gap is about 2.2 eV, which is close to the band gap deduced from the diffuse reflectance spectrum. Since Rb 5s electrons contribute minimally around the Fermi level, the band gap is mainly determined by the $^{2}_{\infty}[\mathrm{GeBiS_4}^-]$ layer. This explains why $RbGeBiS_4$ and $CsGeBiS_4$ have similar band gaps. The partial density of states analysis shows that the S 3p, Bi 6p, and Ge 4p orbitals hybridize strongly near the Fermi level. The S

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(23) Wu, P.; Ibers, J. A. *J. Solid State Chem.* **1993**, *107*, 347−355.
(24) Bucher, C. K.; Hwu, S.-J. *Inorg. Chem.* **1994**, *33*, 5831−5835.

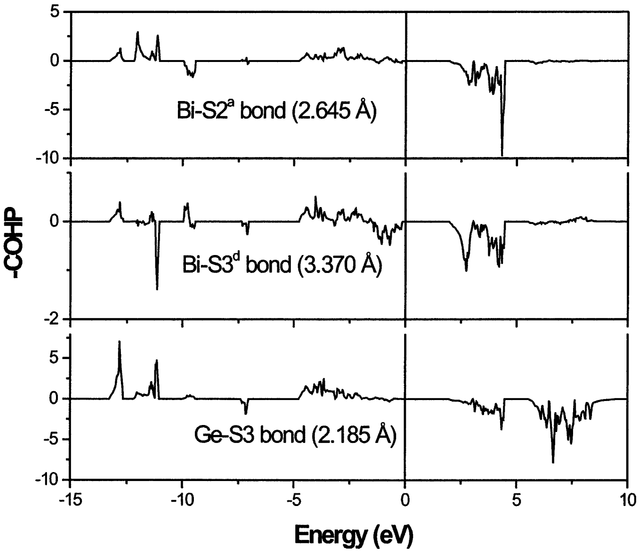

Figure 11. COHP for selected Bi−S and Ge−S bonds in $RbGeBiS_4$. A positive value at a specific energy implies that the states are bonding, and a negative value implies that the states are antibonding.

3p and Ge 4p orbitals are found mostly in the valence band, but the Bi 6p orbitals lie mainly in the conduction band. Analysis of selected Bi−S and Ge−S bonds in $RbGeBiS_4$ was performed by the COHP calculation; some of these results are displayed in Figure 11. Within the BiS_7 polyhedron (Figure 3), Bi−S2^a is the shortest bond and Bi−S3^d is the longest bond, and within the GeS_4 tetrahedron (Table 2), Ge−S3 is the shortest bond. Note that the weighted overlap population of Bi−S3^d is very small. Thus, the interactions between Bi and the S3^d or S2^c atoms (dashed lines in Figure 3) are mainly ionic in character because these atoms are too far away from Bi to form covalent bonds. From the COHP calculation we find that the Ge−S bond is stronger than the Bi−S bond; this causes Ge 4p orbitals to lie mainly in the valence band.

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Supporting Information Available: Crystallographic files in CIF format for $RbSiBiS_4$, $RbGeBiS_4$, $CsSiBiS_4$, and $CsGeBiS_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Schevciw, O.; White, W. B. *Mater. Res. Bull.* **1983**, *18*, 1059−1068.