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Synthesis and Structures of the Quaternary Sulfides $KGaSnS_4$, $KInGeS_4$, and $KGaGeS_4$

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The new quaternary compounds $KGaSnS_4$, $KInGeS_4$, and $KGaGeS_4$ have been synthesized by the reaction of K_2S_5 with elemental Ga or In, Sn or Ge, and S at 900°C. The crystal structures of the three compounds have been determined by single-crystal X-ray diffraction techniques. Crystal data: $KGaSnS_4$—space group $P\bar{1}$, $Z = 4$, $a = 7.152(2)$, $b = 7.847(2)$, and $c = 15.163(3)$ Å, $\alpha = 83.78(2)°$, $\beta = 87.21(2)°$, $\gamma = 63.83(2)°$ ($T = 153$ K), $R(F^2) = 0.147$ for 3068 observations and 130 variables, $R(F) = 0.073$ for 2432 observations having $F_o^2 > 3\sigma(F_o^2)$; $KInGeS_4$—space group $P\bar{1}$, $Z = 4$, $a = 7.200(5)$, $b = 7.739(5)$, and $c = 15.037(10)$ Å, $\alpha = 91.83(3)°$, $\beta = 99.26(4)°$, $\gamma = 112.01(4)°$ ($T = 294$ K), $R(F^2) = 0.124$ for 4832 observations and 131 variables, $R(F) = 0.048$ for 1956 observations having $F_o^2 > 3\sigma(F_o^2)$; $KGaGeS_4$—space group $P2_1/a$, $Z = 4$, $a = 6.853(2)$, $b = 15.956(5)$, and $c = 7.108(2)$ Å, $\beta = 111.95(1)°$ ($T = 115$ K), $R(F^2) = 0.060$ for 2235 observations and 65 variables, $R(F) = 0.027$ for 1925 observations having $F_o^2 > 3\sigma(F_o^2)$. While the three crystal structures differ, they show close similarities. All three structures are made up of layers of metal-centered tetrahedra separated by potassium ions. The main group metal atoms are disordered to varying degrees among the tetrahedra. In each structure the tetrahedra form corner-sharing chains along the *a* axis and these chains are connected by pairs of edge-sharing tetrahedra. The layers in $KInGeS_4$ and $KGaGeS_4$ have the same structure while that in $KGaSnS_4$ is different, owing to the different ways the edge-sharing tetrahedral pairs connect the chains. All three compounds are poor conductors. © 1992 Academic Press, Inc.

Introduction

In the course of a search for potential new superconductors, we have attempted the synthesis of new quaternary chalcogenides that are within or near the "islands" in the three-dimensional elemental quantum configuration space described by Villars and Phillips (*1*). Three such islands encompass all of the strong superconductors ($T_c > 10$ K). Some quaternary sulfides containing an alkali metal, a metal of the iron triad, Ga or In, or Ge or Sn would be inside one of those islands. To date the synthesis of these desired quaternary compounds has been unsuccessful. However, we have synthesized and characterized a new group of related compounds with the general formula K/Ga or In/Sn or Ge/S_4. These compounds are outside the aforementioned islands and in fact are poor conductors. The literature on related chalcogenides is very limited. Goodchild *et al.* (*2*) found that compounds Cu or Ag/Al, Ga, or In/Si, Ge, or Sn/Se_4 have an ordered defect-chalcopyrite structure derived from the diamond structure. For Tl/Al, Ga, or In/Si, Ge, or Sn/S_4, Nakamura *et al.* (*3, 4*) report an orthorhombic layered structure. Two other related compounds, $BaHgSnS_4$ (*5*) and $BaCdSnS_4$ (*6*), have two-

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dimensional network structures formed from edge-sharing tetrahedra, but these structures differ in the way tetrahedral pairs are connected. Indeed, since with chalcogenides the Al and Si groups prefer tetrahedral coordination, it is not surprising that the tetrahedron is the basic building block of all of the structures mentioned above. But owing to the different ways such tetrahedra may be connected and to the influence of the cation, different structural types are found. Similarly, the structures of $KGaSnS_4$, $KInGeS_4$, and $KGaGeS_4$ described here are different from one another and from those discussed above.

Experimental

Syntheses. The compound $KGaSnS_4$ was prepared by the reaction of K_2S_5 (prepared from the stoichiometric reaction of elemental K (AESAR, 99%) and S (Alfa, 99.9995%) in liquid ammonia under an atmosphere of argon) with Ga ingot (Johnson Matthey, 99.999%), Sn powder (Johnson Matthey, 99.999%), and elemental S in a quartz tube. The typical loading ratio was 1 : 2 : 2 : 3. The quartz tube was evacuated ($\approx 10^{-5}$ Torr), sealed, and then heated gradually to 500°C where it was kept for 24 hr before being successively brought to 700°C for 24 hr and 900° for 100 hr. Next, the tube was cooled at a rate of 4°C/hr to 300°C and then the furnace was shut off. Colorless plate-like crystals formed in the tube. Semiquantitative EDAX analysis with the microprobe of a Hitachi S-570 scanning electron microscope revealed the presence of all four elements in a ratio of approximately 1 : 1 : 1 : 4.

The synthesis of $KInGeS_4$ and $KGaGeS_4$ was carried out in a similar manner. In and Ge powders (both Johnson Matthey, 99.999%) were used. For both samples EDAX analysis confirmed the presence of the four elements in the approximate ratio of 1 : 1 : 1 : 4. All three compounds are stable in air and do not decompose significantly in water.

Crystallographic study of $KGaSnS_4$. A plate-like crystal measuring approximately 0.30 by 0.15 by 0.09 mm was selected for data collection. The lattice constants were determined by a least-squares analysis of the setting angles for 25 reflections in the range $42° < 2\theta$ (Cu$K\alpha_1$) $< 46°$ that had been automatically centered on an Enraf–Nonius CAD4 diffractometer at 153 K. The refined cell constants and additional relevant crystal data are given in Table I. The reduced cell given in Table I does not embody higher symmetry, as tested by the method of Le Page (*7*). Intensity data were collected by the ω-2θ scan technique on the CAD4 diffractometer. Six standard reflections measured every 3 hr throughout data collection showed no significant variation in intensity.

All calculations were carried out on a Stardent computer with programs and methods standard in this laboratory (*8*). Conventional atomic scattering factors (*9, 10*) were used and anomalous dispersion corrections (*11*) were applied. A preliminary averaging of the redundant low-angle data suggested that the correct space group was the centrosymmetric one, $P\bar{1}$. This choice was subsequently confirmed by the satisfactory refinement. Initial positions for all the atoms were determined by the direct methods program SHELXS86 (*12*). No significant peaks were found in a difference electron-density map calculated after initial refinement of the structure. With the composition established, the data were corrected for absorption and averaged. An isotropic refinement led to an R index of 0.14. However, the thermal parameters of the two Ga atoms were unrealistically small (0.04(5) and 0.66(5) Å^2) and those of the two Sn atoms were surprisingly large (1.57(5) and 2.09(5) Å^2). This suggested that there is disorder of Ga and Sn among the four metal sites. Consequently, the Sn and Ga atoms were allowed to disorder over these four sites

TABLE I

CRYSTAL DATA AND EXPERIMENTAL DETAILS FOR $KGaSnS_4$, $KInGeS_4$, AND $KGaGeS_4$

	$KGaSnS_4$	$KInGeS_4$	$KGaGeS_4$
Form weight	355.77	354.77	309.67
Space group	C_i^1–$P\bar{1}$	C_i^1–$P\bar{1}$	C_{2h}^5–$P2_1/a$
a (Å)	7.152(2)	7.200(5)	6.853(2)
b (Å)	7.847(2)	7.739(5)	15.956(5)
c (Å)	15.163(3)	15.037(10)	7.108(2)
α (°)	83.78(2)	91.83(3)	90
β (°)	87.21(2)	99.26(4)	111.95(1)
γ (°)	63.83(2)	112.01(4)	90
V (Å^3)	759	763	721
Z	4	4	4
T of data collection (K)	153[a]	294	115[b]
Crystal volume (mm^3)	3.7×10^{-3}	7.1×10^{-4}	9.8×10^{-2}
Crystal shape	Plate, bounded by $\{01\bar{1}\}$, (110), $(\bar{1}0\bar{1})$, (011), $\{001\}$, $(\bar{2}\bar{3}1)$	Plate, bounded by $\{011\}$, $\{001\}$, $\{2\bar{1}\bar{1}\}$, $(\bar{2}1\bar{2})$	Rectangular parallelepiped, bounded by $\{001\}$, $\{010\}$, $\{20\bar{1}\}$, $(\bar{1}6\bar{1})$
Radiation	Cu$K\alpha$ ($\lambda(K\alpha_1) = 1.54056$ Å)	Graphite monochromated Mo$K\alpha$ ($\lambda(K\alpha_1) = 0.7093$ Å)	Graphite monochromated Mo$K\alpha$ ($\lambda(K\alpha_1) = 0.7093$ Å)
Linear absorption coefficient (cm^{-1})	455	83.6	94.3
Transmission factors[c]	0.016–0.151	0.282–0.862	0.037–0.127
Detector aperture (mm)	Horizontal, 3.0; vertical, 4.0; 20 cm from crystal.	Horizontal, 5.5; vertical, 5.0; 32 cm from crystal.	Horizontal, 5.0; vertical, 5.5; 32 cm from crystal.
Take-off angle (°)	3.0	2.5	2.5
Scan speed (° min^{-1})	3.3[d] in 2θ	2.0 in 2θ	$2.5° \leq 2\theta \leq 50°$, 5.0 in 2θ. $50° \leq 2\theta \leq 62°$, 3.0 in 2θ.
Scan type	ω–2θ	θ–2θ	θ–2θ
Scan range (°)	0.9° below $K\alpha_1$ to 0.9° above $K\alpha_2$	0.9° below $K\alpha_1$ to 0.9° above $K\alpha_2$	1.1° below $K\alpha_1$ to 1.1° above $K\alpha_2$
$\lambda^{-1} \sin \theta$, limits (Å)	0.0227–0.6270 $9° \leq 2\theta(\mathrm{Cu}K\alpha_1) \leq 150°$	0.0338–0.7155 $2.75° \leq 2\theta(\mathrm{Mo}K\alpha_1) \leq 61°$	0.0308–0.7261 $2.5° \leq 2\theta(\mathrm{Mo}K\alpha_1) \leq 62°$
Background counts	$\frac{1}{4}$ of scan range on each side of reflection[c]	10 sec at each end of the scan	$2.5° \leq 2\theta \leq 50°$, 4 sec at each end of the scan; $50° \leq 2\theta \leq 61°$, 7 sec at each end of the scan
Data collected	$\pm h \pm k \pm l$ ($2° \leq 2\theta(\mathrm{Cu}K\alpha_1) \leq 45°$); $\pm h \pm k -l$ ($45° \leq 2\theta(\mathrm{Cu}K\alpha_1) \leq 75°$)	$\pm h \pm k +l$	$\pm h \pm k \pm l$
p factor	0.03	0.04	0.04
No. of unique data including $F_0^2 < 0$	3068	4832	2235
No. of unique data with $F_0^2 > 3\sigma(F_0^2)$	2432	1956	1925
No. of variables	130	131	65
$R(F^2)$	0.146	0.124	0.060
$R_w(F^2)$	0.181	0.135	0.076
R [on F for $F_0^2 > 3\sigma(F_0^2)$]	0.073	0.048	0.027
Error in observation of unit weight (e^2)	2.50	1.08	1.42

[a] 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.

[b] The low-temperature system is based on a design by J. C. Huffman, Ph.D. thesis, Indiana University (1974).

[c] The analytical method was used for the absorption correction (J. de Meulenaer and H. Tompa, *Acta Crystallogr.* **19**, 1014 (1965)).

[d] Reflections with $\sigma(I)/I > 0.33$ were rescanned up to a maximum of 60 sec.

with the constraints that the Sn and Ga occupancies at a given site sum to unity, that they have the same thermal parameters at a given site, and that the composition be $KGaSnS_4$. The final cycle of anisotropic refinement was carried out on F_o^2, use being made of all of the data (3068 observations, 130 variables). The final values of R and R_w on F_o^2 are 0.146 and 0.181, respectively, and the value of the conventional R index on F_o for those 2432 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.073.

Crystallographic study of $KInGeS_4$. A plate-like crystal measuring approximately 0.23 by 0.18 by 0.02 mm was selected. Preliminary examination on the CAD4 diffractometer revealed that the crystal was a twin with the second component being oriented relative to the first one by a 180° rotation about the common a^* axis. As a more satisfactory crystal could not be found, data collection proceeded on the twinned crystal. Test scans of several strong reflections from the major component indicated widths in χ, ϕ, and 2θ of less than 0.7°. From a calculation of the setting angles of reflections from the two twin components we found that except for the $0kl$ reflections, which overlap completely, there were no other pairs where all three angles are within 0.5° with each other. There were only 39 pairs of reflections where the differences of all three setting angles are within 0.7°. Thus data could be collected from the major component with a separate scale factor being assigned to the $0kl$ data. Intensity data were subsequently collected by the θ-2θ scan technique on a Picker FACS-1 diffractometer in a manner standard for this laboratory. The lattice constants were determined from least-squares analysis of the setting angles of 19 reflections in the range $40° < 2\theta$ $(MoK\alpha_1) < 42°$ that had been automatically centered at 294 K. The refined cell constants and additional relevant crystal data are given in Table I. The reduced cell does not embody higher symmetry (*7*). Six standard reflections measured every 100 reflections throughout data collection showed no significant variation in intensity.

Again as the refinement proceeded it became apparent that the In and Ge atoms were disordered over the four metal sites. A model similar to that described above was used. The final cycle of anisotropic refinement on F_o^2 resulted in final values of R and R_w on F_o^2 of 0.124 and 0.135, respectively (4832 observations, 131 variables) and in a value of the conventional R index on F for those 1956 reflectins having $F_o^2 > 3\sigma(F_o^2)$ of 0.048. Comparison of F_o^2 and F_c^2 for the 39 pairs of reflections mentioned above indicates that overlap did not occur.

Crystallographic study of $KGaGeS_4$. A crystal selected for data collection was a rectangular parallelepiped of approximate dimensions 0.28 by 0.44 by 0.84 mm. Intensity data were collected by the θ-2θ scan technique on the Picker FACS-1 diffractometer. The lattice constants were determined from least-squares analysis of the setting angles of 56 reflections in the range $36° < 2\theta$ $(MoK\alpha_1) < 39°$ that had been automatically centered at 115 K. The refined cell constants and additional relevant crystal data are given in Table I. Six standard reflections measured every 100 reflections throughout data collection showed no significant variations in intensity.

Although it is difficult to distinguish between Ge and Ga atoms, we assumed that they were disordered over the two metal sites, since disorder was apparent in the two other structures. Constraints similar to those described above were applied to the model. After correction for absorption the redundant reflections hkl, $h\bar{k}l$, $\bar{h}k\bar{l}$, and $\bar{h}\bar{k}\bar{l}$, were averaged to afford a residual of 0.035. The final cycle of anisotropic refinement on F_o^2 led to values of R and R_w on F_o^2 of 0.060 and 0.076, respectively (2235 observations, 65 variables) and to a value of the conventional R index on F for those 1926 reflections having $F_o^2 > 3\sigma(F_o^2)$ of 0.027.

TABLE II

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $KGaSnS_4$

Atom	x	y	z	B_{eq}^{a} (Å^2)
$M(1)^b$	0.36424(13)	0.16809(11)	0.061828(56)	1.41(3)
$M(2)^b$	0.06117(15)	0.50777(12)	0.397372(64)	1.35(3)
$M(3)^b$	0.00507(15)	0.24276(13)	0.241272(70)	1.18(4)
$M(4)^b$	0.50444(18)	0.25660(16)	0.265151(83)	1.20(4)
K(1)	0.07178(62)	0.78153(44)	0.14104(26)	3.2(1)
K(2)	0.65219(70)	0.18693(45)	0.51637(27)	3.4(1)
S(1)	0.42152(49)	0.16690(39)	0.90444(20)	1.80(7)
S(2)	0.00655(48)	0.24524(44)	0.08537(20)	1.83(8)
S(3)	0.46944(45)	0.38087(38)	0.11881(20)	1.61(7)
S(4)	0.10620(55)	0.25319(37)	0.50466(22)	2.10(8)
S(5)	0.14842(47)	0.44583(38)	0.72346(22)	1.89(8)
S(6)	0.37586(51)	0.51218(42)	0.35172(23)	1.96(8)
S(7)	0.84323(44)	0.05973(37)	0.30324(20)	1.57(7)
S(8)	0.34342(44)	0.06196(39)	0.29293(20)	1.57(7)

[a] $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ here and in succeeding tables.

[b] The contents of Sn (Sn/(Sn + Ga)) at four metal sites are 0.87(1) in $M(1)$, 0.56(1) in $M(2)$, 0.40(1) in $M(3)$, and 0.18(1) in $M(4)$.

For all three structures residual electron densities have heights about 2% of the height of the heaviest element in a given structure. No unusual trends were found in an analysis of F_o^2 versus F_c^2 as a function of F_o^2, setting angles, and Miller indices. None of the structures shows additional potential symmetry, as tested by the program MISSYM (*13*). Final values of the atomic parameters and equivalent isotropic thermal parameters for the three compounds appear in Tables II–IV. Final anisotropic thermal parameters and structure amplitudes are given in Tables V and VI, respectively.[1]

TABLE III

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $KInGeS_4$

Atom	x	y	z	B_{eq}^{a} (Å^2)
$M(1)^a$	0.10182(15)	0.00202(14)	0.602917(63)	2.59(3)
$M(2)^a$	0.41088(16)	0.34041(15)	0.056386(66)	2.55(4)
$M(3)^a$	0.64276(12)	0.25668(12)	0.263629(51)	2.42(3)
$M(4)^a$	0.15365(16)	0.29401(15)	0.243914(69)	2.34(4)
K(1)	0.34515(47)	0.67719(39)	0.47421(19)	4.2(1)
K(2)	0.16877(69)	0.74108(49)	0.12918(28)	6.8(2)
S(1)	0.10863(57)	0.24161(45)	0.51170(23)	4.1(1)
S(2)	0.57689(49)	0.00489(43)	0.36105(22)	3.3(1)
S(3)	0.04093(61)	0.99315(49)	0.27157(28)	4.9(1)
S(4)	0.62192(57)	0.64956(48)	0.09656(23)	4.1(1)
S(5)	0.53264(53)	0.12973(49)	0.10707(21)	3.8(1)
S(6)	0.09547(51)	0.28783(57)	0.08944(22)	4.3(1)
S(7)	0.00102(48)	0.53173(48)	0.70328(21)	3.4(1)
S(8)	0.48027(49)	0.46135(44)	0.30706(22)	3.2(1)

[a] The contents of In (In/(In + Ge)) at four metal sites are 0.52(1) at $M(1)$, 0.29(1) at $M(2)$, 0.95(1) at $M(3)$, and 0.24(1) at $M(4)$.

TABLE IV

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $KGaGeS_4$

Atom	x	y	z	B_{eq}^{a} (Å^2)
$M(1)^a$	0.086753(41)	0.582600(15)	0.473789(39)	0.949(8)
$M(2)^a$	0.342900(38)	0.724439(15)	0.275287(39)	0.890(8)
K	0.27323(12)	0.396357(42)	0.17912(10)	2.07(2)
S(1)	0.33740(11)	0.998846(42)	0.251671(97)	1.52(2)
S(2)	0.36010(10)	0.590906(37)	0.37605(10)	1.30(2)
S(3)	0.47792(10)	0.798313(37)	0.562032(91)	1.16(1)
S(4)	0.018685(92)	0.762196(40)	0.068023(90)	1.16(1)

[a] The contents of Ge (Ge/(Ge + Ga)) at two metal sites are 0.48(4) at $M(1)$ and 0.52(4) at $M(2)$.

Results and Discussion

Selected distances and angles for $KGaSnS_4$, $KInGeS_4$, and $KGaGeS_4$ are given in Table VII. Figure 1 provides a perspective view of these structures and Fig. 2 provides the labeling scheme. In these structures the Ga or In and the Sn or Ge atoms are disordered to varying degrees over the metal sites. This is not surprising because these metals have similar sizes and coordination preferences. In fact, each of these metals is tetrahedrally coordinated by four sulfur atoms. The tetrahedra form layers through the sharing of corners and edges. The M–S bond lengths, which range from 2.216(1) to 2.428(3) Å, are comparable to those found in similar sulfides built from tetrahedra: Ge–S bond lengths vary from 2.181(3) to 2.262(3) Å in $Na_6Ge_2S_7$ (*14*) and from 2.150(4) to 2.247(4) Å in Na_2GeS_3 (*15*); Sn–S bond lengths vary from 2.345(7) to

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[1] See NAPS document No. 04911 for 46 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or $15.55 for photocopy. All orders must be prepaid.

TABLE VII

Selected Bond Lengths (Å) and Bond Angles (°)

	KGaSnS$_4$	KInGeS$_4$		KGaGeS$_4$
M(1)–S(1)	2.398(3)	2.332(3)	*M*(1)–S(1)	2.255(1)
M(1)–S(1)	2.402(3)	2.373(4)	*M*(1)–S(1)	2.259(1)
M(1)–S(2)	2.373(3)	2.311(3)	*M*(1)–S(2)	2.232(1)
M(1)–S(3)	2.363(3)	2.295(4)	*M*(1)–S(3)	2.216(1)
M(2)–S(4)	2.349(3)	2.281(4)	*M*(2)–S(2)	2.237(1)
M(2)–S(4)	2.368(3)	2.299(4)	*M*(2)–S(3)	2.234(1)
M(2)–S(5)	2.319(4)	2.223(4)	*M*(2)–S(4)	2.234(1)
M(2)–S(6)	2.336(3)	2.242(4)	*M*(2)–S(4)	2.241(1)
M(3)–S(2)	2.361(3)	2.425(3)		
M(3)–S(5)	2.307(3)	2.409(3)		
M(3)–S(7)	2.314(3)	2.428(3)		
M(3)–S(8)	2.323(3)	2.423(3)		
M(4)–S(3)	2.304(3)	2.238(4)		
M(4)–S(6)	2.328(4)	2.289(4)		
M(4)–S(7)	2.288(3)	2.243(3)		
M(4)–S(8)	2.281(3)	2.243(3)		
S(1)–*M*(1)–S(1)	95.4(3)	94.4(1)	S(1)–*M*(1)–S(1)	97.66(2)
S(1)–*M*(1)–S(2)	106.7(1)	110.2(1)	S(1)–*M*(1)–S(2)	108.72(3)
S(1)–*M*(1)–S(2)	111.2(1)	110.6(1)	S(1)–*M*(1)–S(2)	110.79(3)
S(1)–*M*(1)–S(3)	110.3(1)	113.6(1)	S(1)–*M*(1)–S(3)	104.83(3)
S(1)–*M*(1)–S(3)	117.4(1)	114.4(1)	S(1)–*M*(1)–S(3)	116.44(3)
S(2)–*M*(1)–S(3)	113.8(1)	112.4(1)	S(2)–*M*(1)–S(3)	116.59(3)
S(4)–*M*(2)–S(4)	94.7(1)	97.0(1)	S(2)–*M*(2)–S(3)	104.85(2)
S(4)–*M*(2)–S(5)	111.3(1)	113.5(1)	S(2)–*M*(2)–S(4)	108.97(3)
S(4)–*M*(2)–S(5)	117.4(1)	116.3(1)	S(2)–*M*(2)–S(4)	112.78(3)
S(4)–*M*(2)–S(6)	108.4(1)	106.2(1)	S(3)–*M*(2)–S(4)	114.18(2)
S(4)–*M*(2)–S(6)	112.8(1)	109.8(1)	S(3)–*M*(2)–S(4)	115.39(3)
S(5)–*M*(2)–S(6)	111.0(1)	112.6(1)	S(4)–*M*(2)–S(4)	100.80(2)
S(2)–*M*(3)–S(5)	108.5(1)	110.1(1)		
S(2)–*M*(3)–S(7)	109.0(1)	111.2(1)		
S(2)–*M*(3)–S(8)	108.6(1)	108.4(1)		
S(5)–*M*(3)–S(7)	114.4(1)	112.2(1)		
S(5)–*M*(3)–S(8)	115.0(1)	113.7(1)		
S(7)–*M*(3)–S(8)	101.1(1)	101.0(1)		
S(3)–*M*(4)–S(6)	107.4(1)	105.2(2)		
S(3)–*M*(4)–S(7)	112.5(1)	116.6(1)		
S(3)–*M*(4)–S(8)	111.6(1)	114.3(1)		
S(6)–*M*(4)–S(7)	109.4(1)	107.1(1)		
S(6)–*M*(4)–S(8)	112.9(1)	112.5(1)		
S(7)–*M*(4)–S(8)	103.1(1)	101.1(1)		

KGaSnS$_4$		KInGeS$_4$		KGaGeS$_4$	
K(1)–S(1)	3.465(6)	K(1)–S(1)	3.272(4)	K–S(1)	3.300(1)
K(1)–S(1)	3.842(5)	K(1)–S(1)	3.587(5)	K–S(1)	3.624(1)
K(1)–S(2)	3.471(5)	K(1)–S(1)	3.712(5)	K–S(2)	3.227(1)
K(1)–S(2)	3.548(6)	K(1)–S(2)	3.182(4)	K–S(2)	3.365(1)
K(1)–S(3)	3.215(4)	K(1)–S(2)	3.261(5)	K–S(3)	3.341(1)
K(1)–S(5)	3.355(5)	K(1)–S(7)	3.242(4)	K–S(3)	3.687(1)
K(1)–S(6)	3.816(5)	K(1)–S(8)	3.434(4)	K–S(4)	3.295(1)
K(1)–S(7)	3.334(5)	K(1)–S(8)	3.668(4)	K–S(4)	3.402(1)
K(2)–S(4)	3.152(4)	K(2)–S(3)	3.309(5)		
K(2)–S(4)	3.501(6)	K(2)–S(4)	3.676(6)		
K(2)–S(4)	3.716(6)	K(2)–S(4)	3.690(6)		
K(2)–S(6)	3.191(6)	K(2)–S(5)	3.234(5)		
K(2)–S(6)	3.362(5)	K(2)–S(6)	3.364(6)		
K(2)–S(7)	3.518(5)	K(2)–S(6)	3.478(5)		
K(2)–S(8)	3.303(4)	K(2)–S(7)	3.420(5)		

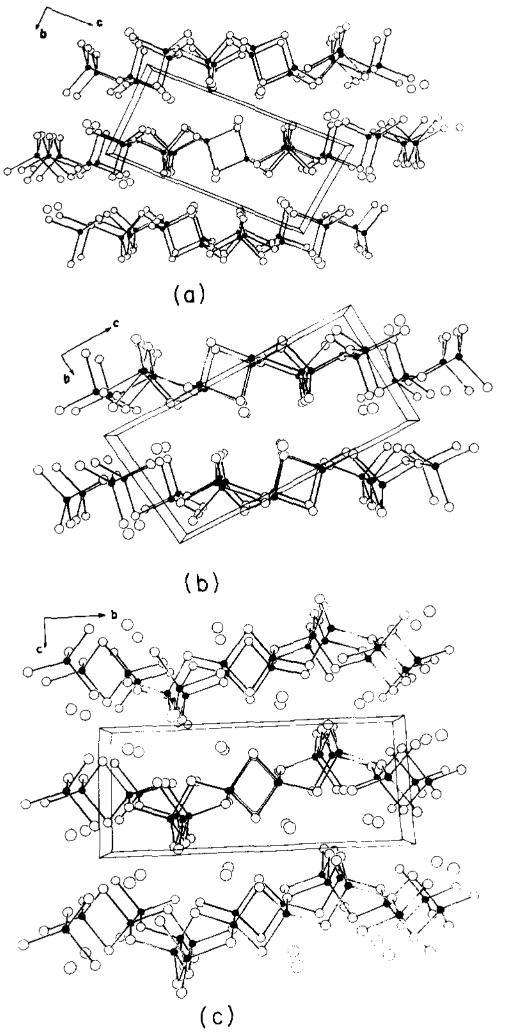

FIG. 1. Views of the three structures down the *a* axis with cell outlines. (a) $KGaSnS_4$, (b) $KInGeS_4$, (c) $KGaGeS_4$. Here small closed circles are main group metal atoms, small open circles are sulfur atoms, and large circles are potassium atoms.

2.430(6) Å in $Na_6Sn_2S_7$ (*14*) and from 2.353(3) to 2.427(2) Å in Ba_2SnS_4 (*16*). As can be seen from Tables II–IV and Table VII, these *M*–S bond lengths increase monotonically with the content of the larger main group metal (Sn for $KGaSnS_4$ and In for $KInGeS_4$). In $KGaGeS_4$ the variation of the *M*–S bond length is small because Ga and Ge have similar sizes. In all three structures, K ions fill the gaps between the layers. In $KGaGeS_4$, the K ion is 8-coordinate with the K–S distances ranging from 3.227(1) to 3.687(1) Å. In $KGaSnS_4$ and $KInGeS_4$, atom K(1) is 8-coordinate with the K–S distances ranging from 3.182(4) to 3.842(5) Å, while atom K(2) is 7-coordinate with the K–S distances ranging from 3.152(4) to 3.716(6) Å.

Figure 3 is a view of the tetrahedra in a layer. There are chains of corner-sharing tetrahedra along the *a* axis in all three structures. These chains are connected by pairs of edge-sharing tetrahedra. The metal sites *M*(1) and *M*(2) in the $KInGeS_4$ and $KGaSnS_4$ structures and the *M*(1) site in the $KGaGeS_4$ structure are at the centers of the tetrahedra that form edge-sharing pairs. The metal sites *M*(3) and *M*(4) in the $KInGeS_4$ and $KGaSnS_4$ structures and the *M*(2) site in $KGaGeS_4$ structure are at the centers of the tetrahedra that share only corners. The S–*M*–S bond angles in the edge-sharing tetrahedra vary from 94° to 117° while those in the corner-sharing tetrahedra vary from 101° to 117°.

The three crystal structures described here differ because of dissimilar cells. But

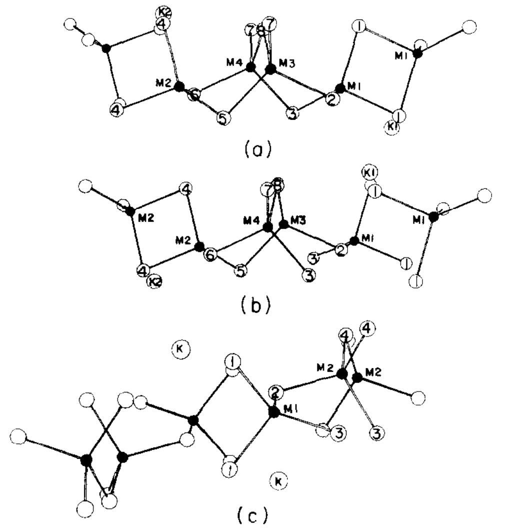

FIG. 2. Drawing of the structures of (a) $KGaSnS_4$, (b) $KInGeS_4$, and (c) $KGaGeS_4$ with labeling scheme. The atoms labeled with number only are sulfur atoms.

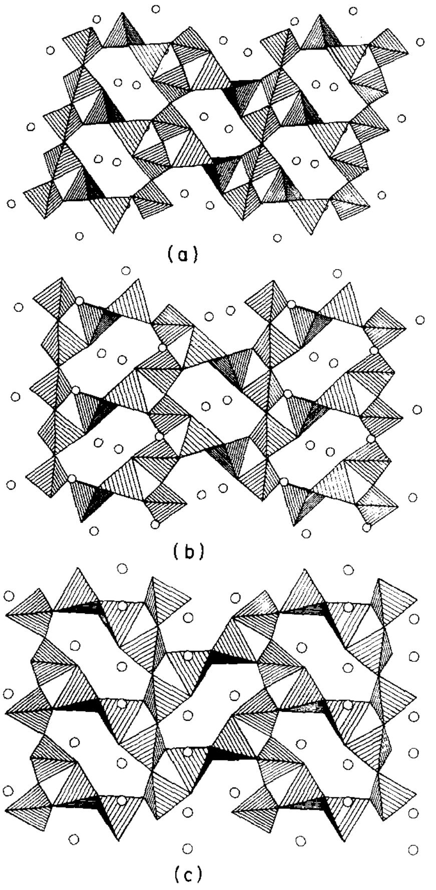

FIG. 3. Connections of tetrahedra in the layers of (a) $KGaSnS_4$, (b) $KInGeS_4$, and (c) $KGaGeS_4$. The open circles represent potassium atoms.

only two kinds of metal–sulfur layers are found, differing in the way the edge-sharing tetrahedral pairs connect the chains. The pairs in $KGaSnS_4$ are distributed nearly symmetrically along both sides of a corner-sharing tetrahedral chain and are parallel to each other. The same kind of layer structure is adopted by $TlInSiS_4$ (*4*), which has an orthorhombic structure. In $KInGeS_4$ and $KGaGeS_4$ the pairs adopt a zigzag pattern that is also found in the layers in high-temperature GeS_2 (*17*).

Attempts have been made to measure the electrical resistivities of these compounds with a two-probe method. However, the resistances of all three compounds exceed the limit of the experiment. Their resistivities are estimated to be above $1 \times 10^5\ \Omega \cdot \text{cm}$.

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