$KCu_{0.9}Bi_{2.7}S_5$: New Semiconducting Quaternary Bismuth Sulfide

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Bismuth chalcogenides are quite interesting due to their potential as useful thermoelectric materials.[1-4] Recently, many new ternary and quaternary compounds have been discovered that possess promising thermoelectric property.[5,6] Furthermore, fundamental interest in these compounds is growing due to their structural diversity they exhibit. For example, the compounds of a general formula of ABi_3Q_5 (A=K, Rb, Cs; Q=S, Se, Te)[7-11] are known to have six different structure types. The polymorphism is made possible by subtle changes in the edge-sharing modes between the infinite BiQ_6 (Q=S, Se) octahedral chains found in the frameworks. Various edge-sharing modes between the octahedral chains can form many types of building units, resulting in a large number of new bismuth chalcogenide frameworks. This is because each BiQ_6 octahedron in one chain has maximum 10 edges available for edge-sharing with others in the neighboring chains. If all the 10 edges are shared with ten other BiQ_6 octahedra in six neighboring chains, then NaCl-type structure is formed.

If fewer edges of an octahedron are to be shared, there are many possible ways of edge-sharing modes to be imagined. For example, (1×3)[12] building bar units, formed by sharing edges of BiQ_6 octahedra between three chains, are found in α-$RbBi_3Se_5$.[9] (2×3) building bar units, formed by the two (1×3) building bar units, are found in α-$RbBi_3Se_5$,[9] γ-$RbBi_3S_5$,[9] γ-$RbBi_3Se_5$,[9] $CsBi_3S_5$,[10] $K_2Bi_{6.33}S_{10}$,[13] and $K_2Bi_8S_{13}$.[13] Furthermore, (1×2) building bar units in Bi_2S_3,[14] (2×2) units in α-$RbBi_3S_5$,[11] (1×4) units in $CsBi_3Se_5$,[9] and even (1×8) units in KBi_3S_5[7,8] are found. This suggests that proper utilization of various types of building bar units in well designed reactions will lead to many new compounds with open frameworks or low-dimensional characteristics.

Recently, quaternary A/Bi/M/Q (M=Zn, Cd, Mn, Cu; Q=S, Se) systems have been explored and many new compounds of $Cs_2Bi_2MS_5$ (M=Zn, Cd, Mn),[15] $K_3Bi_5Cu_2S_{10}$,[16] $RbBi_{2.66}CuSe_5$,[16] ABi_2CuS_4 (A=K, Cs),[16,17] and $A_3Bi_5Cu_2S_{10}$ (A=Rb, Cs)[17] are prepared. They contain infinite linear chains of BiQ_6 octahedra as well as MQ_4 tetrahedra. Once again, (1×3) octahedral building bar units in $RbBi_{2.66}CuSe_5$[16] and (1×2) building bar units in $Cs_2Bi_2MS_5$ (M=Zn, Cd, Mn),[15] $K_3Bi_5Cu_2S_{10}$,[16] ABi_2CuS_4 (A=K, Cs),[16,17] and $A_3Bi_5Cu_2S_{10}$ (A=Rb, Cs)[17] are found. Furthermore, the presence of additional MQ_4 tetrahedral infinite chains complicates the connectivity between them. The tetrahedral metal ion plays an important role as a binder in connecting the octahedral BiQ_6 building bar units enriching the structural diversity of bismuth chalcogenides. Here, we report on the synthesis, structural, and optical characterization of the new quaternary bismuth chalcogenide compound of $KCu_{0.9}Bi_{2.7}S_5$.

The structure of $KCu_{0.9}Bi_{2.7}S_5$ is isostructural with that of $RbBi_{2.66}CuSe_5$.[16] It has a three-dimensional framework with tunnels running parallel to a-axis as shown in Figure 1. Its unique three-dimensional structure is built from the linear infinite BiS_6 octahedral chains and CuS_4 tetrahedral chains. The linear infinite BiS_6 octahedral chain is formed by edge-sharing along the crystallographic a-axis. The linear CuS_4 tetrahedral chain is formed *via* vertex-sharing of tetrahedrons along the crystallographic a-axis. The (1×3) octahedral building bar unit (see Figure 1) is formed by sharing edges of each BiS_6 octahedron in the central chain with 4 neighboring octahedra in two adjacent chains. These (1×3) building bar units are then sharing edges of their terminal octahedra with the neighboring ones to form 2-D stepwise layers as shown in Figure 2. These layers are interconnected with each other by sharing S(1) vertex of terminal octahedra in (1×3) building bar units to form a 3-D framework with tunnels. Cu^- ion is sitting in a tetrahedron of

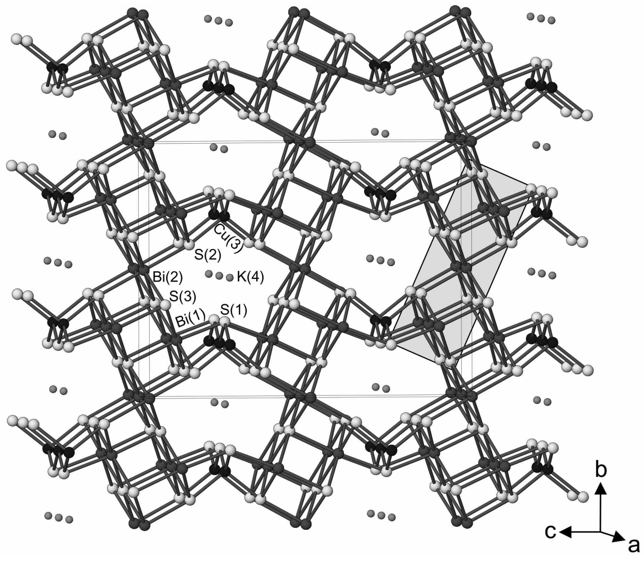

Figure 1. Packing diagram of the three-dimensional framework of $KCu_{0.9}Bi_{2.7}S_5$ with the atom-labelling scheme. The shaded area indicates a (1×3) building bar unit.

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S atoms; two S(1) atoms, shared vertexes of octahedra, and the two S(2) atoms, one in each layer. Cu^+ ion secures the connection between the layers by forming Cu-S bonds. The tunnel in $KCu_{0.9}Bi_{2.7}S_5$ is composed of a 10-membered ring of two Cu-S bonds and eight Bi-S bonds (see figure 1). In the tunnels K^+ ion is sitting in a trigonal prism of S atoms.

In the $[Cu_{0.9}Bi_{2.7}S_5]_n^{n-}$ framework, there are two crystallographically unique Bi atoms. Each Bi atom has a distorted octahedral geometry. Bi^{3+} ion is known to show various degree of distortion in octahedral geometry due to stereochemically active $6s^2$ lone pairs. Bi(1) located at a general position has distorted octahedral geometry with Bi-S bond distances varying between 2.756(2) Å and 2.961(2) Å and S-Bi-S angles varying between 86.62(9)° to 92.97(9)°. Bi(2) located at *m2m* shows more regular octahedral geometry with Bi-S bond distances varying between 2.817(3) Å and 2.876(2) Å and S-Bi-S angles between 87.77(8)° and 92.23(8)°. The Bi(1) shows a distortion toward a trigonal pyramid with three short Bi-S bonds (2.756(2)-2.792(2) Å) and three trans lying long ones (2.934-2.961(2) Å). This type of distortion is quite common in the known bismuth chalcogenide compounds. If the three short ones are almost equal in distance, then the three opposite long ones are almost equal. If one of the short ones gets longer, then the opposite long one gets shorter to make the average Bi-Q distance unchanged. For the $Bi(1)S_6$ octahedron, Bi(1)-S(1) gets longer at 2.792(2) Å among the three short ones and trans lying Bi(1)-S(3) gets shorter at 2.934(4) Å among the three long ones. This suggests that regardless of the degree of distortion, the average Bi-S bond distances are maintained almost equal at ~2.8 Å. Another type of distortion, found at Bi(2), is toward a tetragon with four equal basal bonds of Bi(2)-S(3) at 2.876(2) Å and two axial short bonds of Bi(2)-S(2) at 2.817(3) Å. This type of distortion is not unusual and is found in many bismuth chalcogenide compounds. The average Bi-S distances at 2.86(9) for Bi(1) and 2.86(3) Å for Bi(2) are compared well with other known bismuth chalcogenide compounds in the literature. Selected bond distances and angles are given in Table 1.

Table 1. Selected Bond Distances (A) and Angles (deg) for $KCu_{0.9}Bi_{2.7}S_5$ with Standard Deviations in Parentheses

bond	distance	angle	degree
Bi(1)-S(1)	2.7924(16)	S(1)-Bi(1)-S(3)	175.36(10)
Bi(1)-S(3)	2.934(4)	S(1)-Bi(1)-S(3)	92.97(9) (× 2)
Bi(1)-S(2)	2.756(2) (× 2)	S(1)-Bi(1)-S(2)	89.09(9) (× 2)
Bi(1)-S(3)	2.961(2) (× 2)	S(2)-Bi(1)-S(2)	94.95(10)
		S(2)-Bi(1)-S(3)	89.18(6) (× 2)
Bi(1)-Cu(3)	3.3181(5)	S(2)-Bi(1)-S(3)	87.78(8) (× 2)
		S(2)-Bi(1)-S(3)	175.42(7) (× 2)
		S(3)-Bi(1)-S(3)	86.62(9)
		S(3)-Bi(1)-S(3)	90.41(9) (× 2)
Bi(2)-S(3)	2.876(2) (× 4)	S(2)-Bi(2)-S(2)	180.0
Bi(2)-S(2)	2.817(3) (× 2)	S(2)-Bi(2)-S(3)	92.23(8) (× 4)
		S(3)-Bi(2)-S(3)	180.00(11)
		S(3)-Bi(2)-S(3)	90.14(9) (× 2)
		S(2)-Bi(2)-S(3)	87.77(8) (× 4)
		S(3)-Bi(2)-S(3)	89.86(9) (× 2)
Cu(3)-S(1)	2.352(3) (× 2)	S(3)-Bi(2)-S(3)	180.0
Cu(3)-S(2)	2.451(4) (× 2)	S(2)-Bi(2)-S(3)	87.77(8) (× 4)
		S(1)-Cu(3)-S(1)	119.5(2)
K(4)-S(1)	3.169(5) (× 2)	S(2)-Cu(3)-S(2)	103.24(17)
K(4)-S(2)	3.293(3) (× 4)	S(1)-Cu(3)-S(2)	108.24(6) (× 4)

As assigning -2 charges on S and +1 charge on K and Cu ions, charges on Bi atoms are expected to be +3 suggesting valence-precise semiconductor nature. Optical diffuse reflectance measurement reveals the presence of optical band gap at 0.85 eV confirming the semiconductor nature and suggesting a most likely direct band gap semiconductor as shown in Figure 3. This value can not be compared with those of known quaternary A/Bi/Cu/S compounds at present due to lack of their band gap data. However, this value is somewhat smaller than that of the known ternary bismuth sulfide compounds of ABi_3S_5 (A=K, Rb)[9] at ~1.2 eV and comparable to that of layer compound of γ-$RbBi_3Se_5$[9] at 0.8

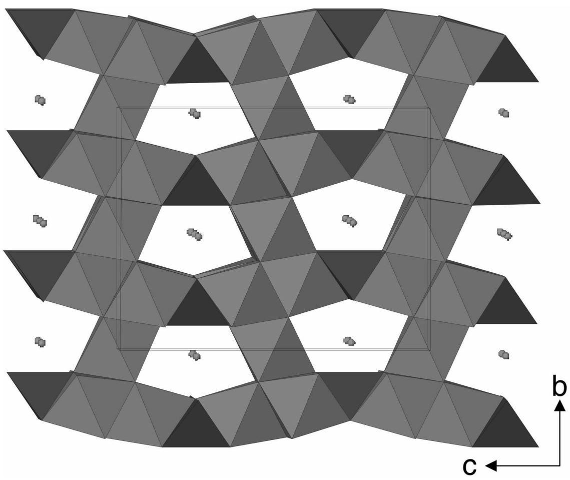

Figure 2. Polyhedral representation of the three-dimensional framework of $KCu_{0.9}Bi_{2.7}S_5$.

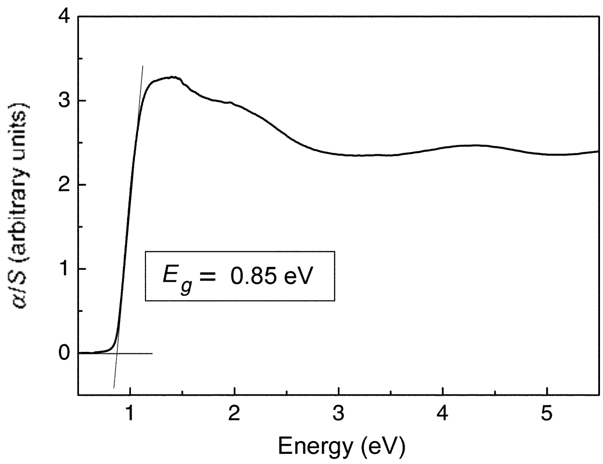

Figure 3. Solid State UV/Vis-Near infrared absorption spectrum showing band gap transition for $KCu_{0.9}Bi_{2.7}S_5$. The band gap is estimated from the crossing point of the solid lines.

eV.

The result presented here further illustrates the structural diversity associated with bismuth metal ions. The varying degree of distortion and the edge-sharing ability of BiQ_6 (Q=S, Se, Te) octahedra can tolerate many different types of building units which are interconnected via edge-sharing and/or vertex-sharing to produce new structural compounds. In addition, incorporation of Cu^+ ions forming the additional tetrahedral building units complicates the connectivity between the various types of building units. At present, the controlling and formation of the building units in the quaternary bismuth chalcogenide compounds are not well understood. However, many novel compounds with different structural building units and connectivity and their structure related properties are expected in the quaternary A/Bi/M/Q (M=transition metal, Q=S, Se, Te) system.

Experimental Section

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. Chemicals in this work were used as obtained: (i) Cu powder, 99.5 % purity, -325 mesh; Bi powder, 99%, -325 mesh, Cerac Inc., Milwaukee, WI, (ii) S powder, 99.5% purity; K metal, 98% purity, Aldrich Chemical Co., Inc., Milwaukee, WI, (iii) DMF, analytical reagent, DongYang Chemicals Co., Seoul. Potassium monosulfide (K_2S) were prepared in liquid ammonia from potassium and elemental sulfide in a 2 : 1 ratio.

$KCu_{0.9}Bi_{2.7}S_5$. 0.165 g (1.5 mmol) of K_2S, 0.104 g (0.5 mmol) of Bi, 0.032 g (0.5 mmol) of Cu, and 0.160 g (5.0 mmol) of S powder were mixed together and loaded in a Pyrex tube (9 mm diameter) which was then flame-sealed under vacuum (~10^{-3} torr). The tube was placed in a computer-controlled furnace and heated at 500 °C for 5 days, then cooled slowly to 150 °C at a rate of 2 °C/hr, and then to 50 °C at a rate of 20 °C/hr. Black needle-shaped crystals were obtained by removing excess potassium polysulfides with degassed DMF. A quantitative microprobe analysis performed on a large number of single crystals with the EPMA system gave an average composition of $K_{1.2}Cu_{0.9}Bi_{2.7}S_5$. This compound is insoluble in all common organic solvents and stable with respect to hydrolysis and air oxidation. The homogeneity of $KCu_{0.9}Bi_{2.7}S_5$ was confirmed by comparing the observed and calculated X-ray powder diffraction patterns. The d_{hkl} spacings observed for the bulk materials were compared, and found to be in good agreement with the d_{hkl} spacings calculated from the single crystal data using POWD10.[18]

Crystallographic Study. The X-ray single crystal data were collected at room temperature on a Siemens P4 four circle diffractometer with graphite monochromated Mo-Kα radiation using the ω-2θ scan mode. The stability of the crystal was monitored by measuring three standard reflections periodically (every 97 reflections) during the course of data collection. No crystal decay was observed. An empirical absorption correction based on 6ψ scans was applied to the data. The structure was solved by direct methods using SHELXTL[19] and refined by full-matrix least square techniques provided in the SHELXTL package of programs.[19]

Two bismuth atoms, three sulfur atoms, and a potassium atom are found. After least-squares refinement (R_1/wR_2 = 7.64/21.57), the isotropic temperature factors for Bi(2) and Cu(3) atoms were almost twice as large as others. A refinement of their multiplicity indicated partial occupancies on these sites with R_1/wR_2 = 5.12/13.13. At this stage, a model with bismuth and copper atom vacancies seemed to be reasonable. Occupancies of the rest of the atoms were refined and only Bi(1) atom was found to have a less than full occupancy while fixing the refined partial occupancies of Bi(2) and Cu(3). The multiplicity refinements of Bi(1) slightly lowered R_1/wR_2 = 5.09/13.09. The occupancies were refined individually and finally fixed at 0.491, 0.184, and 0.226 for Bi(1), Bi(2), and Cu(3) atoms respectively. The Cu/Bi/S ratio was in good agreement with the EPMA data. All atoms were refined anisotropically to give a final R_1/wR_2 = 3.79/9.29. All calculations were performed on a Pentium PC. The crystallographic data and detailed information of structure solution and refinement are listed in Table 2. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 3.

Table 2. Crystal Data and Structure Refinement for $KCu_{0.9}Bi_{2.7}S_5$

Empirical formula	$Bi_{2.7}$ $Cu_{0.9}$ K S_5	
Formula weight	837.64	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Cmcm (#63)	
Unit cell dimensions	a = 4.0628(4) Å	α = 90°.
	b = 13.7595(12) Å	β = 90°.
	c = 17.567(2) Å	γ = 90°.
Volume	982.04(19) $Å^3$	
Z	4	
Density (calculated)	5.665 Mg/m^3	
Absorption coefficient	52.682 mm^{-1}	
F(000)	1425	
Crystal size	0.40 × 0.04 × 0.02 mm^3	
Theta range for data collection	2.32 to 27.45°.	
Index ranges	$-1 \le h \le 5$, $-17 \le k \le 2$, $-1 \le l \le 22$	
Reflections collected	1013	
Independent reflections	663 [R(int) = 0.0330]	
Completeness to theta = 27.45°	100.0%	
Absorption correction	Empirical	
Max. and min. transmission	0.8406 and 0.3059	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	663 / 0 / 36	
Goodness-of-fit on F^2	1.112	
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0929	
R indices (all data)	R1 = 0.0439, wR2 = 0.0953	
Extinction coefficient	0.00156(16)	
Largest diff. peak and hole	2.920 and -4.122 e.$Å^{-3}$	

Table 3. Atomic Coordinates (× 10^4), Occupancy and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $KCu_{0.9}Bi_{2.7}S_5$

atom	*x*	*y*	*z*	Occupancy (%)	*U (eq)*
Bi(1)	10000	2759(1)	3989(1)	98	21(1)
Bi(2)	5000	5000	5000	73	20(1)
Cu(3)	5000	2909(2)	2500	90	29(1)
K(4)	10000	5280(3)	2500	100	27(1)
S(1)	10000	2048(3)	2500	100	19(1)
S(2)	5000	4015(2)	3594(2)	100	17(1)
S(3)	10000	3665(3)	5501(2)	100	23(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

UV/Vis/Near-IR Spectroscopy. Optical band gap measurements were made at room temperature with a Shimadzu UV-3101PC UV-Vis-NIR Scanning Spectrophotometer equipped with ISR-3100 integrating sphere and controlled by a personal computer. $BaSO_4$ powder was used as reference at all energies (100% reflectance). Reflectance data were collected from 2600 nm to 200 nm at room temperature and then the digitized spectra were processed using the Origin6.0 software program. Absorption data were calculated from the reflectance data using the Kubelka-Munk function.[20]

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Supplementary Material Available: Tables of anisotropic thermal parameters of all atoms, and a listing of calculated and observed (10Fo/Fc) structure factors are available on request from the correspondence author.

References

1. Chung, D. Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science* **2000**, *287*, 1024-1027.
2. Chung, D. Y.; Iordanidis, L.; Choi, K. S.; Kanatzidis, M. G. *Bull. Korean Chem. Soc.* **1998**, *19*, 1283-1293.
3. Kanatzidis, M. G. *Semiconduct. Semimet.* **2001**, *69*, 51-100.
4. Kanatzidis, M. G.; Chung, D.-Y.; Iordanidis, L.; Choi, K.-S.; Brazis, P.; Rocci, M.; Hogan, T.; Kannewurf, C. In *Materials Research Society Symposium Proceedings*; 1999; Vol. 545, pp 233-246.
5. Mrotzek, A.; Kanatzidis, M. G. *Accounts Chem. Res.* **2003**, *36*, 111-119.
6. Chung, D.-Y.; Hogan, T. P.; Rocci-Lane, M.; Brazis, P.; Ireland, J. R.; Kannewurf, C. R.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2004**, *126*, 6414-6428.
7. Chondroudis, K.; Kanatzidis, M. G. *J. Solid State Chem.* **1998**, *136*, 328-332.
8. McCarthy, T. J.; Tanzer, T. A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 1294-1301.
9. Iordanidis, L.; Bilc, D.; Mahanti, S. D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 13741-13752.
10. Schmitz, D.; Bronger, W. *Z. Naturforforsch., B: Anorg. Chem. Org. Chem.* **1974**, *29*, 438-439.
11. Kanisheva, A. S.; Mikhailov, Y. N.; Lazarev, B. V.; Trippel, A. F. *Dokl. Akad. Nauk. SSSR.* **1980**, *252*, 96-99.
12. The (1 × 3) refers to a cross section with one octahedron-high in one direction and 3 octahedra-wide in other direction. Therefore, the linear infinite BiQ_6 octahedral chain can be noted as (1 × 1).
13. Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L. H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. X. *Chem. Mater.* **1996**, *8*, 1465-1474.
14. Lukaszewicz, K.; Stepen'-Damm, Y.; Pietraszko, A.; Kajokas, A.;Grigas, J. *Pol. J. Chem.* **1999**, *73*, 541-546.
15. Huang, F. Q.; Somers, R. C.; McFarland, A. D.; Van Duyne, R. P.; Ibers, J. A. *J. Solid State Chem.* **2003**, *174*, 334-341.
16. Huang, F. Q.; Mitchell, K.; Ibers, J. A. *J. Alloy Compd.* **2001**, *325*, 84-90.
17. Yang, Y. T.; Brazis, P.; Kannewurf, C. R.; Ibers, J. A. *J. Solid State Chem.* **2000**, *155*, 243-249.
18. Smith, D. K.; Nichols, M. C.; Zolensky, M. J. E. POWD10: *A FORTRAN IV Program for Calculating X-ray Powder Diffraction Patterns, Version 10*; Pennsylvania State University: 1983.
19. Sheldrick, G. M. *SHELXTL NT* Version 6.12; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2000.
20. (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966. (b) Tandon, S. P.; Gupta, J. P. *Phys. Stat. Sol.* **1970**, *38*, 363.