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Synthesis and Characterization of the New Quaternary Two-Dimensional Materials KCu_2NbQ_4 (Q = Se, S)

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Reaction of K_2Se_5 or K_2S_5 with elemental Nb, Cu, and Se or S affords KCu_2NbSe_4 or KCu_2NbS_4. The structure of KCu_2NbSe_4 has been determined by single crystal X-ray diffraction methods. KCu_2NbSe_4 crystallizes with four formula units in the space group C^{16}_{2v}-$C2cm$ of the orthorhombic system in a cell of dimensions a = 5.663(2) Å, b = 18.791(5) Å, c = 7.645(3) Å at −167°C. The structure consists of two-dimensional metal-chalcogen layers separated by K^+ cations. The Nb atom and two independent Cu atoms are in tetrahedral sites, and there appears to be some substitutional disorder among these sites, as judged from the isotropic thermal parameters. The $CuSe_4$ and $NbSe_4$ tetrahedra share edges and corners to make up the two-dimensional layers. If we arbitrarily choose a cutoff of 4.00 Å then the K atom is coordinated by nine Se atoms. The metal tetrahedra have their expected dimensions with Nb–Se distances varying from 2.392(3) to 2.452(3) Å and Cu–Se distances from 2.427(2) to 2.440(4) Å. There are short metal–metal interactions with Nb–Cu distances at 2.831(1) and 2.833(4) Å. From Weissenberg photography KCu_2NbS_4 is found to be isostructural: cell dimensions at room temperature are a = 5.76 Å, b = 18.46 Å, c = 7.45 Å.

Introduction

Recently we demonstrated that the reactive flux method (*1*) can be applied readily to the synthesis of ternary polytellurides (*2*) and even quaternary chalcogenides (*3*). The materials synthesized by this method often show unusual structures. For example, one-dimensional chains are found in $K_4Ti_3S_{14}$ (*1*), $Na_2Ti_2Se_8$ (*4*), α- and β-$KCuS_4$ (*5*), K_3AuSe_{13}(*6*), $K_4Hf_3Te_{17}$ (*2*), $K_2Hg_3Q_4$ (Q = S, Se) (*7*), $K_2CuNbSe_4$ (*3*), and $K_3CuNb_2Se_{12}$ (*3*); polychalcogenide molecular species are found in $K_4Ta_2S_{11}$ (*8*) and $K_3Nb_2Se_{11}$ (*8*). In this paper, we describe new quaternary two-dimensional mixed-metal materials in the K/Cu/Nb/Q (Q = Se, S) system, namely KCu_2NbSe_4 and KCu_2NbS_4, that were synthesized by the reactive flux method.

Experimental

Synthesis. KCu_2NbSe_4 was prepared from a stoichiometric reaction of K_2Se_5 (199 mg, 0.42 mmol) with powders of elemental Nb (78 mg, 0.84 mmol), Cu (107 mg, 1.68 mmol), and Se (99 mg, 1.26 mmol) (Nb, 99.8%, AESAR; Cu, 99.5%, ALFA; Se, 99.5%, Aldrich). K_2Se_5 was made from the stoichiometric reaction of elemental K (99%, AESAR) with Se in liquid ammonia under an atmosphere of argon. In a glove box the starting materials were loaded into a quartz tube that was subsequently evacuated to 10^{-4} Torr and sealed. It was then

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placed in a furnace that was heated from room temperature to 870°C in 12 hr, held at 870°C for 4 days, and then slowly cooled to 270°C at a rate of 4°C/hr, and finally cooled to room temperature in 3 hr. The product consisted of red needle-like single crystals suitable for X-ray diffraction analysis.

KCu_2NbS_4 was prepared from a reaction of K_2S_5 (143 mg, 0.6 mmol) with elemental Nb (112 mg, 1.2 mmol), Cu (152 mg, 2.4 mmol), and S (57.6 mg, 1.8 mmol). K_2S_5 was made from the stoichiometric reaction of elemental K with S (100.0%, Mallinckrodt) in liquid ammonia under an atmosphere of argon. The starting materials were loaded as described above. The tube was then placed in a furnace that was heated from room temperature to 500°C in 7 hr, held at 500°C for 24 hr, then heated to 850°C in 5 hr, kept there for 4 days, and then slowly cooled to 450°C at a rate of 4°C/hr, and finally cooled to room temperature in 5 hr. Orange, plate-like single crystals extracted from the surface of the melt were suitable for X-ray diffraction analysis. Chemical analyses of four crystals of each material selected at random were performed with the electron microprobe of an EDAX-equipped Hitachi S-570 LB scanning electron microscope, and afforded the compositions K : Cu : Nb : Se = 1.1 : 2.4 : 1.0 : 4.7, and K : Cu : Nb : S = 1.1 : 2.4 : 1.0 : 4.8, respectively.

Crystallography. A single crystal of KCu_2NbSe_4 was mounted on an Enraf–Nonius CAD-4 X-ray diffractometer and the unit cell dimensions, symmetry, and systematic absences were determined. The material is orthorhombic and the systematic absences correspond to space groups *Cmcm*, *C*2*cm*, or *Cmc*2$_1$. The crystal was then transferred to a Picker FACS-1 diffractometer. The intensity data were collected at −167°C by methods standard in this laboratory (*9*) with use of the θ-2θ technique in the range $3° \leq 2\theta(\mathrm{Mo}K\alpha_1) \leq 67°$. Six standards chosen from diverse regions of reciprocal space were monitored every 4 hr during the data collection and showed no significant change. In the solution and refinement of the structure all calculations were carried out on a Stellar GS2000 computer with the use of programs standard (*9*) in this laboratory. The structure was solved through the use of the program SHELX-86 (*10*). Of the three possible space groups, a solution that made chemical sense and displayed a low combined figure of merit could only be found in *C*2*cm*, an alternative setting of *Ama*2. An analytical absorption correction was applied (*11*) once the composition KCu_2NbSe_4 was established. Upon correction for absorption, 3266 measured reflections were reduced to a set of 1737 unique reflections by averaging the hkl and $hk\bar{l}$ reflections. The reflections hkl and $\bar{h}kl$ were not averaged. Rather, they were used to determine the sense of the polar axis in the chosen crystal. Of the 100 reflections for which F_0^2 differed by more than 5% between hkl and $\bar{h}kl$ reflections, the chosen sense of the polar axis accounted for 77 of the differences. Refinement on F_0 of the model with isotropic thermal parameters led to values of 0.88, 0.08, and 0.17 Å^2 for atoms Nb(1), Cu(1), and Cu(2), respectively, and an *R* index of 0.087. As these metal atoms all exhibit tetrahedral coordination, the thermal parameters are suggestive of some substitutional disorder among these sites. A refinement in which each site was allowed to be an admixture of Nb and Cu, with the positional and thermal parameters of each constrained to be equal and with the overall constraint that Nb : Cu = 1 : 2 led to a slight improvement in the *R* index (0.083), to more reasonable thermal parameters (0.23, 0.75, and 0.90 Å^2 for Nb(1), Cu(1), and Cu(2), respectively), and to Nb occupancies of 62(3)%, 18(2)%, and 20(3)% in the three metal sites. Because such a refinement is markedly affected by the isotropic thermal parameters, which in turn are affected by the absorption correction, we choose to assume an ordered model for the final refinement and for further discussion, even though there is probably some substitutional disorder among the metal sites. The final cycle of refinement was carried out on F_0^2 and involved 1737 observations and 21 variables. The relatively high R index probably results from our inability to model the absorption correction and the disorder completely. The results of the refinement and crystallographic details are given in Table I. The final parameters are given in Table II. Final structure amplitudes are given in Table III.[1]

TABLE I

CRYSTAL DATA AND EXPERIMENTAL DETAILS

Formula	KCu_2NbSe_4
F.W.	574.94
Space group	C_{2v}^{16}-$C2cm$
a (Å)	5.663(2)
b (Å)	18.791(5)
c (Å)	7.645(3)
Vol. (Å^3)	813.5
Z	4
T (°C)	-167^a
d(calc.) gcm^{-3}	4.693
μ(cm^{-1})	247
λ(Mo$K\alpha_1$) (Å)	0.70926
Crystal shape	Plate bounded by $\{010\}$, $\{100\}$, $(00\bar{1})$, $(1,0,\overline{10})$, $(\bar{1},0,\overline{15})$
Crystal volume (mm^3)	$6.04\ 10^{-4}$
Transmission factors^b	0.281–0.442
Takeoff angle (deg)	2.5
Scan type	θ–2θ
Scan range (deg)	1.0 below $K\alpha_1$ to 1.2 above $K\alpha_2$
θ limits (deg)	$3 < 2\theta < 67$
Scan speed (deg/min)	2.0
Data collected	$\pm h, k, \pm l$
p factor	0.04
No. of data collected	3266
No. of unique data	1737
No. of unique data with $F_0^2 > 3\sigma(F_0^2)$	1301
Variables	21
R (F^2)	0.157
R_w (F^2)	0.215
$R(F)$ ($F_0^2 \geq 3\sigma(F_0^2)$)	0.087
Error in observation of unit weight (e^2)	2.34

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

[b] The analytical method as employed in the Northwestern absorption program AGNOST was used for the absorption correction (*11*).

TABLE II

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR KCu_2NbSe_4

Atom	Wyckoff notation	x	y	z	B^a (Å^2)
Nb(1)	4b	0.50019(62)	0.110988(83)	1/4	0.88(3)
Cu(1)	4a	0.52103(93)	0	0	0.08(4)
Cu(2)	4b	0	0.10775(13)	1/4	0.17(4)
Se(1)	4b	0.25381(93)	0.003682(88)	1/4	0.44(3)
Se(2)	4b	0.2498(11)	0.21352(10)	1/4	0.96(3)
Se(3)	8c	0.74932(96)	0.109231(68)	−0.00761(15)	0.55(2)
K(1)	4b	0.7535(14)	0.31714(23)	1/4	1.67(7)

[a] $B = 8\pi^2\langle u^2\rangle$

Weissenberg photography on the S analogue, KCu_2NbS_4, indicated that the two materials are isostructural; cell constants at 25°C are a = 5.76, b = 18.46, c = 7.45 Å.

Results

KCu_2NbSe_4 is a new two-dimensional layered material comprised of Cu_2NbSe_4 layers parallel to (010) (Fig. 1); these layers are isolated by K^+ cations. The shortest Se · · · Se distance is 3.706(2) Å and hence in a formal sense one may describe this compound as one of Se(−II),K(I), Cu(I), and Nb(V). The Nb atom and the two crys-

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[1] See NAPS document No. 04880 for 9 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 for photocopy, \$7.75. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling. \$1.50 for postage of any microfiche orders.

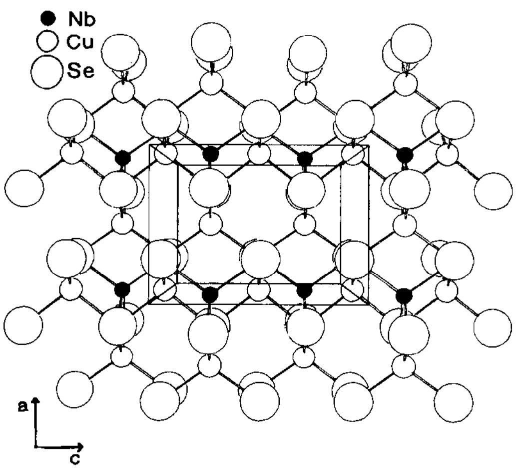

FIG. 1. Projection of one layer of the KCu_2NbSe_4 structure down [010]. The K atoms are not shown. Here and in Fig. 2 Cu atoms are medium open circles, Nb atoms are small filled circles, and Se atoms are large open circles.

tallographically independent Cu atoms are tetrahedrally coordinated by Se atoms in the structure. The $Cu(2)Se_4$ and $NbSe_4$ tetrahedral units are edge sharing alternately along [100]; the $Cu(1)Se_4$ and $Cu(2)Se_4$ tetrahedra are corner sharing along [100] and [001]; the $Cu(1)Se_4$ and $NbSe_4$ tetrahedra are edge sharing along [001] in an infinite alternating pattern (Fig. 2), similar to the one-dimensional alternating metal chain in $K_2CuNbSe_4$ (*3*). The Nb–Se distances (Table IV) are 2.392(3) and 2.452(3) Å, comparing well with those in K_3NbSe_4 (*12*) (Nb–Se, 2.387(1)–2.403(1)Å) and $K_2CuNbSe_4$ (*3*) (Nb–Se, 2.413(1)Å). Similarly, the Se–Nb–Se angles show normal tetrahedral values, varying from 108.7(1) to 110.9(1)°, consistent with those found in $K_2CuNbSe_4$ (109.02(6)–110.24(6)°) and in K_3NbSe_4 (108.49(3)–111.68(5)°). The Cu–Se bond distances range from 2.427(2) to 2.440(4) Å, perhaps slightly shorter than the Cu–Se distance (2.457(1)Å) in $K_2CuNbSe_4$. The Se–Cu–Se angles about the two independent Cu atoms in the present structure are somewhat different: atom Cu(2) is in a normal tetrahedral environment (108.2(2)–110.8(1)°), while atom Cu(1) is in a more distorted tetrahedral environment (103.3(3)–115.6(1)°). The K atom exhibits

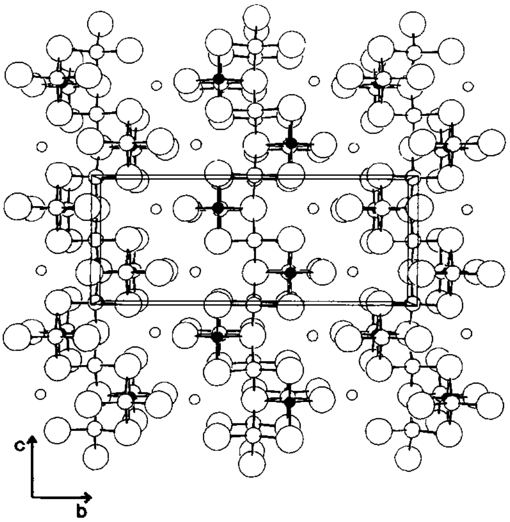

FIG. 2. Projection of the KCu_2NbSe_4 structure down [100]. K atoms are small open circles.

TABLE IV

SELECTED DISTANCES (Å) AND ANGLES (deg) FOR KCu_2NbSe_4

2Nb–Cu(1)	2.831(1)	K(1) · · · Se(3)	3.638(6)
Nb–Cu(2)	2.831(4)		3.638(6)
	2.833(4)		3.674(6)
Nb–Se(1)	2.452(3)		3.674(6)
Nb–Se(2)	2.392(3)	2Cu(1)–Cu(2)	3.887(4)
2Nb–Se(3)	2.423(2)	Se(1)–Cu(1)–Se(1)	103.3(3)
2Cu(1)–Se(1)	2.439(2)	Se(1)–Cu(1)–Se(3)	109.0(1)
2Cu(1)–Se(3)	2.427(2)		109.6(1)
Cu(2)–Se(1)	2.427(4)	Se(3)–Cu(1)–Se(3)	115.6(1)
Cu(2)–Se(2)	2.440(4)	Se(1)–Cu(2)–Se(2)	108.2(2)
2Cu(2)–Se(3)	2.428(3)	Se(1)–Cu(2)–Se(3)	110.8(1)
Se(1) · · · Se(1)	3.825(2)	Se(3)–Cu(2)–Se(2)	109.2(1)
Se(1) · · · Se(2)	3.943(2)	Se(3)–Cu(2)–Se(3)	108.4(2)
2Se(1) · · · Se(3)	3.961(2)	Se(2)–Nb–Se(1)	109.0(1)
2Se(1) · · · Se(3)	3.976(2)	Se(2)–Nb–Se(3)	110.9(1)
2Se(1) · · · Se(3)	3.997(2)	Se(3)–Nb–Se(1)	108.7(1)
2Se(2) · · · Se(3)	3.811(2)	Se(3)–Nb–Se(3)	108.8(1)
2Se(2) · · · Se(3)	3.965(3)	Cu(1)–Se(1)–Cu(1)	103.2(1)
2Se(2) · · · Se(3)	3.969(3)	Cu(1)–Se(1)–Nb	70.7(1)
Se(3) · · · Se(3)	3.706(2)	Cu(2)–Se(1)–Cu(1)	113.0(1)
Se(3) · · · Se(3)	3.939(3)	Cu(2)–Se(1)–Nb	71.0(1)
K(1) · · · Se(1)	3.505(5)		
K(1) · · · Se(2)	3.419(7)		
	3.454(7)		
	3.866(1)		
	3.866(1)		

ninefold coordination if we arbitrarily choose a cutoff of 4.00 Å for the K · · · Se distances; it is found between the double chains. There are three crystallographically distinct Se atoms: atom Se(2) bridges the Nb and Cu(2) atoms; Se(3) triply bridges all the metal atoms; atom Se(1) is coordinated to four metal atoms and this type of coordination, though uncommon, is found in $Nb_4Br_{10}Se_3(NCMe)_4$ (*13*), where a Se atom is bonded to all four Nb atoms. In the present structure Nb–Cu distances are 2.831(1), 2.831(4), and 2.833(4) Å, somewhat shorter than that in $K_2CuNbSe_4$ (2.873(1)Å). The Se · · · Se distances show no apparent correlation with edge sharing.

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