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Synthesis and Characterization of Cu_3NbSe_4 and KCu_2TaSe_4

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Cu_3NbSe_4 has been synthesized from a stoichiometric reaction of the elements at 950°C. The material, which has the sulvanite (Cu_3VS_4) structure, crystallizes in space group T_d^1–$P\bar{4}3m$ of the cubic system with one formula unit in a cell with $a = 5.638(1)$ Å at -165°C. Cu_3NbSe_4 has a three-dimensional structure with edge-sharing of $CuSe_4$ and $NbSe_4$ tetrahedra and corner-sharing among $CuSe_4$ tetrahedra extending equally in all directions. KCu_2TaSe_4 was prepared from a reaction of K_2Se_5, Cu, Ta, and Se in the ratio 1 : 4 : 2 : 3 at 850°C. KCu_2TaSe_4 crystallizes in space group C_s^4–Cc of the monoclinic system with four formula units in a cell of dimensions $a = 5.660(1)$, $b = 18.829(4)$, $c = 7.662(2)$ Å, $\beta = 90.04(3)°$ at -165°C. In this structure the Ta and two independent Cu atoms are in tetrahedral sites. The $CuSe_4$ and $TaSe_4$ tetrahedra share edges and corners to make up two-dimensional layers. These layers are separated from one another by K^+ ions. KCu_2TaSe_4 is not isostructural with KCu_2NbSe_4, although the structures are similar.

Introduction

Previously, the compounds K_3MQ_4 (M = Nb, Ta; Q = S, Se) (*1*), K_2CuMSe_4 (M = Nb, Ta) (*2, 3*), and KCu_2NbQ_4 (Q = S, Se) (*4*) were synthesized and characterized in this laboratory. As the alkali metal content decreases in this series of compounds the structures change from separated K^+ and MQ_4^{3-} ions, to one-dimensional infinite chains composed of alternating edge-shared $CuSe_4$ and MSe_4 tetrahedra isolated from one another by K^+ ions,[1] to two-dimensional metal chalcogen layers separated by K^+ ions. This increase in dimensionality with decreasing alkali metal content appears to be a general trend (*5*). To confirm this trend in the present series of compounds a structure of one compound of the type Cu_3MQ_4 (M = Nb or Ta; Q = S or Se) was needed. In this paper we describe the synthesis and structural characterization of Cu_3NbSe_4. We also describe the synthesis and structure of a new member of the KCu_2MQ_4 family, namely KCu_2TaSe_4, which, although not isostructural with KCu_2NbSe_4, again comprises two-dimensional metal–chalcogen layers separated by K^+ ions.

Experimental

Synthesis. Cu_3NbSe_4 was synthesized from a stoichiometric reaction of the elements (Cu, 99.99%, Aldrich; Nb, 99.8% AESAR; Se, 99.99%, Aldrich). The starting materials were loaded into a quartz tube that was subsequently evacuated to 10^{-4} Torr and sealed. The tube was then placed in a furnace that was held at 950°C for 4 days. The reaction tube was then cooled to 200°C at a rate of 4°/hr, and finally to 25°C over 2

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[1] This same structure is also shown by the isostructural compound $K_2AgTaSe_4$ (space group $Fddd$, a = 6.047(2), b = 13.453(2), c = 23.309(4) Å at -165°C). $K_2AgTaSe_4$ was prepared by the reaction of K_2Se_5, Ag, Ta, and Se at 950°C.

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hr. Several red-orange crystals so obtained were examined by the electron microprobe of an EDAX-equipped Hitachi S-570 LB scanning electron microscope and were found to have the composition Cu : Nb : Se = 3 : 1 : 4.

KCu_2TaSe_4 was prepared from a reaction of K_2Se_5, Cu, Ta, and Se in the ratio 1 : 4 : 2 : 3 (Ta, 99.9% Aldrich). K_2Se_5 was made from a stoichiometric reaction of elemental K (99%, AESAR) with Se in liquid ammonia under an atmosphere of dry, oxygen-free argon. In a dry box the starting materials were loaded into a quartz tube that was subsequently evacuated to 10^{-4} Torr and sealed. The tube was placed in a furnace that was heated from room temperature to 500°C and held there for 24 hr. Subsequently the temperature was raised to 850°C and held there for 4 days before it was cooled to room temperature at a rate of 4°/hr. Several orange crystals were examined by the EDAX technique described above and found to have the composition K : Cu : Ta : Se = 1 : 2 : 1 : 4.

Crystallography. Weissenberg photography indicated that Cu_3NbSe_4 crystallizes in the cubic system in space groups $Pm\bar{3}m$, $P432$, or $P\bar{4}3m$. A crystal was placed in the cold stream of an Enraf-Nonius CAD4 diffractometer, and the unit cell was obtained by a least-squares analysis of the setting angles of 25 reflections automatically centered in the range of $32 \leq 2\theta(\text{Mo}K\alpha_1) \leq 38°$ at −165°C. Intensity data were collected by the θ–2θ scan technique. Six standard reflections, chosen from diverse regions of reciprocal space and monitored every 3 hr during data collection, showed no significant change. An analytical absorption correction was applied (*6*) to the data. The structure was solved by direct methods in space group T_d^1–$P\bar{4}3m$ (*7*) and refined on F^2 by full-matrix least-squares methods (*8*). The conventional $R(F)$ index for those reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.021. Some crystallographic details are given in Table I. The final positional and equivalent isotropic thermal parameters are given in Table II. Anisotropic thermal parameters and structure amplitudes are given in Table IS.[2]

TABLE I

CRYSTAL DATA AND EXPERIMENTAL DETAILS

Formula	KCu_2TaSe_4	Cu_3NbSe_4
Formula weight	663	599
Space group	C_s^4–Cc	T_d^1–$P\bar{4}3m$
a, Å	5.660(1)	5.638(1)
b, Å	18.829(4)	
c, Å	7.662(2)	
β, deg.	90.04(3)	
Vol. $Å^3$	816.6(3)	179.22(6)
Z	4	1
ρ(calc.) g cm^{-3}	5.393	5.554
Temperature, °C	-165^a	-165
Monochromated $\lambda(\text{Mo}K\alpha_1)$, Å	0.70930	0.70930
μ, mm^{-1}	36.8	30.5
Crystal size, mm	0.061 × 0.205 × 0.056	0.075 × 0.172 × 0.086
Transmission factors	0.117–0.207	0.091–0.184
Crystal vol., mm^3	0.7×10^{-3}	1.1×10^{-3}
Take-off angle, deg.	3.5	3.5
Scan type	θ–2θ	θ–2θ
Scan range, θ deg.	±1.0	±1.0
Data collected	$2 \leq \theta \leq 35°$; $\pm h, \pm k, \pm l$	$2 \leq \theta \leq 30°$; $\pm h, \pm k, \pm l$
No. of data collected	7114	4384
No. of unique data	3554	246
No. of unique data with $F_o^2 > 2\sigma(F_o^2)$	3296	241
$R(F)(F_o^2 > 2\sigma(F_o^2))$	0.030	0.021
$R_w(F^2)$	0.084	0.064

[a] The low temperature system for the Nonius CAD4 diffractometer is from a design by Professor J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. T. de Vic, 31320 Castanet-Tolosan, France.

Weissenberg photography indicated that KCu_2TaSe_4 crystallizes in the monoclinic crystal system in space group C_s^4–Cc or C_{2h}^6–$C2/c$. A tabular crystal was mounted in the cold stream of an Enraf-Nonius CAD4 diffractometer, and the unit cell was obtained by a least-squares analysis of the setting angles of 25 reflections automatically

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[2] See NAPS document No. 05012 for 20 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. $1.75 for postage of any microfiche orders.

TABLE II

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT COEFFICIENTS (Å^2) FOR Cu_3NbSe_4

Atom	x	y	z	U(eq)^a
Nb	0	0	0	0.0043(2)
Se	0.25021(5)	0.25021	0.25021	0.0065(2)
Cu	$\frac{1}{2}$	0	0	0.0090(2)

^{a} $U(\mathrm{eq}) = \frac{1}{3} \sum_i \sum_j (U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j)$.

centered in the range of $24 \leq 2\theta(\mathrm{Mo}K\alpha_1) \leq 36°$ at -165°C. Intensity data were collected by the θ–2θ scan technique. Six standard reflections, chosen from diverse regions of reciprocal space and monitored every 3 hr during data collection, showed no significant change. In the solution and refinement of the structure, the noncentrosymmetric space group C_s^4–Cc was chosen, since averaging of the absorption corrected data led to a satisfactory residual of 0.030 in point group m. The structure was solved by direct methods (*7*) and refined on F^2 by full-matrix least-squares methods (*8*). The conventional $R(F)$ index for those reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.030. Some crystallographic details are given in Table I. The final positional and equivalent isotropic thermal parameters are given in Table III. Anisotropic thermal parameters and structure amplitudes are given in Table IIS.^{2}

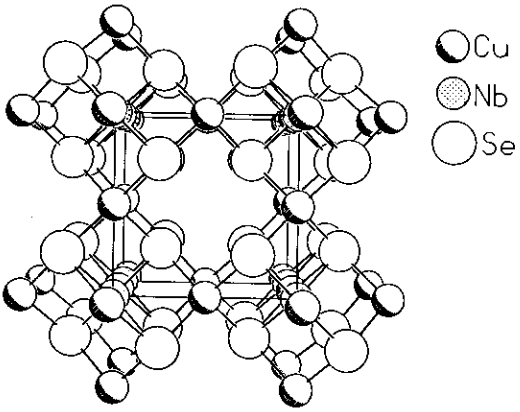

FIG. 1. A sketch of the structure of Cu_3NbSe_4.

Results

Cu_3NbSe_4 has a three-dimensional structure (Fig. 1) in which there is edge-sharing of $CuSe_4$ and $NbSe_4$ tetrahedra and corner-sharing among $CuSe_4$ tetrahedra extending equally in all directions. Each Se atom is surrounded by three Cu atoms at three of the corners of a nearly regular tetrahedron, and a Nb atom not at the fourth corner of the tetrahedron but at the inverse position. This is the sulvanite (Cu_3VS_4) structure (*9*). Selected bond distances and angles are given in Table IV. The Cu–Se distance is 2.442(1) Å, while the Nb–Se distance is 2.443(1) Å. These distances are comparable with those found in $K_2CuNbSe_4$ (Cu–Se: 2.457(1) Å, Nb–Se: 2.413(1) Å (*2*)) and in

TABLE III

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT COEFFICIENTS (Å^2) FOR KCu_2TaSe_4

Atom	x	y	z	U(eq)
Ta	0.1389	0.11048(1)	0.9056	0.0066(1)
Se(1)	0.3859(2)	0.00369(3)	0.9057(2)	0.0076(3)
Se(2)	0.3866(2)	0.21335(4)	0.9058(2)	0.0151(3)
Se(3)	−0.1072(2)	0.10951(5)	1.1629(1)	0.0098(3)
Se(4)	−0.1072(2)	0.10954(5)	0.6484(1)	0.0099(3)
Cu(1)	0.6387(4)	0.10805(4)	0.9057(3)	0.0104(3)
Cu(2)	0.1185(3)	0.00005(9)	1.1556(2)	0.0103(4)
K	0.8822(4)	−0.31746(9)	0.4059(3)	0.0215(7)

TABLE IV

SELECTED BOND LENGTHS (Å) AND ANGLES (DEG) FOR Cu_3NbSe_4

Nb–Se	2.443(1)	Se–Nb–Se	109.5
Cu–Se	2.442(1)	Se–Cu–Se	109.4(1)
Nb–Cu	2.819(1)	Se–Cu–Se	109.6(1)
		Cu–Se–Cu	109.4(1)
		Nb–Se–Cu	70.5(1)

TABLE V

SELECTED BOND LENGTHS (Å) AND ANGLES (DEG.) FOR KCu_2TaSe_4

Ta–Se(1)	2.449(1)	Se(1)–Ta–Se(2)	109.29(4)
Ta–Se(2)	2.391(1)	Se(2)–Ta–Se(3)	110.13(4)
Ta–Se(3)	2.414(1)	Se(2)–Ta–Se(4)	110.17(4)
Ta–Se(4)	2.412(1)	Se(1)–Ta–Se(3)	108.86(4)
Ta–Cu(1)	2.829(2)	Se(1)–Ta–Se(4)	108.87(4)
Ta–Cu(1)	2.831(2)	Se(3)–Ta–Se(4)	109.49(4)
Ta–Cu(2)	2.831(2)		
Ta–Cu(2)	2.830(2)	Se(1)–Cu(1)–Se(2)	108.20(9)
		Se(1)–Cu(1)–Se(3)	110.86(8)
Cu(1)–Se(1)	2.431(2)	Se(1)–Cu(1)–Se(4)	110.87(8)
Cu(1)–Se(2)	2.443(2)	Se(2)–Cu(1)–Se(3)	109.56(9)
Cu(1)–Se(3)	2.439(3)	Se(2)–Cu(1)–Se(4)	109.60(9)
Cu(1)–Se(4)	2.441(3)	Se(3)–Cu(1)–Se(4)	107.75(8)
Cu(2)–Se(1)	2.443(2)	Se(1)–Cu(2)–Se(1)	103.41(7)
Cu(2)–Se(1)	2.442(2)	Se(1)–Cu(2)–Se(3)	108.71(7)
Cu(2)–Se(3)	2.426(2)	Se(1)–Cu(2)–Se(4)	108.61(7)
Cu(2)–Se(4)	2.428(2)	Se(1)–Cu(2)–Se(4)	109.42(7)
		Se(3)–Cu(2)–Se(1)	109.43(7)
K–Se(2)	3.422(3)	Se(3)–Cu(2)–Se(4)	116.46(7)
K–Se(2)	3.463(3)		
K–Se(3)	3.609(3)	Ta–Se(1)–Cu(1)	70.87(5)
K–Se(4)	3.609(3)	Cu(1)–Se(1)–Cu(2)	112.80(8)
K–Se(1)	3.507(2)	Cu(1)–Se(1)–Cu(2)	112.83(8)
K–Se(2)	3.876(3)	Ta–Se(1)–Cu(2)	70.68(5)
K–Se(2)	3.874(3)	Ta–Se(1)–Cu(2)	70.73(5)
K–Se(3)	3.704(3)	Cu(2)–Se(1)–Cu(2)	103.31(7)
K–Se(4)	3.699(3)		

KCu_2NbSe_4 (Cu–Se: 2.427(2)–2.440(4) Å; Nb–Se: 2.392(3)–2.452(3) Å (*4*)).

The structure of KCu_2TaSe_4 is closely related to that of its Nb analogue (*4*), although the latter crystallizes in the orthorhombic rather than the monoclinic system. The crystal structure of KCu_2TaSe_4 shows a two-dimensional layered network and these layers are separated along the *b* axis (Fig. 2). Similar to that in KCu_2NbSe_4, three crystallographically distinct metal atoms in KCu_2TaSe_4 are in tetrahedral sites surrounded by Se atoms. In this compound Se–Ta–Se angles range from 108.86(4) to 110.17(4)°, while Se–Cu(1)–Se angles vary from 107.75(8) to 110.87(8)°, and Se–Cu(2)–Se angles range from 103.41(7) to 116.46(7)° (Table V). These are slightly different from those found in KCu_2NbSe_4: Se–Nb–Se, 108.7(1) to 110.9(1)°; Se–Cu(1)–Se, 103.3(3) to 115.6(1)°; and Se–Cu(2)–Se, 108.2(2) to 110.8(1)°. The Cu–Se(1)–Cu angles in KCu_2TaSe_4 range from 103.31(7) to 112.83(8)° and the Ta–Se(1)–Cu angles range from 70.68(5) to 70.87(5)°, comparable with those found in KCu_2NbSe_4 (Cu–Se(1)–Cu: 103.2(1)–113.0(1)°; Nb–Se(1)–Cu: 70.7(1)–71.0(1)° *4*)). The Cu–Se and Ta–Se distances range from 2.426(2) to 2.443(2) Å and 2.391(1) to 2.449(1) Å, respectively, similar to those found in $K_2CuTaSe_4$ (Cu–Se: 2.450(2) Å; Ta–Se: 2.394(2) Å (*3*)). There are four independent Se atoms in KCu_2TaSe_4. Among them, both atoms Se(3) and Se(4) triply bridge all the metal atoms. These are different from those found in KCu_2NbSe_4 where three crystallographically distinct Se atoms have different coor-

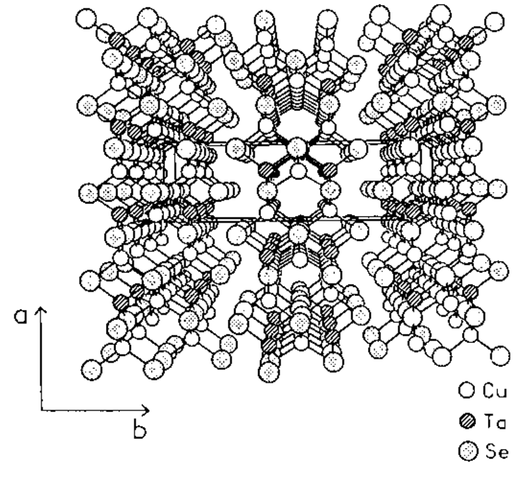

FIG. 2. A perspective view of the structure of KCu_2TaSe_4 down *c**.

dination geometries. But such differences between the two structures are not surprising, as the Ta compound is monoclinic while the Nb compound is orthorhombic. Moreover, the metal atoms are ordered in the Ta structure while there is some disorder between Nb and Cu in the Nb structure.

Returning to dimensionality versus alkali metal content we find that since Cu_3NbSe_4 has a three-dimensional structure the trend noted earlier now extends from K_3MQ_4 through to Cu_3MQ_4 and is consistent with that derived earlier from numerous structures in the literature (*5*).

Acknowledgments

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