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Bench-Top Synthesis of Solid-State Copper(I) Sulfides, $KCu_{7-x}S_4$ ($x = 0.0, 0.12, 0.34$), via Nonaqueous Electrochemistry

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The ability to synthesize solid-state materials without extensive heating is attractive, especially for those applications where a “low-temperature” reaction is critical. In conventional solid-state synthesis,[1,2] slow diffusion rates dictate high temperature and long duration. By dissolving solids in a solvent, the energy necessary to induce diffusion can be greatly reduced and consequently phase nucleation may be achieved at lower temperatures. Designing reactions that are driven by electrical potential may offer promising alternatives to the conventional synthesis of extended solids. We have demonstrated the feasibility of this approach by the electrochemical synthesis of solid-state potassium copper(I) sulfide phases in an amine solution. We have grown whiskers of the $KCu_{7-x}S_4$ series, where $x = 0.00$−0.34, 2 cm in length, in as little as 4 h at ca. 110 °C. Preliminary studies suggest that fine-tuning of electronic structures can be achieved in situ. The implication of current findings is that selective phase nucleation, philosophically similar to “molecular design”, may ultimately be possible in the solid state.

Electrochemistry has been used for the production of a limited number of chemicals for almost as long as electricity has been commercially available.[3] Two major branches soon emerged, namely, low-temperature aqueous electrochemistry and molten salt electrochemistry.[4−7] These techniques have been employed for the synthesis of technologically useful magnetic and electronic materials ranging from the growth of bulk crystals to the epitaxial growth of oriented thin films. Despite the advantages and long history, the development of electrochemical (E-Chem) techniques in exploratory synthesis of solid-state materials is still in a stage of infancy.[8]

Our initial attempt is to employ E-Chem methods for selective synthesis of low-dimensional conducting solids. In fact, this aspect of electrochemistry has been demonstrated by the synthesis of low-dimensional organic solids.[9] An ingenious class of conducting organic solids made of charge-transfer salts, including TTF−TCNQ (the first organic metal) and $(TMTSF)_2PF_6$ (the first organic superconductor; at 12 Kbar, $T_c \sim 1.0$ K), have been grown onto the electrode via intimately mixed organic solutions.

Analogous phenomena are found in the E-Chem synthesis of conducting inorganic solids. In this study, the synthesis can be simply carried out in a two-electrode cell. A copper electrode is employed for electrocrystallization. Ethylenediamine, the solvent of choice for polychalcogenide chemistry,[8,10] and an equimolar mixture of K_2S_n and CuCl are used.[11] It is noted that, prior to this study, a compound reportedly identified as KCu_7S_4 was synthesized in polycrystalline form at 400−800 °C by conventional solid-state methods.[12,13] This research shows that single crystals of the extended $KCu_{7-x}S_4$ series, including KCu_7S_4 ($x = 0$), can now be prepared by electrocrystallization at approximately the boiling point of water. Nonstoichiometry and mixed-valence are introduced via electrochemical doping. Only the end member ($x = 0$) corresponds to an electron-precise phase consisting of closed-shell K^+, Cu^+, and S^{2-} ions.

We have observed preferential crystal growth along the pseudo-one-dimensional copper sulfide chain. The Cu−S chain (Figure 1) propagates along the direction parallel to the needle axis. The extended structure consists of Cu_4S_4 columns interconnected by tetrahedral

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(11) In a typical reaction, 1.0 g of K_2S (AlfaÆesar) and 0.5 g of CuCl (98+%, Aldrich) were loaded into a 100 mL round-bottom flask in a nitrogen-purged drybox. A rubber septum was used to seal off the flask to protect the system from the atmosphere. About 50 mL of ethylenediamine (99%, Aldrich, dried over CaH_2 and distilled) was injected into the reaction flask. The resulting solution was heated to ca. 110 °C in a sand bath for ca. 10 h to dissolve reactant mixtures. Two parallel plate electrodes (1.5×1.5 cm^2) made from copper foil (99.9%, AlfaÆesar) were immersed in the solution and connected to a constant-voltage source. The applied voltage was between 0.5 and 3.5 V. In this particular system, the higher the voltage larger the x value of the $KCu_{7-x}S_4$ crystals obtained.

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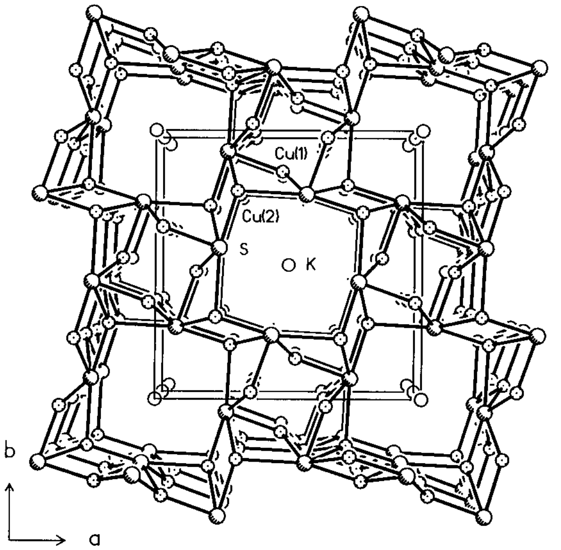

Figure 1. Unit cell of the $KCu_{7-x}S_4$ phase viewed down along the needle axis. The Cu_4S_4 column is made of three-coordinated copper, Cu(1), and bridging sulfur. Two adjacent columns are interconnected by tetrahedrally coordinated copper cations, Cu(2). These two structural units alternate to form an open framework around the 4-fold symmetry axis where the K^+ cations reside.

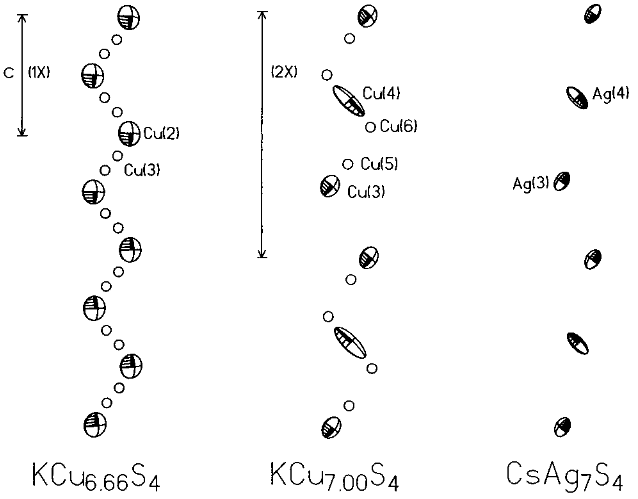

Figure 2. Disordered tetrahedral copper chain in the $KCu_{6.66}S_4$ and $KCu_{7.00}S_4$ phases and, for comparison, an analogous Ag chain in $CsAg_7S_4$[9] are plotted. The copper sites are partially occupied, and the refined percent occupancies[16] are 54.2(6)% and 6.2(6)% for Cu(2) (8h) and Cu(3) (16i) in $KCu_{6.66}S_4$ and 91(1)%, 82(1)%, 7(1)%, and 11(2)% for Cu(3) (8g), Cu(4) (4d), Cu(5) (8g), and Cu(6) (8g) in $KCu_{7.00}S_4$, respectively. The disordering patterns of the $KCu_{6.88}S_4$ phase are similar to those of the $KCu_{6.66}S_4$ phase. The *c* axis is doubled in $KCu_{7.00}S_4$, similar to that in the silver analogue. The anisotropic atoms are presented at 50% probability, and the shaded octants and open circles represent major vs minor occupancy sites, respectively.

Table 1. Crystallographic Data for $KCu_{7-x}S_4$ ($x = 0.0, 0.12, 0.34$)

chemical formula	$KCu_{7.00(2)}S_4$	$KCu_{6.88(5)}S_4$	$KCu_{6.66(4)}S_4$
fw[a]	612.5	604.5	590.7
space group	*P*4/*n* (No. 85)	*I*4/*m* (No. 87)	*I*4/*m* (No. 87)
a, Å	10.177(2)	10.176(2)	10.179(2)
c, Å	7.722(2)	3.834(2)	3.790(2)
V, Å^3	799.8(3)	397.1(2)	392.7(2)
Z	4	2	2
T, K	295	298	298
ρ_{calc},[a] g cm^{-3}	5.086	5.056	4.996
λ, Å	0.710 69	0.710 69	0.710 69
linear abs coeff, cm^{-1}	197.38	195.50	191.98
R[b]	0.030	0.039	0.027
R_w[c]	0.038	0.049	0.031

[a] Calculated based upon the refined structural formula (see text). [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R_w = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2}$.

chains, according to the notation adopted by Whangbo and Canadell.[14] Recent band structure calculations[15] show that the electron interactions are characterized primarily by covalent interaction through regular Cu−S bonds (2.30−2.34 Å) within the Cu_4S_4 column. The contribution of the interchain Cu−S (2.25−2.63 Å) and Cu−Cu bonds (2.82−2.92 Å along the Cu_4S_4 column, 2.28 Å along the Cu chain, and 2.61−2.70 Å between column and chain) to the electron interaction is much weaker. This suggests that the conducting pathway is primarily along the needle axis, and it is tempting to think that the E-Chem reaction facilitates continued growth preferentially along the conducting chain. Fast growth is attributed to ion deposition at the tip of the freshly grown $KCu_{7-x}S_4$ "microelectrodes". In fact, crystals grow orthogonal to the plate electrode, parallel to the electric field.

Single-crystal X-ray diffraction studies[16] show that these phases adopt the $(NH_4)Cu_7S_4$ structure[17] and the nonstoichiometry is due to copper vacancies occurring in the tetrahedral chain (Figure 2). The latter gives rise to the general formula $KCu_{3-x}[Cu_4S_4]$.[18] (Crystallographic data are summarized in Table 1. The final positional and thermal parameters for the $x = 0.34$ phase are listed in Table 2, while those of the $x = 0.0$ and 0.12 phases are reported in Table S2, Supporting Information.) In the average structure of $KCu_{6.66}S_4$, we have seen zigzag Cu(2) chains with disordered coppers residing between (open circles). We observed this type of disorder at room temperature for all phases with $x \neq 0$, but a different disordering pattern and subsequent superlattice for $x = 0$.

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(16) The diffraction data for the $KCu_{7-x}S_4$ ($x = 0.00, 0.12, 0.34$) crystals were collected on a Rigaku AFC7R four-circle diffractometer. The unit-cell parameters and the orientation matrix were determined by a least-squares fit of 16−35 randomly located reflections with $16.0° < 2\theta < 30.4°$, $16.1° < 2\theta < 27.5°$, and $12.7° < 2\theta < 19.8°$, respectively. Data were collected using an $\omega - 2\theta$ scan mode at 8°/min (≤3 rescans). There was no detectable decay during the data collection, according to the intensities of three standard reflections which were measured every 100 reflections. Lorentz-polarization and empirical absorption corrections (ψ scans) were applied to the data. Space groups were chosen on the basis of extinction conditions and successful structure solution. The structures were solved by direct methods with SHELXS-86, and refined on $|F|$ with SHELXTL-PLUS by least-squares, full-matrix techniques. Scattering factors for all atoms were taken from the source program used. The references for the crystallographic analysis are cited in the following publication: Mackay, R.; Wardojo, T. A.; Hwu, S.-J. *J. Solid State Chem.* **1996**, *125*, 255.

(17) Gattow, V. G. *Acta Crystallogr.* **1957**, *10*, 549.

(18) The *x* value is calculated based on the refined occupancy of tetrahedral copper. The chemical composition is confirmed indirectly by the two following pieces of evidence: First, the temperature-dependent resisitivity shows a strong correlation with the value of *x*, and the $x = 0$ sample shows a semiconducting behavior as expected. Second, a normalized volume vs *x* plot gives a nearly linear correlation where the cell volume decreases with increasing *x*.

Table 2. Positional and Thermal Parameters[a] for $KCu_{6.66}S_4$

atom	x	y	z	B_{eq} (Å^2)	occupancy (%)
K	0	0	0	1.66(8)	100
Cu(1)	0.0274(1)	0.3578(1)	0	1.97(8)	100
Cu(2)	0.3030(3)	0.2244(2)	0	4.18(8)	54.4(6)
Cu(3)	0.2695(8)	0.2434(9)	0.188(2)	1.2(2)	6.2(6)
S	0.2388(1)	0.4348(1)	0	1.18(8)	100

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} \ldots + 2hka^*b^*U_{12})$.

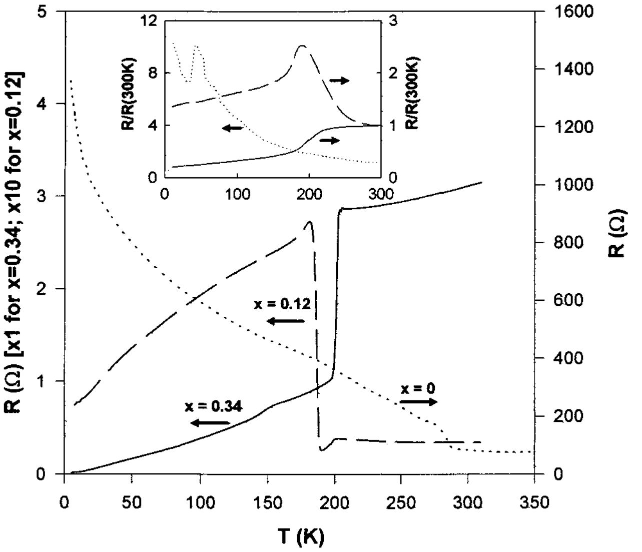

Figure 3. R vs T plots of three phases in the $KCu_{7-x}S_4$ series. The inset presents the relative resistance curves for pressed pellet samples of oriented whiskers.[19] The semiconducting-to-metallic transition observed for the $x = 0.12$ phase and abrupt transitions in the more copper-deficient $x = 0.34$ phase are unusual. See text.

The temperature-dependent resistivity shows a strong variation with x (Figure 3).[19] Four-probe measurements were performed on both pressed pellet and single-crystal samples. Single-crystal dimensions were typically 5 μm × 50 μm × 3 mm. The conductivity increases with x, being semiconducting ($dR/dT < 0$) when $x = 0$ and metallic (e.g., $\rho \sim 100$ $\mu\Omega$ cm at 300 K for $x = 0.34$) when $x \neq 0$. Figure 3 also reveals several resistivity anomalies. These transitions observed in the single-crystal measurements are much sharper than those in the pellets, perhaps because the pellets average the anisotropy. Tight binding calculations suggest that these transitions are not driven by the electronic structure.[15]

These fascinating transitions found in resistivity were further examined by ac calorimetry measurements.[20] Figure 4 shows the derived heat capacity (of the sample plus addenda, including thermocouples and silver paint), C_p, near the transitions for various values of x. Huge C_p anomalies are seen at 292, 186/193, and 208 K, corresponding well with the resistivity transitions observed in Figure 3. The shapes of and the entropy changes at these transitions appear to be similar (except for the 193 K transition for the $x = 0.12$ crystal), indicating that these transitions may have similar origins, despite the dissimilar behavior of the resistance at the transitions. C_p measurements on the $x = 0.34$ samples with a differential scanning calorimeter allow semiquantitative values to be assigned to the ac calorimetry measurements. The entropy change during the 208 K transition is ca. R ln 9/mol of Cu(2), where R is the ideal gas constant, in rough agreement with an ordering of the vacancies on the Cu zigzag chains (one vacancy for every 3 Cu ions). These values are much larger than expected for an electronic transition such as the charge density wave seen in some quasi-one-dimensional metals. A model based on diffusive one-dimensional ordering transitions is proposed and described elsewhere.[21]

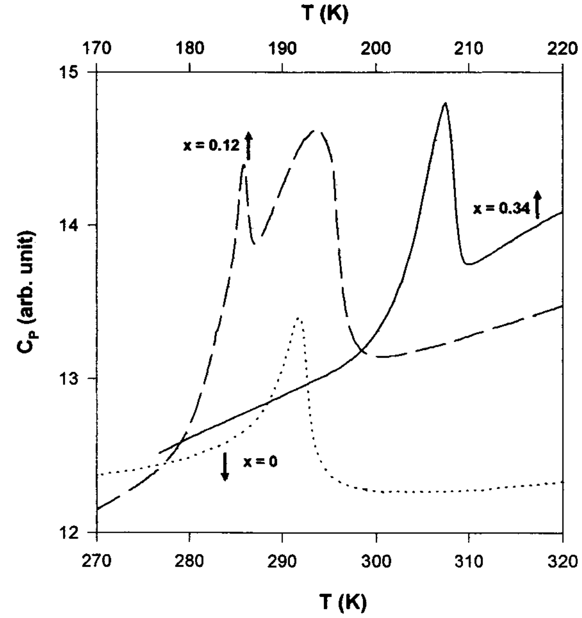

Figure 4. AC calorimetry measurements on single crystals near the transitions.

The $x = 0.12$ crystals show two transitions at 186 (T1) and 193 K (T2). We have assumed that T1 has the same origin as the transitions observed in the $x = 0$ and $x = 0.34$ crystals, but the origin of T2 is not known.

The sharp, nearly 4-fold drop in resistance at 208 K in the $x = 0.34$ crystals is unusual. A similar resistivity anomaly was observed in $K_3Cu_8S_6$ at ~55 K.[22,23] There is a small secondary transition in the resistance at 153 K, which is also seen in the ac calorimetry.[21] Preliminary investigations based on the profile refinements of low-temperature X-ray diffraction data show evidence of a tetragonal-to-monoclinic phase transition between 185 and 195 K for the $x \neq 0$ phases.[24] The sharp drop in the resistance, as well as the plethora of phase changes that are strongly dependent on the stoichiometry of the compound, are rare, making the title system worthy of future study.

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(19) For the $KCu_{6.88}S_4$ phase, the temperature-dependent resistivity curve of a pressed pellet sample (see Figure 3, inset) is similar to that of the "KCu_7S_4" phase reported by Ohtani et al. (refs 12 and 13). The cell constants for "KCu_7S_4" are $a = 10.163$ (5) Å, $c = 3.8380$ (4) Å. The calculated cell volume is 396.4 Å, which is comparable with that of the $KCu_{6.88}S_4$ phase (see Table 1).

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In summary, we have further demonstrated the versatility of E-Chem methods in the synthesis of extended inorganic solids. By this effective electrocrystallization via a nonaqueous solvent, we have synthesized potassium copper(I) sulfide single crystals with controlled chemical compositions, which is impossible by conventional methods thus far.[25] The E-Chem doping provides a precision with which nonstoichiometry and mixed valency can be controlled. The outcome of this renewed technique is remarkable in that bulk extended solids can be synthesized in a matter of several hours, at temperatures as low as the boiling point of water. In all likelihood, abundant opportunities, in terms of selective synthesis of inorganic solids, await in the field of electrochemistry.

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Supporting Information Available: Tables of detailed crystallographic data for the $KCu_{7-x}S_4$ series, positional and thermal parameters, and selected bond distances and angles (8 pages); structure factors (4 pages). Ordering information is given on any current masthead page.

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(25) In a recent report on the stoichiometry, space group and polymorphism of $TlCu_7S_4$, the polycrystalline samples of the $TlCu_{7-x}S_4$ ($0 \leq x < 0.55$) series have been synthesized by conventional methods. Berger, R.; Morén, L. *J. Alloys Compd.* **1996**, *237*, 33.