



Cu₇Bi₆S₁₀Cl₅ – Mobile Copper(I) Cations Inside Dendritic Channels of a Rigid Framework

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7 **Cu₇Bi₆S₁₀Cl₅ – Mobile Copper(I) Cations Inside Dendritic Channels**
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10 **of a Rigid Framework**
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14 **Andreas Heerwig^[a] and Michael Ruck*^[a]**
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18 *Dedicated to Professor Bernd Harbrecht on the Occation of his 60th Birthday*
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23 **Keywords:** Bismuth; Cation mobility; Copper; Covalent polyhedra networks; One-dimensional
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25 ionic conductors
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31 **Running title:** Mobile Cu cations in dendritic channels
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1
2 **Abstract.** The melting reaction of Cu, CuCl, S, and Bi₂S₃ yields black, shiny needles of the sulfide
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4 chloride Cu₇Bi₆S₁₀Cl₅. The compound decomposes peritectically above 639(5) K. Cu-*K*-XANES
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6 data confirm the oxidation state +I of Cu. Cu₇Bi₆S₁₀Cl₅ crystallizes in the monoclinic space group
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8 *C2/m* with *a* = 2878.3(9) pm, *b* = 396.59(9) pm, *c* = 1156.5(4) pm, and *β* = 111.55(3) ° at *T* =
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10 293(2) K. Three S and four Cl anions coordinate each of the three independent Bi cations in the
11
12 shape of mono-capped trigonal prisms. The [BiS₃Cl₄] polyhedra share edges and faces resulting in
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14 furrowed layers parallel ($\bar{2}$ 01). Localized as well as disordered Cu cations occupy trigonal or
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16 tetrahedral voids in the packing of anions. The Joint Probability Density Function (JPDF) reveals
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18 branched and unbranched continuous pathways along [010], which are available for cation
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conduction.

Introduction

Argyrodites like $\text{Ag}_7\text{GeSe}_5\text{I}$ [1], $\text{Cu}_6\text{PS}_5\text{X}$ ($X = \text{Cl}, \text{Br}, \text{I}$) [2], and $\text{Li}_6\text{PS}_5\text{I}$ [3] are famous for their high isotropic ionic conductivity. The three-dimensional arrangement of interconnected conduction paths in their structures is an essential prerequisite for this property. On the other hand, for electrode applications it could be desirable to find anisotropic ionic conductors, which offer electronic transport as well (mixed conductors). Quaternary phases of the systems $M/\text{Bi}/Q/X$ ($M = \text{Cu}, \text{Ag}, Q = \text{S}, \text{Se}$, and $X = \text{Cl}, \text{Br}, \text{I}$) have been shown to be tunable small-gap semi-conductors [4], which especially in the case of the Cu compounds show also ion mobility. Typically, their structures consist of rigid substructures of $[\text{Bi}Q_nX_m]$ polyhedra with disordered Cu^{I} in between. For example, $\text{Cu}_3\text{Bi}_2\text{S}_4\text{Cl}$ [5] or $\text{Cu}_3\text{Bi}_2\text{S}_3\text{I}_3$ [6] are considered to be mixed conductors, where the different phenomena are not unidirectional. Our aim was to reveal a greater range to such highly anisotropic materials, as already successful reported in previous work [7]. Here, we present a new quaternary compound in the system $\text{Cu}/\text{Bi}/\text{S}/\text{Cl}$, which exhibits a rigid bismuth-anion network and inherent disordered Cu^{I} cations.

Experimental Section

Synthesis

A successful synthesis of $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ was achieved using stoichiometric amounts of Bi_2S_3 (Alfa Aesar; 99.9 %), Cu (Chemapol; p. a.), S (Laborchemie Apolda; purified and distilled), and CuCl, which had been synthesized from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Grüssing; p. a.) and NaCl (VWR; p. a.) according to *Kramb* [8]. The starting materials were handled in an Argon filled glove box (M. Braun; $c(\text{O}_2) \leq 1 \text{ ppm}$; $c(\text{H}_2\text{O}) \leq 1 \text{ ppm}$). The reaction was carried out in evacuated ($p \approx 0.1 \text{ Pa}$) silica ampoules (150 mm in length, 15 mm inner diameter) placed in the middle of a tubular furnace. The educts were heated from ambient temperature to 670 K within 24 hours, cooled to 570 K in the same period of time, and tempered at 570 K for two weeks before quenching in water. The product

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2 consisted of hedgehogs of black needles, which exhibit metallic luster exposed to impinging light.

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4 The compound is inert against water and alcoholic solvents, but decomposes in inorganic acids.
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8 9 *Thermal Analysis*

10 A powdered sample of $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ ($m \approx 30$ mg) enclosed in an evacuated ($p \approx 0.1$ Pa) silica
11 micro-ampoule was analyzed using a DTA-DSC device (Labsys DSC 12, Setaram). With a rate of
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16 $\Delta T/t = 5$ K/min the sample was heated to 770 K and subsequently cooled to ambient temperature.

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18 The residua of the thermal analysis were characterized by X-ray powder diffraction.
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23 24 *Spectroscopic Investigation*

25 X-ray absorption near edge spectroscopy was applied to determine the valence of the Cu ions in the
26 material. It was performed at the Doris ring at HASYLAB of DESY in Hamburg. The examination
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took place at the beam line E4 at the Cu-K-edge between 8729 eV and 9977 eV with a step width of
2.4 eV.

Crystallographic Structure Determination

Cu₇Bi₆S₁₀Cl₅ was characterized by powder and single-crystal X-ray diffraction methods. Precession
photographs of a single-crystal showed a monoclinic pattern with reflection conditions that led to
the space groups $C2/m$ or Cm . The lattice constants at 293(2) K were determined from 52 single
indexed reflections of a Guinier photograph with silicon as internal standard: $a = 2878.3(9)$ pm, $b =$
 $396.59(9)$ pm, $c = 1156.5(4)$ pm, and $\beta = 111.55(3)^\circ$. The reflection intensities were measured on a
four-circle diffractometer with scintillation detector (AED2, Siemens/Stoe) using the learnt-profile-
method [9]. An analytical absorption correction was applied [10] based on a microscopic crystal
description that had been optimized using seven ψ -scans [11]. Experimental details are summarized
in Table 1. The crystal structure was solved by direct methods in the space group $C2/m$ (no. 12) and
refined against F^2 [12]. During the first steps of the structure solution three Bi, one Cu, five S and

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2 three Cl positions were found. The differentiation between S and Cl ions was possible by bond-
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4 length bond-strength considerations [13]. Anisotropic displacement parameters were determined for
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6 these atoms. Difference Fourier maps showed numerous maxima, which could be assigned to
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8 partially occupied Cu positions. Those significant within the bias in the Fourier map were included
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10 in the refinement procedure. First the sum of occupancies for all disordered Cu atoms was fixed
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12 based on charge balance and the assumption of the Cu oxidation state +I. As it turned out that the
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14 sum of occupancies of the positions Cu2 x approximates three atoms per unit cell, it was constrained
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16 to that value. Likewise the sums of occupancies of the positions Cu3 x and Cu4 x were constrained to
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18 four and three. For disordered Cu atoms of the same group the identical isotropic displacement
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20 parameter was applied. The crystal structure refinement converged without significant residual
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22 electron densities at reliability indexes $R_1 = 0.021$ for $1735 F_o > 4\sigma(F_o)$ and $wR_2 = 0.046$ for all
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24 2048 data (Table 1). Atomic parameters and selected interatomic distances are listed in Tables 2 and
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26 3. Further details of the crystal structure determination are available from the
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28 Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), E-mail
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30 crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-421386. For graphical
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32 representation of the crystal structure the program Diamond [14] was used.
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40 The calculation of the Joint Probability Density Function (JPDF) was done with JANA [15],
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42 followed by a visualization with VESTA [16]. The Cu2 string was fitted by applying anharmonic
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44 terms of third order to a Cu atom in 0.247(1), 0.14(2), 0.514(3). For the Cu4 string a Cu atom in
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46 0.502(2), 0.260(3), -0.002(8) was refined with a fourth order tensor. Since no large negative
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48 electron density arose in both cases, the anharmonic refinement can be regarded as an adequate
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50 description [17].
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Table 1. Crystallographic data and details of the structure determination for $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$.

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|---------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| Compound | $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ |
| Measuring temperature | 293(2) K |
| Crystal system | monoclinic |
| Space group | $C2/m$ (no. 12) |
| Lattice parameters | $a = 2878.3(9)$ pm $b = 396.59(9)$ pm $c = 1156.5(4)$ pm $\beta = 111.55(3)^\circ$ $V = 1227.9(6) \times 10^6$ pm ³ |
| Z | 2 |
| $\rho_{\text{calc.}} \times \text{cm}^3 / \text{g}$ | 5.94 |
| Crystal size / mm ³ | $0.78 \times 0.04 \times 0.02$ |
| Measuring system | four-circle diffractometer AED2 (Siemens/Stoe) with scintillation detector and graphite monochromator |
| Radiation | Mo- $K\alpha$, $\lambda = 71.073$ pm |
| Measuring range | $2\theta \leq 60^\circ$ $-40 \leq h \leq 40$ $-5 \leq k \leq 5$ $-16 \leq l \leq 16$ |
| Absorption correction | analytical [10]; crystal description optimized using seven ψ -scans [11] |
| $\mu(\text{Mo-}K\alpha) \times \text{mm}$ | 50.1 |
| Transmission factors | 0.20 to 0.30 |
| Measured reflections | 6958 |
| Unique reflections | 2048 |
| R_{int} | 0.028 |
| R_σ | 0.024 |
| Structure refinement | Least squares method; full matrix; based on F^2 |
| Extinction parameter | $13.9(4) \times 10^{-4}$ |
| Parameters; Restrictions | 120; 3 |
| Residual electron density $\Delta\rho \times 10^6$ pm ³ / e | +1.6 to -1.3 |
| R_1 (all F_o) | 0.031 |
| R_1 ($F_o > 4\sigma(F_o)$) | 0.021 |
| wR_2 (all F_o^2) | 0.046 |
| Goof | 1.014 |

Table 2. Wyckoff positions, coordinates, occupancy factors (k) and equivalent isotropic displacement parameters of the atoms in $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ at 293 K. U_{eq} (in pm^2) is defined as one third of the trace of the orthogonalized tensor U_{ij} .

| Atom | Position | x | y | z | k | $U_{\text{eq}}, U_{\text{iso}}$ |
|------|----------|---------------|---------------|---------------|----------|---------------------------------|
| Bi1 | $4i$ | 0.26976(1) | $\frac{1}{2}$ | 0.21694(3) | 1 | 152.7(7) |
| Bi2 | $4i$ | 0.40926(1) | 0 | 0.46296(2) | 1 | 141.3(7) |
| Bi3 | $4i$ | 0.39384(1) | 0 | 0.04258(2) | 1 | 140.1(7) |
| Cu1 | $4i$ | 0.15687(4) | 0 | 0.2914(1) | 1 | 277(2) |
| Cu2a | $4i$ | 0.247(1) | 0 | 0.466(2) | 0.099(7) | 221(9) |
| Cu2b | $8j$ | 0.2566(6) | 0.104(6) | 0.478(1) | 0.135(7) | $U_{\text{iso}}(\text{Cu2a})$ |
| Cu2c | $8j$ | 0.2482(6) | 0.185(5) | 0.488(1) | 0.104(4) | $U_{\text{iso}}(\text{Cu2a})$ |
| Cu2d | $8j$ | 0.2371(7) | 0.286(7) | 0.506(1) | 0.086(8) | $U_{\text{iso}}(\text{Cu2a})$ |
| Cu3a | $4i$ | 0.5348(7) | $\frac{1}{2}$ | 0.190(2) | 0.055(2) | 174(4) |
| Cu3b | $4i$ | 0.5240(5) | $\frac{1}{2}$ | 0.231(2) | 0.25(1) | $U_{\text{iso}}(\text{Cu3a})$ |
| Cu3c | $4i$ | 0.5179(4) | $\frac{1}{2}$ | 0.260(2) | 0.452(3) | $U_{\text{iso}}(\text{Cu3a})$ |
| Cu3d | $4i$ | 0.5125(4) | $\frac{1}{2}$ | 0.288(2) | 0.29(1) | $U_{\text{iso}}(\text{Cu3a})$ |
| Cu3e | $4i$ | 0.473(1) | $\frac{1}{2}$ | 0.282(3) | 0.030(1) | $U_{\text{iso}}(\text{Cu3a})$ |
| Cu4a | $2a$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 0.090(2) | 268(10) |
| Cu4b | $8j$ | 0.5054(5) | 0.411(3) | 0.046(2) | 0.062(3) | $U_{\text{iso}}(\text{Cu4a})$ |
| Cu4c | $4g$ | $\frac{1}{2}$ | 0.313(2) | 0 | 0.219(2) | $U_{\text{iso}}(\text{Cu4a})$ |
| Cu4d | $8j$ | 0.5087(3) | 0.158(2) | 0.0189(7) | 0.118(2) | $U_{\text{iso}}(\text{Cu4a})$ |
| Cu4e | $4i$ | 0.513(3) | 0 | 0.022(6) | 0.041(7) | $U_{\text{iso}}(\text{Cu4a})$ |
| Cu4f | $2b$ | $\frac{1}{2}$ | 0 | 0 | 0.171(2) | $U_{\text{iso}}(\text{Cu4a})$ |
| S1 | $4i$ | 0.20309(7) | $\frac{1}{2}$ | 0.3203(2) | 1 | 160(3) |
| S2 | $4i$ | 0.31045(6) | 0 | 0.3805(2) | 1 | 150(3) |
| S3 | $4i$ | 0.40060(6) | $\frac{1}{2}$ | 0.6074(2) | 1 | 130(3) |
| S4 | $4i$ | 0.48737(6) | 0 | 0.1760(2) | 1 | 163(3) |
| S5 | $4i$ | 0.41240(7) | $\frac{1}{2}$ | -0.0877(2) | 1 | 146(3) |
| Cl1 | $4i$ | 0.20722(6) | 0 | 0.0500(2) | 1 | 175(3) |
| Cl2 | $4i$ | 0.38504(7) | 0 | 0.2433(2) | 1 | 187(3) |
| Cl3 | $2c$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 1 | 266(6) |

Table 3. Selected interatomic distances (in pm) for $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$. Symmetry operators: (i): x, y, z ; (ii): $x, y+1, z$; (iii): $1/2-x, 1/2-y, -z$; (iv): $x, y-1, z$; (v): $1/2-x, -y-1/2, -z$; (vi): $1/2-x, 1/2-y, 1-z$; (vii): $1-x, 1-y, 1-z$; (viii): $1-x, 1-y, -z$; (ix): $1-x, -y, -z$.

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|------|-----------------------|-----------|-------|---------------------|----------|-------|---------------------|----------|-------|------------------------------|----------|
| Bi1– | S1 | 260.7(2) | Cu2a– | S1 ^{vi} | 236(2) | Cu3a– | S5 ^{viii} | 225(3) | Cu4a– | S5 ^{i, viii} | 234.7(2) |
| | S2 ^{i, ii} | 269.3(1) | | S2 | 238(2) | | S4 ^{i, ii} | 238(1) | | S4 ^{i, ii, viii ix} | 295.8(2) |
| | Cl1 ^{i, ii} | 288.9(2) | | S1 ^{i, iv} | 260(1) | | S3 ^{vi} | 239(2) | | | |
| | Cl2 | 321.9(2) | | | | | | | Cu4b– | S5 ^{viii} | 226(1) |
| | Cl1 ⁱⁱⁱ | 338.8(2) | Cu2b– | S1 ^{vi} | 222.6(9) | Cu3b– | S4 ^{i, ii} | 222.7(3) | | S4 | 240(1) |
| | | | | S2 | 227(1) | | S3 ^{vii} | 228.3(5) | | S5 | 258(1) |
| Bi2– | S2 | 264.7(2) | | S1 | 247(1) | | S5 ^{viii} | 289(3) | | S4 ⁱⁱ | 292(1) |
| | S3 ^{i, iv} | 266.3(1) | | | | | | | | | |
| | Cl2 ^{i, iv} | 309.4(2) | Cu2c– | S1 ^{i, vi} | 227(1) | Cu3c– | S4 ^{i, ii} | 224.0(4) | Cu4c– | S5 ^{i, viii} | 246.2(3) |
| | Cl3 ^{i, iv} | 318.04(7) | | S2 | 263(2) | | S3 ^{vii} | 228.3(4) | | S4 ^{i, ix} | 252.1(5) |
| | | | | S2 ^{vi} | 294(2) | | | | | | |
| Bi3– | S4 | 256.5(2) | | | | Cu3d– | S4 ^{i, ii} | 233.3(9) | Cu4d– | S4 | 221.1(9) |
| | S5 ^{i, iv} | 266.1(1) | Cu2d– | S1 | 218(1) | | S3 ^{vii} | 234.4(8) | | S4 ^{ix} | 238.3(8) |
| | Cl2 ^{i, iv} | 313.3(2) | | S2 ^{vi} | 237(2) | | Cl3 | 261(3) | | S5 ^{viii} | 251.1(7) |
| | Cl1 ^{iii, v} | 335.4(2) | | S1 ^{vi} | 240(1) | | | | | S5 | 292.0(8) |
| | | | | | | Cu3e– | Cl3 | 235(3) | | | |
| Cu1– | S1 ^{i, iv} | 234.3(1) | | | | | Cl2 | 240(3) | Cu4e– | S4 | 215(3) |
| | S3 ^{vi} | 235.1(2) | | | | | S4 ^{i, ii} | 245(2) | | S4 ^{ix} | 229(4) |
| | S5 ⁱⁱⁱ | 246.5(2) | | | | | | | | S5 ^{viii, ix} | 282(6) |
| | | | | | | | | | Cu4f– | S4 ^{i, ix} | 219.5(2) |

Results and Discussion

The thermal reaction of Cu, CuCl, S and Bi₂S₃ resulted in shiny black needles of the sulfide chloride Cu₇Bi₆S₁₀Cl₅. With respect to the pseudo-ternary phase diagram the sum formula can be rearranged as 5BiSCl·¹/₂Bi₂S₃·⁷/₂Cu₂S. Heating Cu₇Bi₆S₁₀Cl₅ in evacuated silica ampoules results in peritectoid decomposition at 639(5) K. After slow cooling to ambient temperature, Cu₃Bi₂S₄Cl [5] as well as smaller amounts of CuBiSCl₂ [4] and BiSCl [18] were detected by X-ray powder diffractometry. The decomposition reaction can be written as



The oxidation state +I of the Cu cations was verified by XANES measurements (Fig. 1). The energy of the copper *K* edge of Cu₇Bi₆S₁₀Cl₅ is very similar to the reference CuCl, while there is a large difference to the position of the edge of CuS. The instability of Cu^{II} in sulfidic environment is once more demonstrated [19].

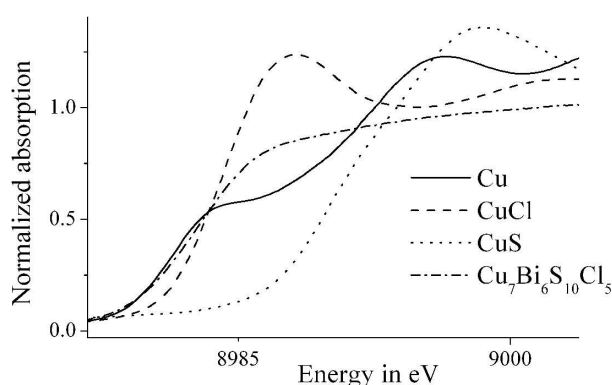
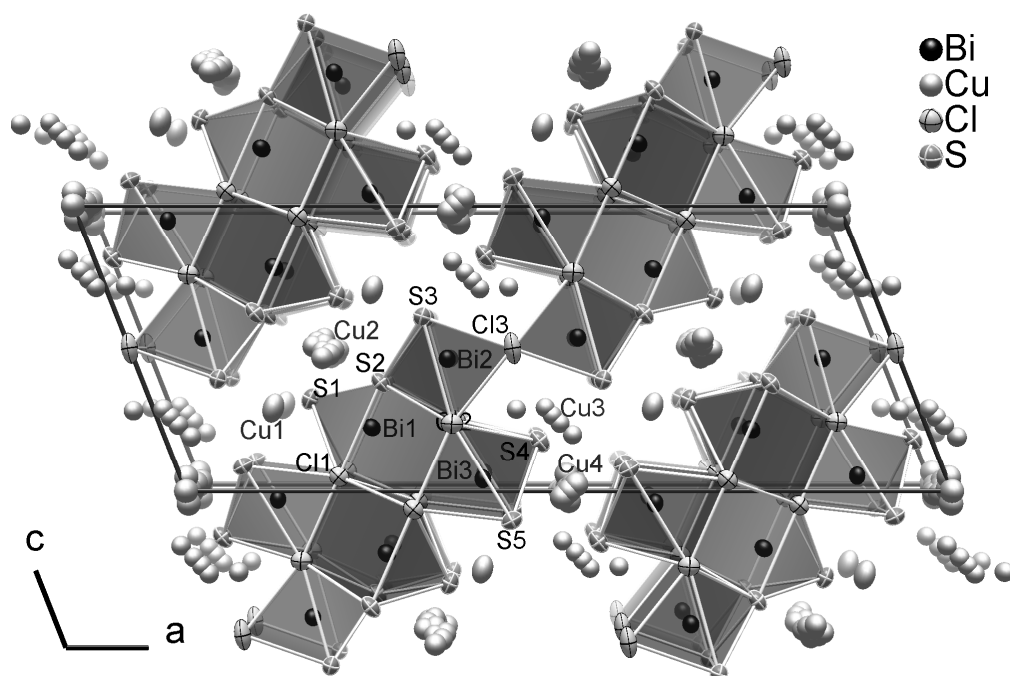


Figure 1. XANES spectrum at the Cu *K* edge of Cu₇Bi₆S₁₀Cl₅ as well as of reference substances.

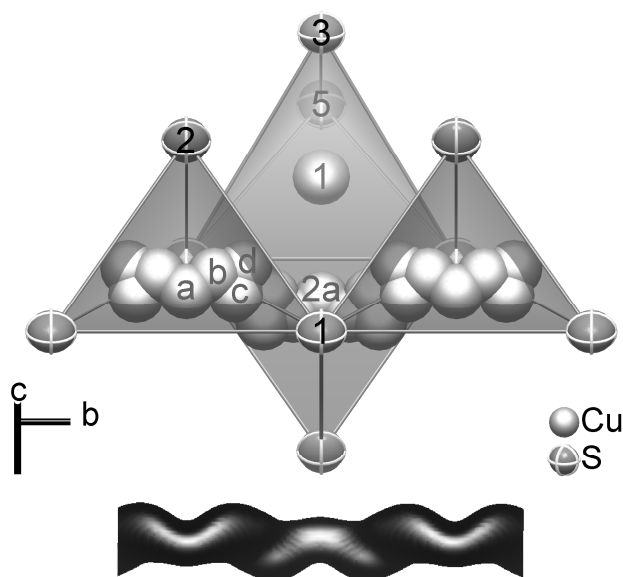
The monoclinic crystal structure of Cu₇Bi₆S₁₀Cl₅ can be subdivided into a layered rigid backbone formed by the Bi cations and the anions, and more or less mobile Cu cations in between (Fig. 2). Each of the three independent Bi cations is coordinated by three S and four Cl anions in the shape of a mono-capped trigonal prism. Such coordination spheres of anions surrounding bismuth cations are already reported for substances like Cu₃Bi₂S₄Cl [5] or Cu₉Bi₉S₁₆Cl₈ [7]. The [BiS₃Cl₄] polyhedra share edges and faces resulting in compact rods with six prisms in the cross section

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2 running along [010] and eventually in corrugated layers $\frac{2}{\infty}[\text{Bi}_6\text{S}_{10}\text{Cl}_5]^{7-}$ parallel $(\bar{2}01)$. The same
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4 connectivity of prisms as in the six-membered rods can also be found in the crystal structure of
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6 $\text{Cu}_3\text{Bi}_2\text{S}_4\text{Cl}$ [5, 20], which is a thermal decomposition product of $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ (vide supra). The
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8 idea of an essentially rigid polyhedral substructure is supported by the astonishingly regular
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10 displacement ellipsoids of the anions, which indicate only minor response of the anions to the
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12 varying occupancies of the Cu positions. Although the anions are well localized, their polarizability
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14 allows exchange of Cu cations between neighboring sites. Every Cl anion is connected to four or
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16 five Bi cations, whereas the S anions coordinate only one to three Bi cations. In other words, the Cl
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18 anions are located inside the polyhedral framework, while the S anions form its interface to the Cu
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20 cations. Consequently the chemical surrounding of the Cu cations is dominated by S anions. The
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22 feature that the mobile Cu ions are coordinated by the more polarizable anions is known from
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24 related compounds like $\text{Cu}_9\text{Bi}_9\text{S}_{16}\text{Cl}_8$ [7] as well.
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Figure 2. Crystal structure of $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ emphasizing the layers of $[\text{BiS}_3\text{Cl}_4]$ prisms. The ellipsoids represent 95 % probability.

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2 The localized Cu1 atom centers a tetrahedron of S anions with $d(\text{Cu-S}) = 234 - 246$ pm. The
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4 next nearest Cu position, Cu2a, is 263 pm away and also coordinated tetrahedrally (Figure3). Since
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6 the two coordination polyhedra share a common edge, an exchange between the two positions
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8 seems to be unlikely. The positions Cu2a to Cu2d form an infinite sequence of closely spaced
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10 positions along [010] with no more than 50 pm between neighboring sites. This feature has been
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12 regarded as an indicator of high ion mobility and low activation energies for hopping from one
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14 position to another [21], which is a necessary condition for a good ionic conductor. An alternative
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16 representation of the electron density using the Joint Probability Density Function (JPDF) reveals a
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18 continuous pathway. The unusually high isosurface level $\eta = 0.2 \text{ e}/(10^6 \text{ pm}^3)$ of this path is a
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20 consequence of two peculiarities: Firstly, all Cu2 sites are almost equally populated, although Cu2b,
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22 Cu2c, and Cu2d are only coordinated trigonally by S. Secondly, the overall population of 1.5 Cu2
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24 atoms per string and translational period b , which corresponds to an average distance of 264 pm
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26 between occupied sites, is rather high.
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56 **Figure 3.** Localized Cu1 and disordered Cu2 cations in the crystal structure of $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$. The
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58 tetrahedra are centered by Cu1 and Cu2a. The ellipsoids represent 95 % probability. Below: The
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60 JPDF of the Cu2 string with an isosurface of $\eta = 0.2 \text{ e}/(10^6 \text{ pm}^3)$.

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The same holds for the series of Cu₄ positions, which show a quite similar density of sites and the same average overall population (Fig. 4). Again the JPDF is continuous at an isosurface level of $\eta = 0.2 \text{ e}/(10^6 \text{ pm}^3)$. Cu₄c is coordinated tetrahedrally, while Cu₄b and Cu₄d have trigonal, and Cu₄a and Cu₄e linear coordination of S anions. The major difference lies in the orthogonal branches of the Cu₄ string formed by the sites Cu₃a to Cu₃e. If the string of Cu₄ positions is regarded the “street” for mobile Cu cations, the Cu₃ positions are the “parking”. Any Cu ion entering or leaving the branch must pass through a triangle of S anions and beat the distance $d(\text{Cu}_{3\text{a}}\text{--Cu}_{4\text{b}}) = 161 \text{ pm}$. Furthermore, the sum of occupancies for the Cu₃ position equals one Cu atom per branch, i.e. the “parking” is occupied. Cu₃a is coordinated by four, Cu₃b as well as Cu₃c by three S anions. Cu₃d and Cu₃e, lying deep in the furrows of the $[\text{Bi}_6\text{S}_{10}\text{Cl}_5]^{7-}$ layers, occupy tetrahedral voids and hold one or two Cl anions in their coordination.

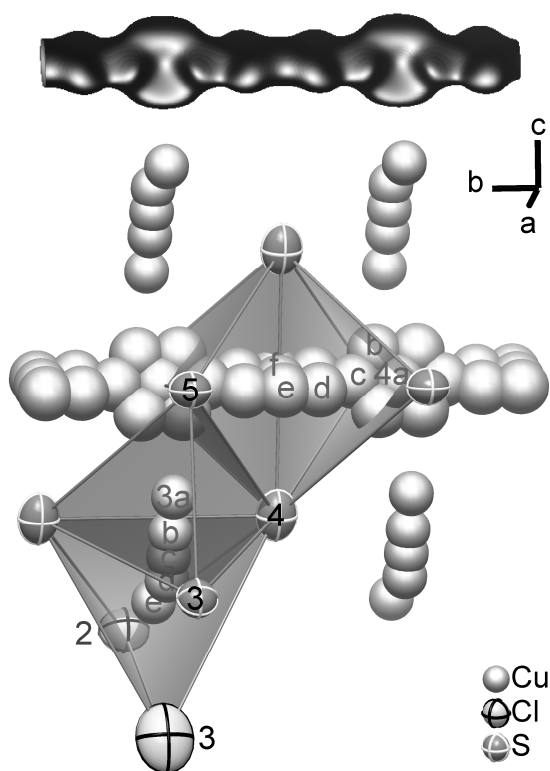


Figure 4. Disordered Cu₃ and Cu₄ cations forming a dendritic one-dimensional substructure in $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$. The tetrahedra shown are centered by Cu₃a, Cu₃e, and Cu₄c. The ellipsoids represent 95 % probability. Above: The JPDF of the Cu₄ string with an isosurface of $\eta = 0.2 \text{ e}/(10^6 \text{ pm}^3)$.

Concluding Remark

On an absolute scale the ionic conductivity of $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ will not be able to compete with argyrodites like $\text{Ag}_7\text{GeSe}_5\text{I}$ [1], $\text{Cu}_6\text{PS}_5\text{X}$ ($X = \text{Cl}, \text{Br}, \text{I}$) [2], and $\text{Li}_6\text{PS}_5\text{I}$ [3], which exhibit tremendous ionic mobility. However, the structural concept of compounds like $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$ seems to be interesting for one-dimensional, i.e. structurally directed, ionic conductivity. The one-dimensional character in combination with the high density of Cu cations may substantially slow down the mobility of individual cations. On the other hand, the group velocity could be acceptable, since only few steps of transport are necessary to deliver a cation at the electrode. Furthermore, back jumps should be less probable than in compounds with less Cu cations on the available sites. The cruces for any imaginable application are the needle-like habitus of the crystals and the intricate crystal growth of a compound decomposing peritectically.

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Supplementary Material

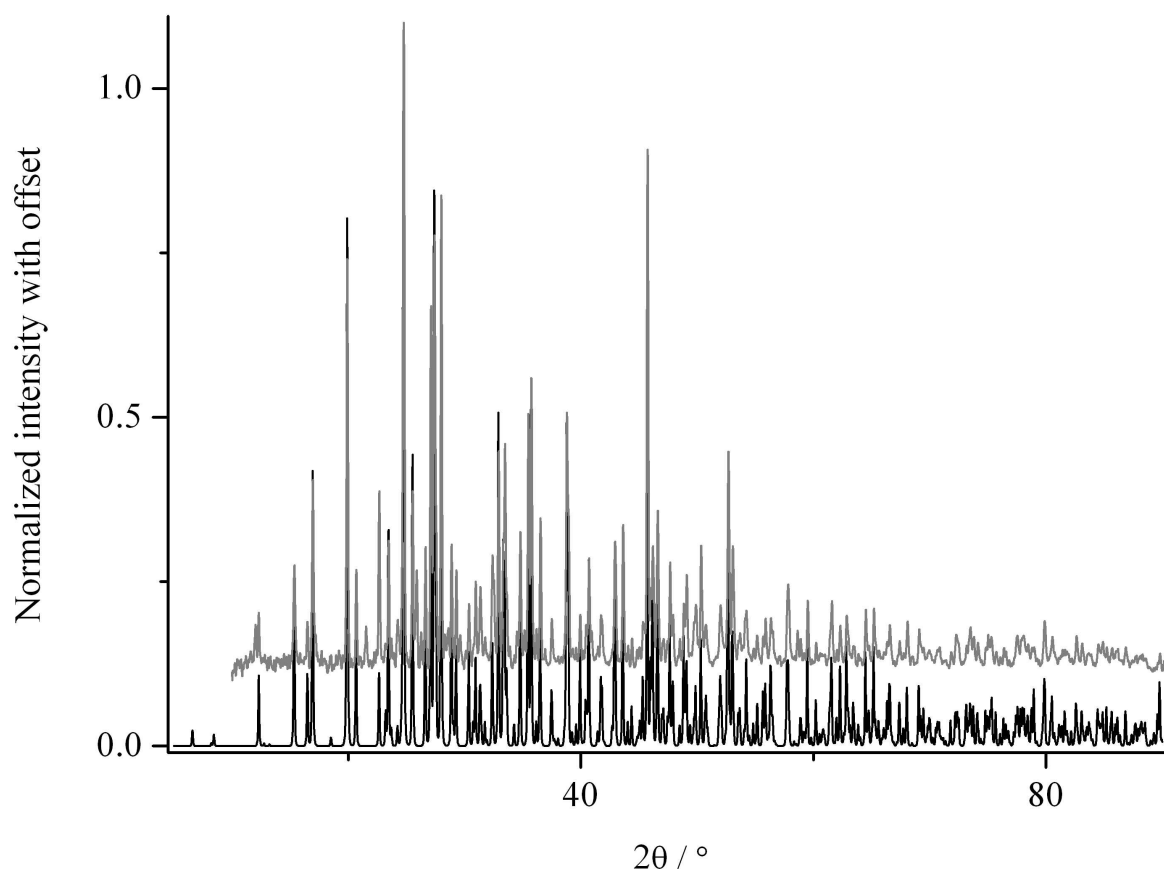


Figure S1. Measured (gray) and calculated (black) powder diffractogram of $\text{Cu}_7\text{Bi}_6\text{S}_{10}\text{Cl}_5$.