

Growth of CuS platelet single crystals by the high-temperature solution growth technique

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Abstract

Millimeter size CuS single crystals with a dark indigo blue color and a plate hexagonal shape have been successfully grown by the high-temperature solution growth technique using the KCl–LiCl eutectic as solvent. Surface microtopographic studies of the crystals indicated that the growth is made by the lateral spreading of the layers. Electrical resistivity measurements clearly show an anomaly at $T \sim 55$ K, related with the low-temperature structural transition, a high residual resistivity ratio of ~ 400 and a sharp superconducting transition at $T \approx 1.7$ K confirming the very good quality of the crystals.

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1. Introduction

Copper sulfides have been extensively studied due to their potential application in optical and electronic devices. They exist in a wide variety of phases, ranging from the copper-rich Cu_2S (chalcocite) to CuS_2 , passing through intermediate compounds like Cu_{2-x}S (digenite), $\text{Cu}_{1.96}\text{S}$ (djurleite), $\text{Cu}_{1.75}\text{S}$ (anilite) or CuS (covellite). Most of these compounds show a semiconducting behavior, but bulk CuS was reported to be a metallic conductor [1,2] that undergoes a superconducting transition at 1.6 K [1]. It crystallizes into a unique hexagonal structure type (space group $P6_3/mmc$), which can be seen as build from alternating CuS and Cu_2S_2 layers (Fig. 1). Studies in this compound have been made mainly in polycrystalline samples, existing only very few measurements made in natural Covellite single crystals, and there is a strong lack of good quality synthetic single crystals. This compound undergoes a structural phase transition at 55 K, from

hexagonal to orthorhombic, that involves a small slipping of the CuS layers with respect to the Cu_2S_2 ones [3]. This transition can be hardly seen in the magnetic and electrical properties when measured in polycrystalline samples [3], which, together with the large Cu^+-Cu^+ interatomic distances, has lead to the conclusion that the structural transition results from van der Waals interactions of the S–S contacts between the CuS and Cu_2S_2 layers and is not driven by a Fermi surface instability [4].

The high electrical conductivity of CuS has been conducted to studies for application as a cathode material for lithium rechargeable batteries [5], thermoelectric cooling [6], solar electric and electronic devices [7] and catalysis [8]. The development of preparation techniques to obtain films, nano and micrometer size crystallites has been a very actual and active field of research [9–15]. However, very little work has been made in order to obtain good quality millimeter size CuS single crystals. To the best of our knowledge, up to this date only one work has been described in order to grow single crystals of CuS [16], by using sodium polysulfide fluxes. However, the crystals presented large amounts (>400 ppm) of sodium as

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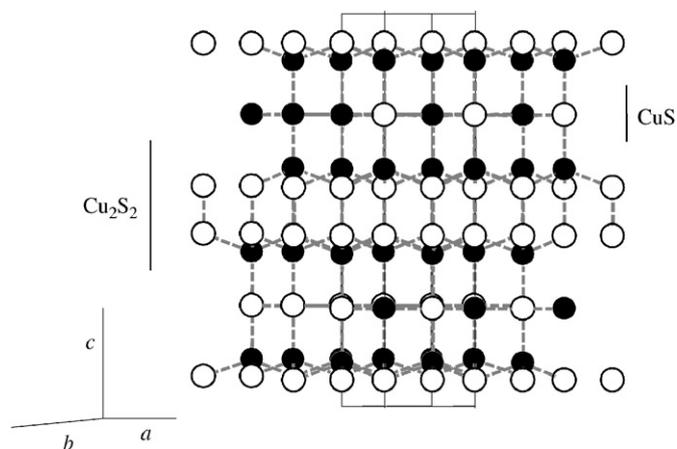


Fig. 1. Projection of the CuS structure on the (100) plane; white circles stand for sulfur atoms and black circles for copper atoms.

impurity. In this paper, we describe the growth and characterization of millimeter size high-quality CuS single crystals by the high-temperature solution growth technique, using the KCl–LiCl eutectic as solvent. The crystals were characterized by X-ray diffraction and their shape, surface morphology and electrical resistivity, this last as a function of the temperature, were also studied in order to determine the growth mechanism and quality of the crystals.

2. Experimental procedure

CuS single crystals were grown by a high-temperature solution growth method, using the KCl–LiCl eutectic as solvent. The starting materials were Cu (Goodfellow, 99.99+%), S (Aldrich, 99.99+%), KCl (Merck, 99.5+%) and LiCl (BDH, 99.5+%). KCl and LiCl were dried at 200 °C under vacuum for 2 h, before being used. The eutectic composition was prepared from a mixture of KCl and LiCl with a 42:58 molar ratio [17], which was heated up to 650 °C inside a quartz ampoule sealed under vacuum. The elemental constituents, with a Cu:S ratio of 1:1.01, were sealed inside a quartz ampoule (10 mm of inner diameter and 100 mm in length) together with the eutectic mixture, under a vacuum atmosphere of 10^{-5} mbar. The proportion between the (Cu+S) mixture and the (KCl–LiCl) eutectic was 1:60. The ampoule was heated up to an average temperature of 480 °C and held at this temperature for 170 h. A temperature gradient of 10 °C was applied between the top (hot junction) and the bottom (cold junction) in order to minimize the S evaporation from the solution. The ampoule was then cooled down to 400 °C at 2 °C/min, remaining at this temperature for 5 h before being removed from the furnace. After cooling down to room temperature the ampoule was broken and the mixture was removed. The eutectic was removed from the CuS crystals by washing the mixture several times with de-ionized water.

The structural characterization of the crystals was performed at room temperature by powder X-ray diffraction on a X'Pert PRO Panalytical diffractometer. The diffraction measurements were made on plate-shaped crystals and top-layer polycrystals were aligned on the surface of a low-noise Si sample holder and using Cu K α radiation, with a 2θ -step size of 0.02° from 10° to 65° and a constant counting time of 5 s per step. The identification of the structure was made by comparing the experimental powder pattern with the CuS-type structure calculated using the program Powder cell [18]; the room temperature lattice c parameter was also refined by using the same software.

The morphology, particle size and microtopographical analysis of the crystal surfaces were made by optical microscopy (Olympus BX51) and a scanning electron microscopy (Jeol JSM-7001F), equipped for energy dispersive X-ray spectroscopy (EDS). Five EDS point analysis were obtained in different parts of the sample. These analyzes were carried out with a spatial resolution of 2.5 μ m at 25 kV.

The quality of the CuS crystals was checked by measuring the electrical resistivity in the 1.4–300 K range, which was performed in a liquid helium cryostat (OXFORD INSTRUMENTS), on $\sim 0.8 \times 0.6 \times 0.01$ mm³ small crystals, by using the four probe method with a 200 μ A electrical current and under a zero applied magnetic field.

3. Results and discussion

After removal from the furnace the ampoule revealed the formation of a dark indigo blue color polycrystalline top layer, consistent with the color of the CuS mineral, covellite. In addition it could be seen the existence of small particles, also with dark indigo blue color, inside the frozen liquid. The polycrystalline top layer and hexagonal plate-shaped CuS crystals could be easily isolated after washing the mixture with water and filtering.

The Cu–S phase diagram is dominated by the Cu_{2–x}S phase, which melts congruently at 1130 ± 2 °C. CuS is a low-temperature phase that decomposes peritectically at 507 ± 2 °C into S-rich liquid and Cu_{2–x}S. Therefore, the CuS synthesis must be done below ~ 500 °C and several methods have already been reported before, in particular to yield polycrystalline or nanostructured samples of this compound [9–15,19,20]. The choice of the KCl–LiCl eutectic as solvent to promote the reaction between Cu and S in order to obtain CuS was quite convenient due to its easy removal by water dissolution and the low melting temperature of the eutectic mixture, (~ 355 °C), well below the CuS decomposition temperature (507 ± 2 °C [21]). Moreover, it was expected a fair solubility of Cu and S at ~ 500 °C by both KCl and LiCl due to the reactivity of the constituent elements [22]. Indeed, the optical observation of the ampoule revealed a total dissolution of both elements in the KCl–LiCl eutectic at 480 °C. A minor

excess of S was considered in the starting composition in order to prevent any small losses of this element by evaporation.

The confirmation of the isolated crystals as CuS was obtained by a comparison of X-ray diffraction pattern of the obtained crystals with the simulation for plate-shaped CuS crystals oriented with the [001] direction perpendicular to the diffraction plane. As shown in Fig. 2, the simulation with $c = 16.3116 \text{ \AA}$ fits well with the powder X-ray diffraction pattern of the product, in fair agreement with reported $c = 16.342(3) \text{ \AA}$ value [3]. No extra reflections, indicating the possible presence of impurity phases, were seen in the diffractogram. EDS analysis of the crystals indicated a Cu:S ratio of 1:1 with no signs of extra elements.

The density difference between the eutectic mixture and the sulfide, together with the temperature gradient in the ampoule, are most probably the reasons for the observed distribution of the synthesized CuS inside the ampoule: as the density of the melt is higher than the density of CuS, there is a promotion for the formation of a CuS layer at the surface of the liquid; however, the existence of a temperature gradient favors the crystallization of CuS in the lower cooled regions, explaining the presence of small isolated CuS crystals inside the liquid. A typical hexagonal plate-shaped single crystal is presented in Fig. 3. The maximum dimension of these single crystals was $1.5 \times 1.5 \times 0.1 \text{ mm}^3$.

The surface micrographs of the crystals are shown in Fig. 4. A layer growth pattern can be observed, and the regular shape of the growth layers indicate that the growth was slow. No evidence of growth spiral patterns could be observed, which points to a non-screw growth mechanism. The existence of flat and smooth layers suggests that the growth was made by the lateral spreading of the layers.

The electrical resistivity ρ of a CuS single-crystalline sample as a function of the temperature is shown in Fig. 5. The resistivity presents a continuous decrease with

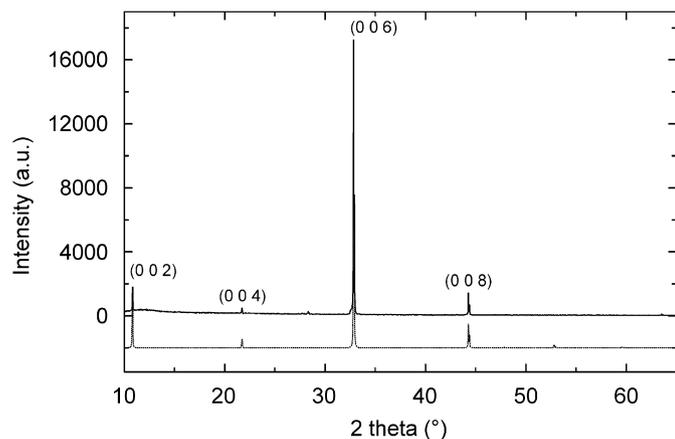


Fig. 2. Experimental powder X-ray diffraction pattern of the plate-shaped crystals and top layer polycrystals, aligned on the surface the sample, and simulation for plate-shaped CuS crystals oriented with the (001) direction perpendicular to the diffraction plane.

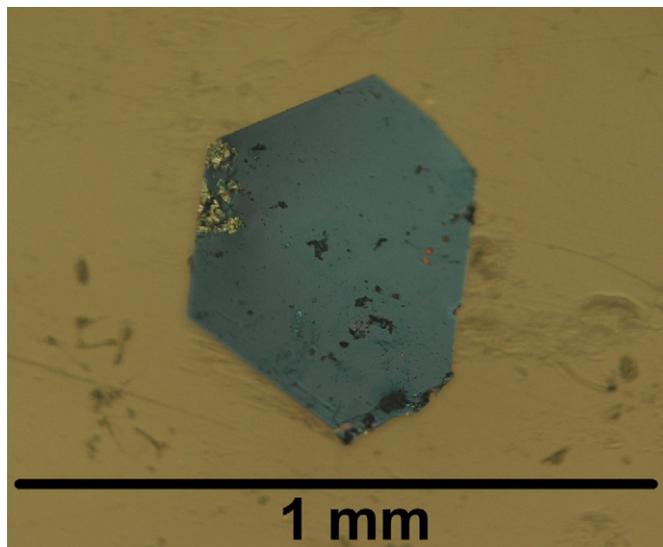


Fig. 3. Example of a CuS single crystal prepared by the high-temperature solution growth technique, using the KCl–LiCl eutectic as solvent.

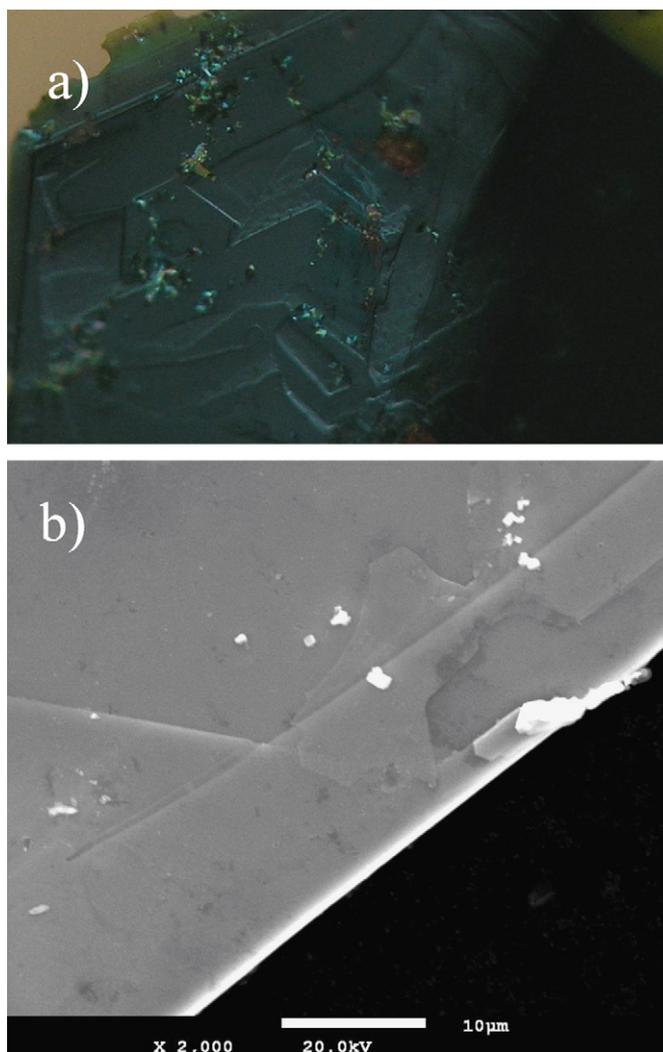


Fig. 4. Optical, (a), and SEM, (b), images of the CuS surface showing a flat and smooth layer growth pattern.

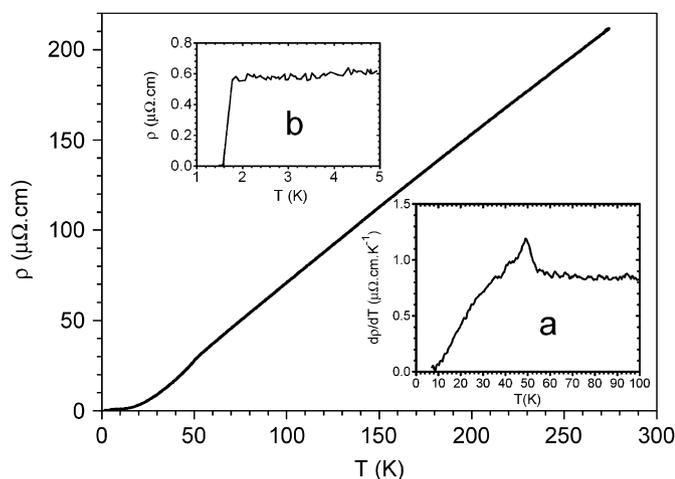


Fig. 5. Electrical resistivity of CuS as a function of temperature; inset (a) shows in detail the derivative of the temperature dependence of resistivity; inset (b) presents the low-temperature region.

decreasing temperature, with resistivity values of ~ 210 and $0.5 \mu\Omega\text{cm}$ at room temperature and 2 K, respectively, indicating a residual resistivity ratio of ~ 400 . The resistivity decrease is linear down to a temperature of ~ 55 K, at which a small anomaly is observed. This anomaly is the fingerprint of the reported structural transition [3] and clearly corresponds to a maximum in $d\rho/dT$ at 49 K (inset a) of Fig. 5, sharper than what was previously published [2]. A very sharp drop in the resistivity is observed below an onset temperature $T_{\text{Con}} \approx 1.8$ K, which corresponds to a transition to the superconducting state, with a critical temperature $T_{\text{C}} \approx 1.7$ K. The resistivity becomes already negligible at 1.55 K and the transition width is about 0.1 K for a 10–90% drop of the resistivity curve (inset b) of Fig. 5. The value of the superconducting temperature and transition width, the clear presence of the anomaly at the structural phase transition and the high residual resistivity ratio all point to a very good quality of the CuS crystals grown in this work.

4. Conclusions

The development of a growth technique for high-quality CuS crystals was investigated. Millimeter size CuS single crystals have been successfully grown by slowly cooling down a solution of Cu and S in the KCl–LiCl eutectic solvent. A competition involving the density difference between the eutectic mixture and the sulfide, and the temperature gradient inside the ampoule, was observed to control the distribution of the synthesized CuS in the liquid phase. The single crystals have a plate hexagonal shape and a dark indigo blue color, in agreement with the color of the CuS mineral covellite. X-ray diffraction measurements and EDS analysis confirmed the crystals as CuS.

Surface microtopographic studies of the as-grown hexagonal single crystals showed the existence of flat and smooth layers, suggesting that the growth was made by the lateral spreading of the layers. No signs of growth spiral patterns could be seen.

The good quality of the crystals was confirmed by electrical resistivity measurements as a function of the temperature, which clearly show an anomaly at $T \sim 55$ K related with the low-temperature structural transition. Furthermore, a high residual resistivity ratio of ~ 400 and a sharp superconducting transition at $T \approx 1.7$ K also point to a very good quality of the CuS crystals grown in this work. These crystals will be further used in a deeper characterization of the CuS compound.

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