

## CuInS<sub>2</sub> grown under elevated pressures; Part 1: Structural and defect characterization

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### Abstract

By using an Argon overpressure large CuInS<sub>2</sub> single crystals could be produced. Upon modification of the temperature gradient over the melt a change of structural features could be induced. Low temperature gradients resulted in the growth of large single crystals, whereas for increased temperature gradients sheet-like material was prepared.

The lamellar material cleaved along the (112) planes as revealed by RHEED and the appearance of Kikuchi lines indicate good crystallinity. Within the limits of x-ray diffraction the material was shown to be single phase CuInS<sub>2</sub>. Photoluminescence data and IR measurements are employed for comparison of the materials with different structural properties. Possible origins for the new lamellar structure will be discussed.

### 1. INTRODUCTION

CuInS<sub>2</sub> has received attention as a possible alternative base material for solar cells[1-15]. The first highly photoactive material in a non-optimum configuration has been reported from our laboratory[3]. Recently a thin film device has been produced exhibiting a 7.3% power conversion efficiency. At room temperature CuInS<sub>2</sub> has the chalcopyrite structure and possesses a band gap of 1.55 eV, which lies near the optimum for homojunction solar cell devices[16].

For applications in high efficiency energy converting systems, such as concentrators, the growth of high quality single crystalline material is mandatory. With a direct energy gap in the optimum range of the theoretical solar conversion efficiency ( $E_g = 1.54$  eV) a minority carrier diffusion length of about 2  $\mu\text{m}$  would be sufficient for effective carrier collection in the relevant spectral range[17, 18].

The performance of CuInS<sub>2</sub> solar cells has lagged behind that of its selenide analog, whose current efficiency has reached 14%. Among the differences in material preparation of the sulfur and selenide chalcopyrite is the significant variation of the overall vapor pressure in the ampoule. The increased pressure due to addition of Ar obviously influences the vapor phase equilibrium constant phenomenologically, it turns out that the increase of the partial pressure of one component (Ar) results in a decrease of the partial pressure of sulphur[19].

## 2. RESULT AND DISCUSSION

### 2.1 Structural Analysis

The gradient freeze technique[20] was used with an Argon overpressure (25 bar at melting point) for the growth of  $\text{CuInS}_2$  from its melt. The experimental details will be published elsewhere[21]. This technique resulted in large  $\text{CuInS}_2$  single crystals of two types of crystals depending on the temperature gradients above the liquid/melt interface. For relatively horizontal temperature gradients single crystals on the order of  $10 \times 10 \times 3 \text{mm}^3$  were obtained. For steeper temperature gradients crystals possessing a lamellar type structure were obtained(Fig. 1). Surprisingly, both types of samples could be easily cleaved, which is not expected for a chalcopyrite structure. The comparison of Debye Scherrer diffraction data with file data shows both materials to be single phase  $\text{CuInS}_2$  within the experimental limitations of the method. The lattice constants inferred from the data are  $a = 5.760 \text{ \AA}$ , and  $c = 11.50 \text{ \AA}$ . Laue diffraction pattern obtained from a cleaved sample show  $[112]$  orientation, an indication that cleavage occurs predominantly along  $(112)$  planes. The natural cleavage planes for  $\text{CuInS}_2$  are  $(110)$  orientated [22, 23]. The quality of the crystals can be seen most readily from x-ray and electron microscopic analyses. The observance of Kikuchi lines, Fig.2, requires near perfection of the crystals, otherwise defects would spread these lines over larger angles. The data confirm the  $[112]$  orientation of the cleavage planes. The occurrence of Kikuchi lines demonstrates quite high crystallinity over extended regions of the sample. The lattice constant determined from the RHEED experiment is  $a=5.76\text{\AA}$  with  $c/a = 2.04$ . Rocking curves were made to determine the relative dislocation density. A FWHM of  $1140''$  is indicative of a structure containing substantial amounts of dislocations, possibly also microcrystallites. The influence of the modification of growth parameters on the structural characteristic has also been investigated.

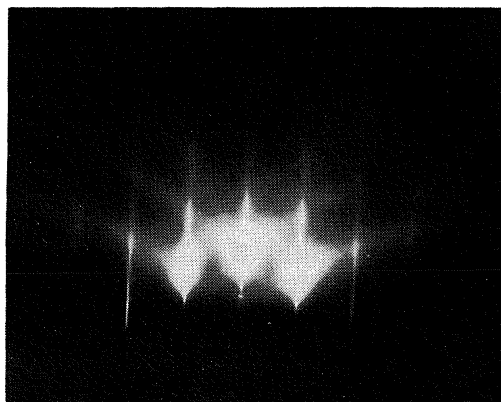
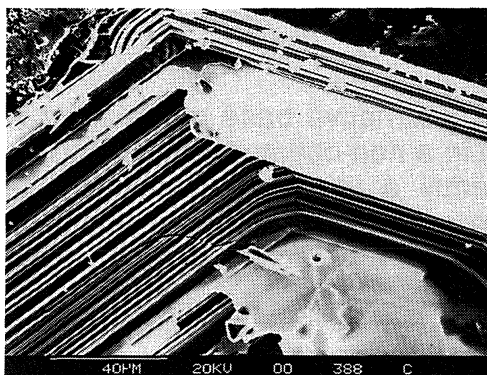


Figure 1: Scanning electron micrograph of the lamellar-type material obtained under elevated argon pressures and large temperature gradients.

Figure 2: RHEED pattern from the  $(112)$  planes.

Although X-ray diffraction and electron microprobe showed the material to be CuInS<sub>2</sub>, within their respective limits, the material exhibited, for instance, a different mechanical behavior compared to the expected one for CuInS<sub>2</sub>. The material could be cleaved and very thin layers could be peeled off with adhesive tape, similar to the procedures known for layered crystals like WSe<sub>2</sub>. An analysis of the (112) planes after cleavage in vacuo by XPS revealed large deviations of the Cu to In ratio from 1[24]. The penetration depth is of the order of ten atomic layers and the fact that the Cu to In ratio is not consistent on both cleaved surfaces means the second phase is probably only a few atomic layers thin, less than the penetration depth. This second phase could have formed during freezing due to the stressed environment brought about by the steep temperature gradient and/or high pressures. The nature of this phase is currently under investigation.

## 2.2 Optical Properties.

Because of the lamellar structure of the material it was possible to cleave the crystals easily. In the MIR for all samples the well known interference fringes occurred caused by multiple reflections between the layers (Fig. 3). As described by Harrick [25] these interferences can be used to determine the thickness of the transmitted layer. Assuming a refractive index of 2.51 for CuInS<sub>2</sub> we calculated that

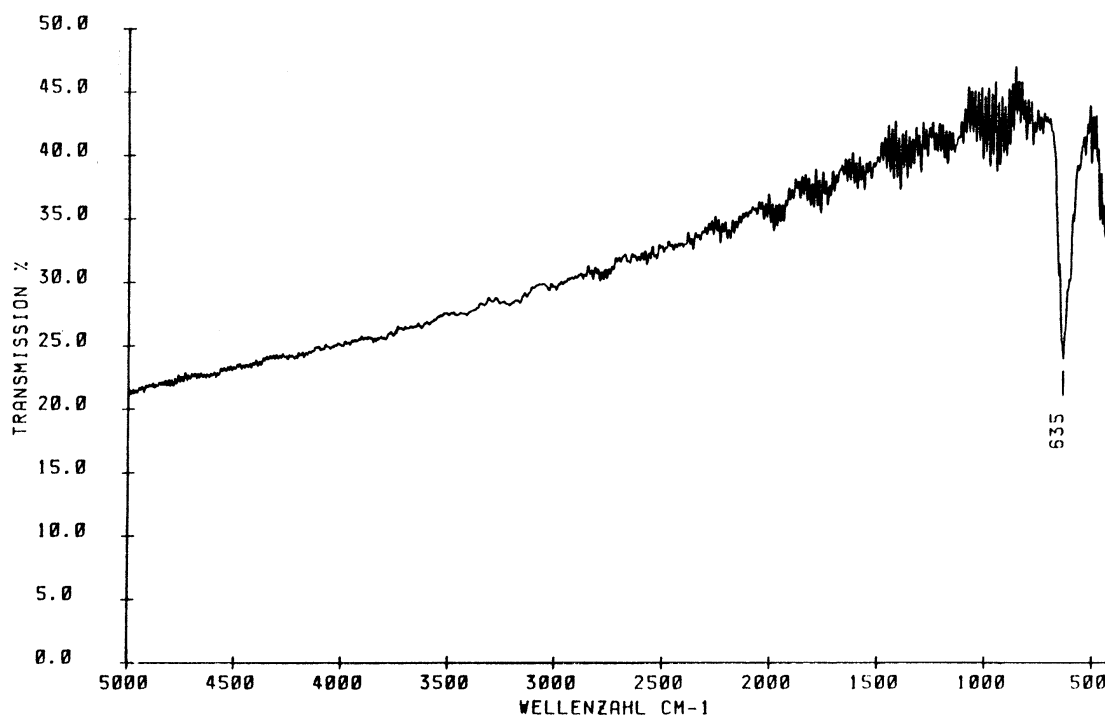


Figure 3: Transmission IR spectrum of the lamellar-type CuInS<sub>2</sub> layer with  $d = 137\mu\text{m}$  (MIR).

the spectrum of figure 1 was taken from a sample with  $d = 137 \mu\text{m}$ . In the FIR layers of 100 to 200  $\mu\text{m}$  thickness are absorbing the whole IR radiation while thinner films with  $d \sim 10 \mu\text{m}$  are transparent (Fig. 4). In reflection the penetration depth of the IR light is estimated between 15  $\mu\text{m}$  (MIR) and 55  $\mu\text{m}$  (FIR), respectively.

Of the 21 optical vibrational modes for  $\text{CuInS}_2$  9 modes are IR-active [26-28]. Since the chalcopyrite lattice is optically anisotropic for the reflection measurements it is necessary to consider the orientation of the sample, the angle of incidence and the polarization of the light. For the electrical vector  $\mathbf{E}$  being perpendicular to the  $\mathbf{c}$ -axis 2 of 3 expected modes have been reported [26-28]. The  $\mathbf{E} \parallel \mathbf{c}$  configuration can not be realized exactly for crystals cleaved along the (112) plane so Koschel et al. [26] extrapolated the spectrum for this orientation resulting in 3 of 6 expected IR-modes. The spectra of Neumann et al. [28] coincide with those of [26] although the orientation of the samples (i.e. cleavage plane) is not mentioned. For clarity in our experiments we did not make any mathematical extrapolations and therefore our spectra for the *normal crystals* show the same spectral features as published by Bodnar et al. [27]. In the spectra of the lamellar-type material (Figs. 4 and 5) the absorption bands are almost masked by strong interferences but nevertheless an additional mode at 217  $\text{cm}^{-1}$  is observed. IR-spectra are available for  $\text{InS}$  [29],  $\beta\text{-In}_2\text{S}_3$  [30],  $\text{In}_6\text{S}_7$  [31],  $\text{CuIn}_5\text{S}_8$  [32], and  $\text{Cu}_3\text{In}_5\text{S}_9$  [33] but for none of them an absorption at 217  $\text{cm}^{-1}$  was reported.

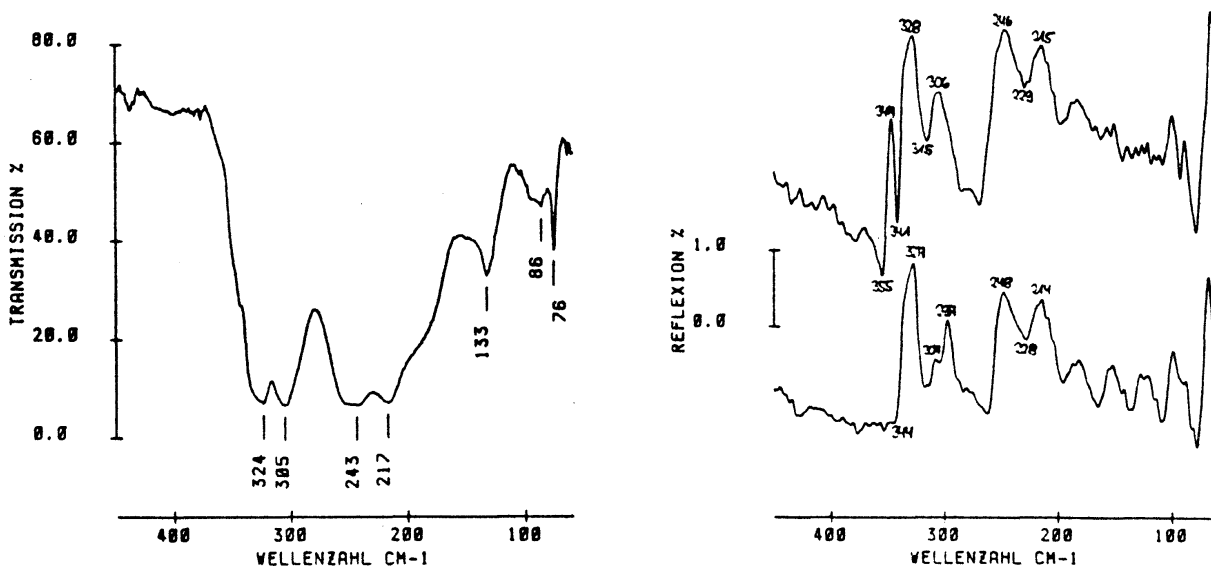


Figure 4: Transmission IR spectrum of a lamellar-type  $\text{CuInS}_2$  layer of about 10  $\mu\text{m}$  thickness (FIR).

Figure 5: IR reflectivity spectra of  $\text{CuInS}_2$  (lamellar-type material): upper curve approximately  $\mathbf{E} \perp \mathbf{c}$ , lower curve approximately  $\mathbf{E} \parallel \mathbf{c}$

The PL spectra of the two sample types investigated are compared in Fig. 6. Fig.6(a) represents single crystal CuInS<sub>2</sub> and exhibits the well known broad band emission at about 1.3 eV [19, 34] and a broadened signal between 1.38 eV and 1.42 eV. The low energy structure has also been found in sub band gap photoresponse measurements [19] and can be attributed to sulfur excess. The energetically higher signal is typical for Cu-rich samples although the shoulder located by 0.04 eV towards lower energy is somewhat less pronounced than in the data presented by Binsma [35, 36].

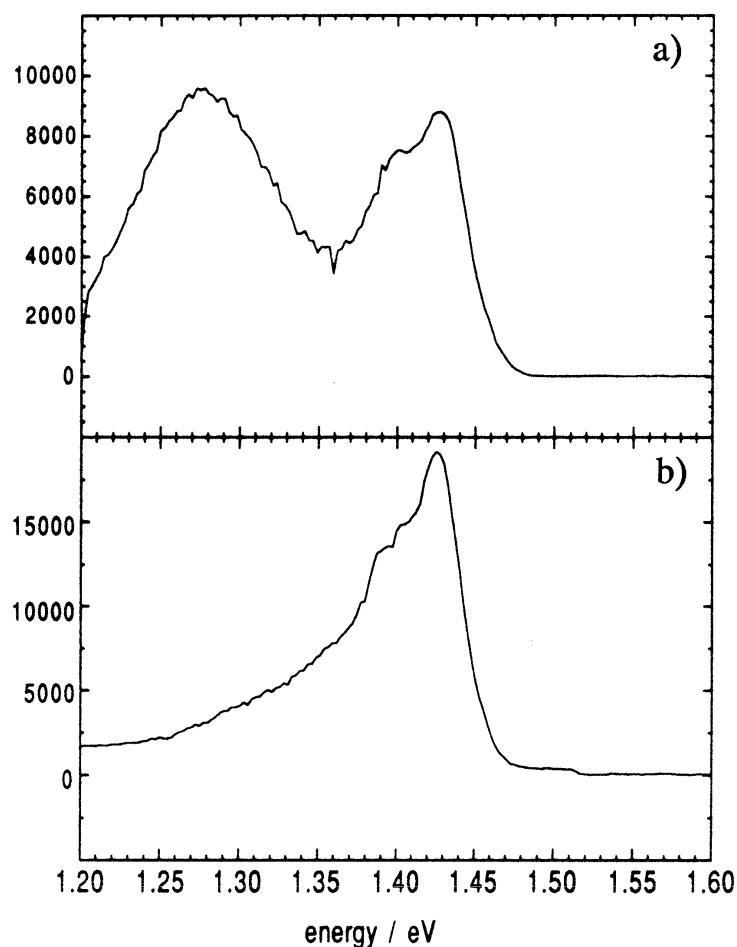
The signal from the lamellar-type material in Fig. 6(b) shows some similarity with the so-called optimized samples of high photoactivity [3] although the features here are more blurred and the peak position corresponds rather to Cu-rich material than to samples with In excess. The missing low energy emission, however, indicates a somewhat increased electronic quality of these samples.

Figure 6:  
Photoluminescence  
spectra at 5K for

(a) "normal"

and

(b) lamellar-type  
CuInS<sub>2</sub> crystals.



### 2.3 The Lamellae structure

The occurrence of layer type material which exhibits a high crystallinity within the layers and surprisingly large minority carrier diffusion lengths as evidenced by

EBIC [38], is unexpected. As the material is grown in a steep temperature gradient where thermodynamic equilibrium conditions are most likely not prevailing, an interpretation based on phase diagrams does not seem justified. Therefore we only can speculate at present on the origin of such structure. It appears that during non-equilibrium growth, a crystalline segment forms. If the growth method induced deviation from stoichiometry exceeds a critical hitherto unknown value, new phases of different composition can be formed. Obviously the new phases allow a comparably easy cleaving of the material as has been found in cleavage experiments under ultra high vacuum conditions. The overall contribution of the interphase amounts to less than 1 % and is difficult to be analyzed by standard X-ray diffraction experiments. The fact that the lamellar growth occurs for many layers indicates that the lattice mismatch between  $\text{CuInS}_2$  and the unknown interphases has to be sufficiently small. The nature of the interphases is intensively investigated by various methods at present.

### 3. CONCLUSIONS

It has been shown that large  $\text{CuInS}_2$  single crystals can be grown using argon overpressure. Two types of crystal morphologies result, one being normal single crystals and the other a lamellar-type structure. Both cleave along the (112) planes. With regards to optical properties, the lamellar-type material exhibits an unaccountable mode at  $217 \text{ cm}^{-1}$  in the IR and multiple reflections arising from the layers reveals a  $10 \mu\text{m}$  layer thickness. Photoluminescence shows the lamellar material to have similar defect characteristics as highly photoactive material previously showing a 10% power conversion efficiency.

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