

# Structural investigations of $\text{CuIn}_3\text{Se}_5$ by TEM

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**Summary:** The structure of the off-stoichiometric In-rich phase  $\text{CuIn}_3\text{Se}_5$  was studied by transmission electron diffraction (TED) and high resolution transmission electron microscopy (HRTEM). The results provide unambiguously a tetragonal structure of this compound. A theoretical model with ordered occupation of vacancies was derived. A detailed comparison between the theoretical model and the experimental findings is given.

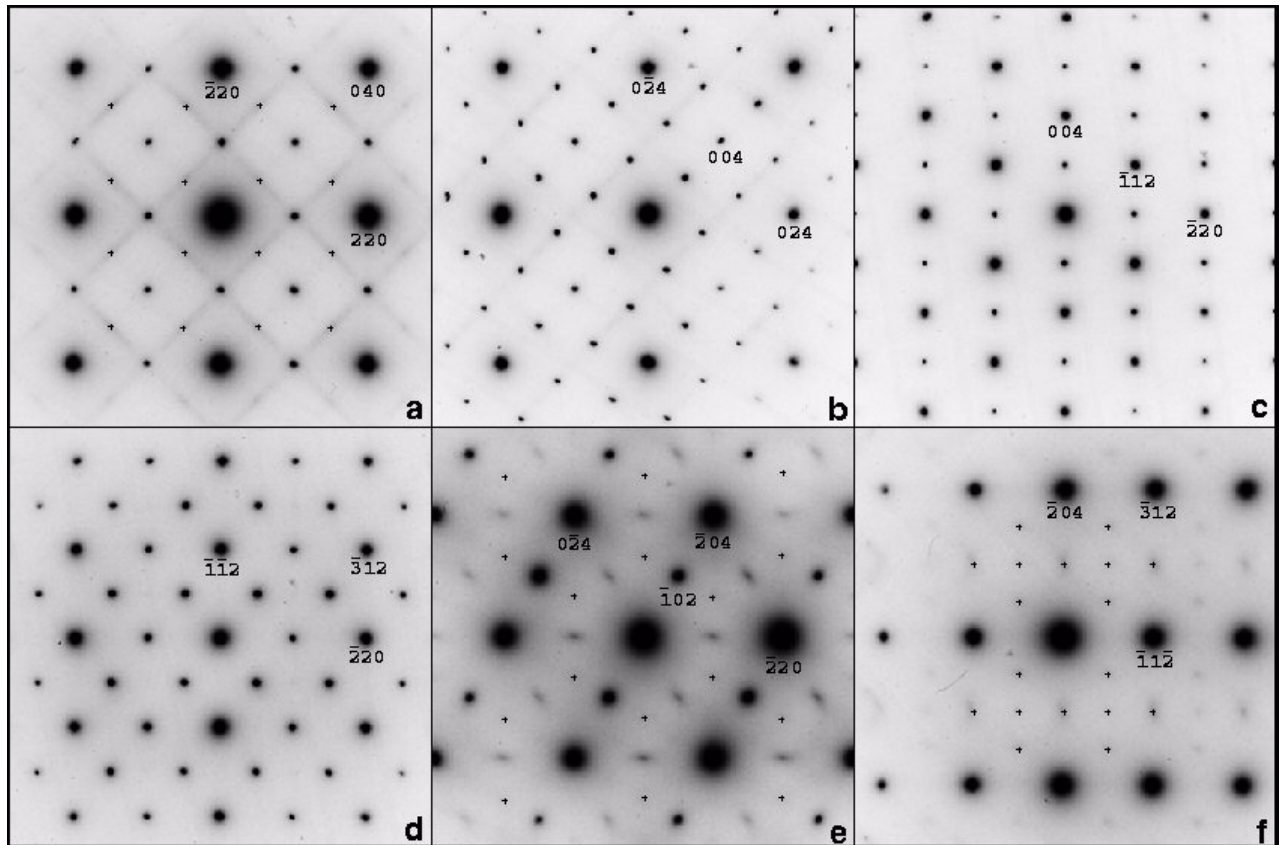
$\text{CuInSe}_2$  and its related off-stoichiometric phases have been extensively studied because of their promising properties for solar energy conversion. The ternary chalcogenide  $\text{CuIn}_3\text{Se}_5$  is often detected as a secondary phase at the surface of In-rich  $\text{CuInSe}_2$  films. Its electronic behaviour has been investigated intensively. However, there are controverse descriptions of the possible crystal structure. In the present work, the structure of off-stoichiometric In-rich  $\text{CuIn}_3\text{Se}_5$  single crystals was studied by TED and HRTEM.

The crystals were grown from the melt by means of the vertical gradient freeze (VGF) method and synthesized directly in a quartz ampoule [1]. TEM specimens were mechanically pre-thinned down to about 20  $\mu\text{m}$  thickness, followed by ion etching. TEM experiments were performed on various PHILIPS microscopes (EM400, CM12, and CM200 FEG).

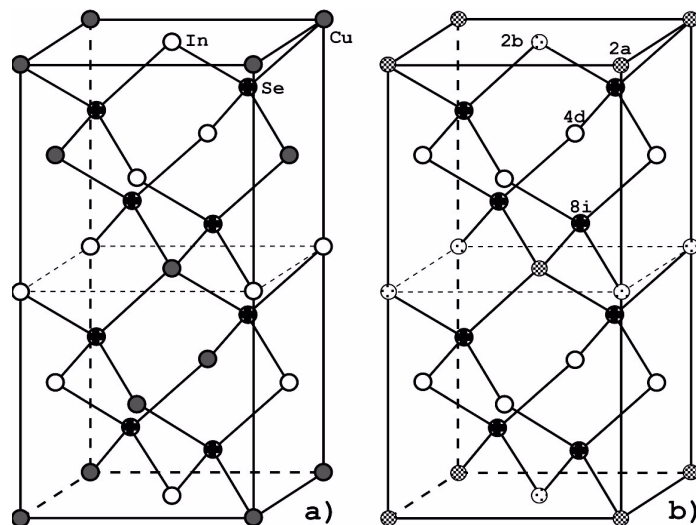
The electron diffraction patterns taken along different zone axes are shown in Figure 1. The comparison of these patterns with corresponding patterns of  $\text{CuInSe}_2$  reveals that the positions of strong reflections, mainly produced by the scattering of the Se sublattice ( $l=4n$  ; even  $[h,k]$  or  $l=4n\pm 2$  ; odd  $[h,k]$ ), remain unchanged. Thus, in both structures there is an identical ordering of anions. The appearance of additional reflections, i.e. the so-called typical off-stoichiometric reflections, shows the difference between the diffraction patterns of  $\text{CuIn}_3\text{Se}_5$  studied and  $\text{CuInSe}_2$ . This is a hint to a different occupation of cations and vacancies in the cation sublattice. A detailed study of these patterns provides that reflections with  $h+k=2n$  and odd  $l$ -indices are vanished while all others are present. Taking into account these results a reciprocal lattice was constructed, which corresponds to a primitive tetragonal lattice belonging to the space group  $P\bar{4}2c$ . In this unit cell the defined cation sites are statistically occupied by metal atoms and vacancies (Figure 2).

Hönle et al. reported on a structure of  $\text{CuIn}_3\text{Se}_5$  with the space group  $P\bar{4}2c$  determined by X-ray powder diffraction using the Guinier method [2]. Contrary to that, Suzuki et al. suggested a structure model for  $\text{CuIn}_3\text{Se}_5$  belonging to the space group  $I\bar{4}2m$  based on electron and X-ray diffraction studies [3]. The experimental results presented here are in good agreement with the structure discussed by Hönle et al. The systematical derivation of the extinction conditions for the structure reported by Hönle et al. also led to the violation of reflections with  $h+k=2n$  and odd  $l$ -indices, consequently. Furthermore, for the  $[110]$  direction the comparison between the experimental and simulated high resolution images on the basis of the structure model reveals the similar contrast patterns (cf. Figure 3, [4]).

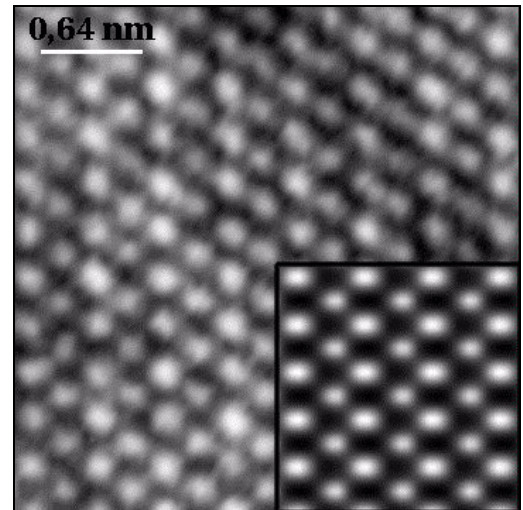
The structure of the In-rich  $\text{CuIn}_3\text{Se}_5$  under investigation is similar to that reported by Hönle et al. In the unit cell the Se atoms occupy the same positions as in the chalcopyrite structure, whereas the cations and vacancies are statistically distributed on the cation sites. The space groups mentioned above belong to different branches of the symmetry tree. This can be derived from the ZnS structure by group theory, where the cation sites are occupied in different manner.



**Figure 1:** Experimental electron diffraction patterns of the  $\text{CuIn}_3\text{Se}_5$  phase in a)  $[001]$ -, b)  $[100]$ -, c)  $[110]$ -, d)  $[111]$ -, e)  $[221]$ - and f)  $[241]$ -directions.



**Figure 2:** Structure models of a)  $\text{CuInSe}_2$  (chalcopyrite) and b)  $\text{CuIn}_3\text{Se}_5$  (identical sublattice of anions and statistical occupation of cations and vacancies on 2a and 2b sites, and full occupation of In on 4d sites).



**Figure 3:** Comparison between experimental and simulated high resolution image in  $[110]$ -direction of the structure model suggested ( $U=200\text{kV}$ ,  $c_s=1,35\text{mm}$ ,  $\alpha=0,5\text{\AA}^{-1}$ ,  $\delta=0,3\text{mrad}$ ).

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## References

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