Experimental determination of orientation relations between high and low pressure phases of copper indium selenide CuInSe$_2$

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CuInSe$_2$ is a ternary I-III-VI$_2$ semiconductor used for high efficiency crystalline solar cells.

At ambient conditions, it crystallizes in the tetragonal chalcopyrite-type (SG: I$4_2$d) which is a superstructure of the cubic zinc-blende type with doubled c lattice parameter. The lattice parameters determined by structural refinement of powder diffraction data are $a = 5.82$ Å and $c = 11.70$ Å with an axial ratio $c/a \approx 2.01$ [1].

At a pressure of approximately 8 GPa CuInSe$_2$ transforms into a phase belonging to the cubic NaCl type with a lattice parameter of $a = 5.35$ Å. The transition is accompanied by a volume decrease of about 10% [2]. The distribution of the cations in the high pressure phase is assumed to be disordered due to its Raman characteristics [3].

The final goal of the experiments is to get information on the transition mechanism. For that purpose the orientation relations between the high and low pressure phases are investigated.

A single crystal of CuInSe$_2$ was loaded into a beryllium-free diamond-anvil cell with an opening angle of 90° [4]. The crystal size was approximately 170*175*50 μm$^3$ and one of its {101} cleavage planes was nearly parallel to the culets. A 4:1 mixture of methanol and ethanol was used as pressure transmitting medium. The indentation of the stainless steel gasket had an initial thickness of 85 mm. The diameter of the sample hole was 275 mm. The pressure was measured using the ruby fluorescence method [5]. After the loading of the cell the pressure was set to 4.9 GPa.

The measurements were performed at beamline BW5 at Hasylab, Hamburg. The beam energy of the synchrotron radiation was $\sim 100$ keV ($\lambda \sim 0.128$ Å). The data were collected with a Perkin Elmer 1621 detector. The measurement was carried out over an $\omega$-range from -42° to 42° with an exposure time of 30 seconds per step.

First, the single crystal was measured with a step width of $\omega=0.5°$. Afterwards the pressure was increased to 8.7 GPa, until the low pressure phase disappeared. The high-pressure phase was measured with a step width of $\omega=0.2°$. The transformation is very sluggish and shows a large hysteresis. The low pressure phase was obtained at 1.4 GPa.

Unfortunately, the programs usually used for texture analysis could not be used, because the intensities of the sample reflections are weak in comparison to those of the diamond anvils and the steel gasket. The reflections have a very narrow width and partly overlap with the reflections of the diamonds and the gasket (Fig. 1). Therefore, a new program was developed transforming the detector coordinate system into the pole figure coordinate system.

The following orientation relations were found: [100]$_{LP}$ $||$ [100]$_{HP}$, [010]$_{LP}$ $||$ [010]$_{HP}$ and [001]$_{LP}$ $||$ [001]$_{HP}$ (Fig. 2).
Figure 1: Diffraction image showing powder rings of the steel gasket, reflection of a diamond anvil and reflections of the high-pressure phase of CuInSe$_2$

Figure 2: Pole figures of the single crystal, high- and low-pressure phases. The white area in the middle of the pole figures represents the non-accessible part of reciprocal space.

References