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2010 J. Phys.: Condens. Matter 22 355801

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High pressure orthorhombic structure of CuInSe₂

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Received 2 May 2010, in final form 13 July 2010

Published 10 August 2010

Online at stacks.iop.org/JPhysCM/22/355801

Abstract

The structural behaviour of CuInSe₂ under high pressure has been studied up to 53 GPa using angle-dispersive x-ray powder diffraction techniques. The previously reported structural phase transition from its ambient pressure tetragonal structure to a high pressure phase with a NaCl-like cubic structure at 7.6 GPa has been confirmed. On further compression, another structural phase transition is observed at 39 GPa. A full structural study of this high pressure phase has been carried out and the high pressure structure has been identified as orthorhombic with space group *Cmcm* and lattice parameters $a = 4.867(8)$ Å, $b = 5.023(8)$ Å and $c = 4.980(3)$ Å at 53.2(2) GPa. This phase transition behaviour is similar to those of analogous binary and ternary semiconductors, where the orthorhombic *Cmcm* structure can also be viewed as a distortion of the cubic NaCl-type structure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The ternary I–III–VI₂ compound semiconductor copper indium diselenide (CuInSe₂) is an analogue of the binary II–VI compound semiconductors. Despite much experimental and theoretical interest in this compound [1–4], very few high pressure studies have been carried out experimentally [5, 6]. This material has attracted much attention because of its variety of potential applications, especially as a candidate material for the fabrication of high-efficiency crystalline solar cells [7]. High pressure crystal structures have played an important role in governing electrical and optical properties of materials, which have a direct effect for photovoltaic applications [6]. In previous high pressure energy-dispersive powder diffraction studies of this material, a structural phase transition from the ambient tetragonal chalcopyrite phase to the face-centred cubic NaCl structure at 7.6 GPa have been reported [5]. This NaCl phase exists up to 29 GPa, the highest pressure obtained in that experiment. However, the peak intensities measured using energy-dispersive techniques were not suitable for Rietveld analysis. Therefore, full structure refinement could not be

performed and the previously reported NaCl-type structure was deduced from the similarity between CuInS₂ and CuInSe₂ for the powder diffraction profiles and volume reduction at the transition pressure [5].

We have embarked on a re-examination of the high pressure structures and transitions in CuInSe₂ using angle-dispersive powder diffraction techniques with the image-plate detector on station 9.1 at the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, UK. We find the same structural phase transition at 7.1 GPa as has been previously reported [5]. On further compression, we have obtained extensive data through another phase transition at 39.2 GPa. This newly discovered phase has now been identified as an orthorhombic distortion of the NaCl structure and is stable up to 53.2 GPa, the maximum pressure reached in this experiment.

2. Experimental details

Single crystals of CuInSe₂ were grown by the horizontal directional freezing method. The growth process was slightly

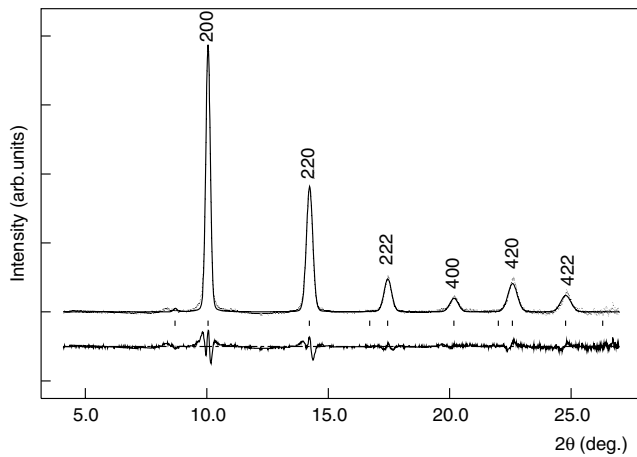


Figure 1. The full Rietveld refinement of the cubic structure at 8.7 GPa. The dotted line shows the observed profile and the solid line shows the calculated profile. The tick marks below the profiles show the calculated peak positions and the difference between the observed and calculated profiles is indicated under the tick marks.

different from that normally employed elsewhere in that the melt was kept initially at 1523 K. The top free surface of the first half of the ingot showed the 112 plane along a length of a few centimetres. Crack free samples of centimetre size can be cut parallel to the free surface. In this particular batch, the p-type single crystal was found to be of very high quality, both with regard to the crystallinity and electrical properties [9]. X-ray powder diffraction showed sharp diffraction peaks of the clean chalcopyrite structure with $a = 5.7783 \text{ \AA}$ and $c = 11.5716 \text{ \AA}$, giving $c/a = 2.0026$. The composition of the crystal, determined by EDS analysis, is 24.4% Cu, 23.7% In and 51.9% Se, which is slightly Cu-rich. The composition is slightly different from the reported [8] preferred composition of 23.5:26.4:50.1 for a large single crystal grown by the vertical Bridgeman method. The first attempt toward a high pressure structural solution was carried out using single-crystal techniques. However, the high quality single-crystal sample was pulverized upon compression. The sample was then finely ground for powder diffraction experiment. Diffraction data were collected on station 9.1 at the SRS using a wavelength of 0.4654 \AA . The two-dimensional powder patterns collected on the image plate were read on a Molecular Dynamics 400A PhosphorImager and then integrated to give conventional one-dimensional diffraction profiles. Details of our experimental setup and pattern integration program have been reported previously [10]. The full conical aperture Diacell DXR-5 and DXR-6 were used, with diamond culet diameters of 200 and $300 \mu\text{m}$ respectively [11]. Samples were loaded with a 4:1 mixture of methanol:ethanol as the pressure-transmitting medium, and the pressure was measured using the ruby-fluorescence technique [12]. All structural parameters, including lattice parameters, were obtained from Rietveld refinement of the full integrated profiles using the program GSAS [13].

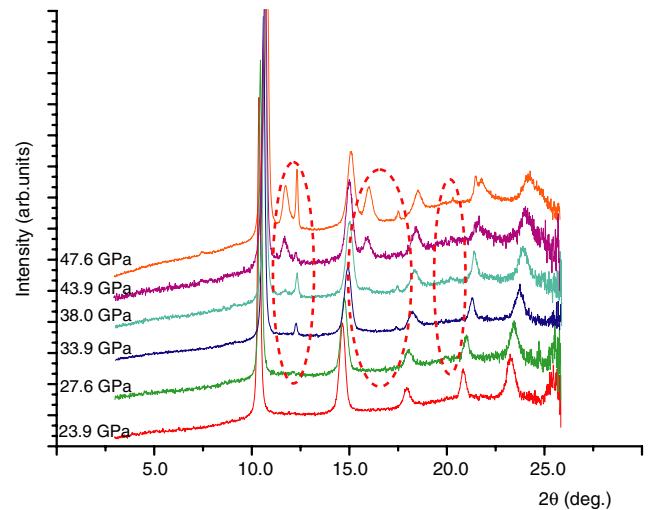


Figure 2. The diffraction patterns collected under pressures between 23.9 and 47.6 GPa. The newly appearing reflections from the orthorhombic phase are indicated by circles.

3. Results and discussion

Ambient temperature–pressure diffraction data were collected to ensure the purity of the powder sample after grinding. The verified samples were then pressurized and put back on the beamline for high pressure measurements. The diffraction pattern collected at ambient pressure showed a very smooth and contaminant free two-dimensional Debye–Scherrer pattern, which can be identified with the tetragonal chalcopyrite $I\bar{4}2d$ structure. On pressure increase the well-known transition from the tetragonal $I\bar{4}2d$ phase to the NaCl phase was observed at 7.1 GPa. However, the diffraction patterns observed for the cubic phase indicate a highly textured powder sample, with substantial intensity variation around the rings. In order to obtain a smooth one-dimensional diffraction profile, a textured sample in the cubic phase was annealed at 453 K for 10 h. The resulting smoother diffraction rings were then used for structure refinement. In order to confirm the structural detail of this high pressure phase, full Rietveld refinement has been performed on powder diffraction profiles collected over the entire pressure range of this phase. The diffraction patterns are contamination free and the full structural detail can be extracted. The first attempt to confirm the reported cubic structure has been carried out. Figure 1 shows the Rietveld refinement of the high pressure cubic structure collected at 8.7 GPa.

The diffraction profiles were collected throughout the first phase transition and beyond 29 GPa, the previous highest pressure reported, and found a new transition at 39 GPa. Figure 2 shows the evolution of the diffraction profile collected at various pressures through the phase transition at the high pressure region. The newly emerging reflections are indicated by circles. From the angle-dispersive patterns, full structural refinement can be performed and the cubic phase has now been confirmed by our experiment. On further compression, we observed a structural phase transition at 39.0 GPa and we have obtained data throughout the phase transition and

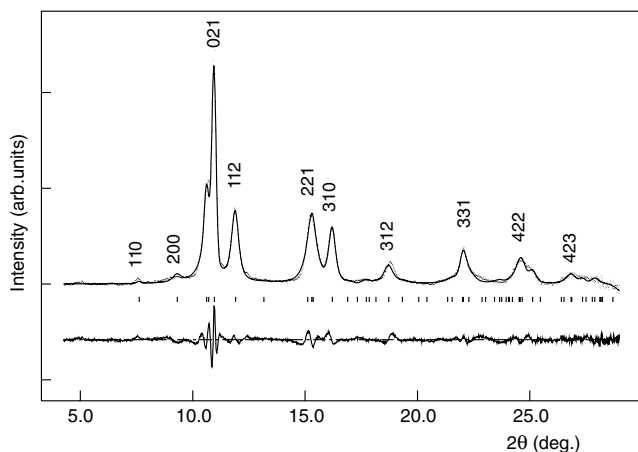


Figure 3. The Rietveld refinement of the diffraction pattern collected at 53.2 GPa. The dotted line shows the observed profile and the solid line shows the calculated profile. The tick marks below the profiles show the calculated peak positions and the difference between the observed and calculated profiles is indicated under the tick marks.

the high pressure phase. The highest pressure reached in this experiment was 53.2 GPa. The structural solution of this newly discovered phase has been carried out. From the integrated diffraction profiles, the high pressure patterns reveal an obvious evolution from the cubic structure. This progression can also be clearly observed from the two-dimensional data recorded on the image plate. Therefore, for the third phase, a structural distortion from the cubic NaCl structure is expected. Based on this information, we have performed the *ab initio* indexing of this high pressure structure.

In the pattern collected at 53.2 GPa, it was possible to measure the positions of ten reflections, including the very weak reflection at 7.5° . Using the indexing program DICVOL [14], an excellent fit to the data was found to be given by an orthorhombic unit cell with lattice parameters of $a = 4.86 \text{ \AA}$, $b = 5.02 \text{ \AA}$ and $c = 4.97 \text{ \AA}$. The pattern could then be indexed, and this revealed reflections with $h+k = \text{odd}$ in all (hkl) and $l = \text{odd}$ in $(h0l)$ to be systematically absent. The lattice symmetry is thus C-face centred. It is worth noting that only the very weak reflection (110) rules out two space groups, $C2cb$ and $Cmca$. The systematic absence conditions given above restrict possible space groups to $Cmcm$, $C2cm$ and $Cmc2_1$.

Full structural refinements have been carried out for all three possible space groups. The $Cmcm$, $C2cm$ and $Cmc2_1$ groups gave identical fit to all of our high pressure data collected at this phase. The highest-symmetry $Cmcm$ has been selected for further full structural analysis. The best fit to the $Cmcm$ structure, with R_{wp} factor = 0.0163, is shown in figure 3 with refined lattice parameters $a = 4.867(8) \text{ \AA}$, $b = 5.023(8) \text{ \AA}$ and $c = 4.980(3) \text{ \AA}$. The required systematic absence corresponds to the 4(c) position of $Cmcm$ ($0, y, 1/4; 0, -y, 3/4; 1/2, 1/2 + y, 1/4; 1/2, 1/2 - y, 3/4$) with $y(\text{Cu-In}) = 0.701(5)$ and $y(\text{Se}) = 0.159(6)$. The structure can be considered as a distortion of the NaCl structure. From figure 4, it can be seen that the $Cmcm$ structure becomes the

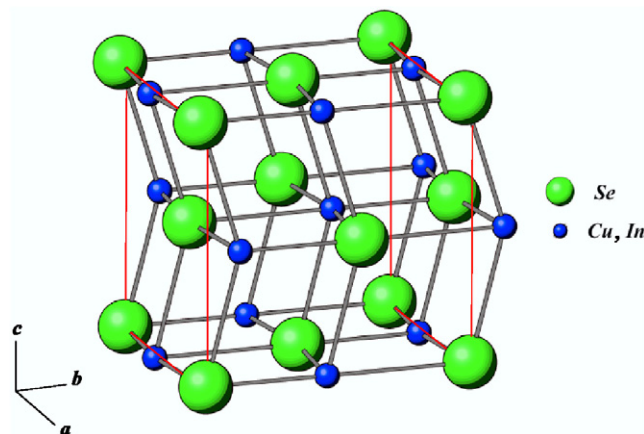


Figure 4. The crystal structure of the high pressure phase III of CuInSe_2 , which can be considered an orthorhombically distorted NaCl structure.

NaCl structure if lattice parameters are all equal, $y = 3/4$ and $1/4$. If $\Delta y \neq 0.5$, then there are displacement of alternate (001) planes in the [010] direction.

The refined lattice parameters of the high pressure cubic structure at 7.4 GPa is $a = 3.7205 \text{ \AA}$. The volume decrease (per formula unit), $\Delta V/V_0$, at the tetragonal–cubic transition is 11%. The unit cell of the orthorhombic $Cmcm$ structure immediately after the transition is $a = 4.897(5) \text{ \AA}$, $b = 5.091(5) \text{ \AA}$ and $c = 5.025(4) \text{ \AA}$, implying a further volume decrease of $\sim 1\%$, and hence the total volume change for the two transitions is 12%.

Under high pressure, the ionicity becomes greater as the atomic separation decreases. The ionicity causes significant changes in the properties of semiconductors [18]. A larger ionicity affects the Coulomb interaction between ions and also the energy of the fundamental gap in the electronic band structure. When the ionicity is large enough, the material becomes a metal. The increasing Coulomb interaction between ions causes an increase in the cohesive energy of the crystal which favours the high-symmetry structure of the increasing coordinate [19]. In the case of CuInSe_2 , its greater ionicity favours the $Cmcm$ structure containing eight-fold coordinated atoms and the rock-salt structure containing six-fold coordinated atoms rather than tetrahedral bonds in the chalcopyrite structure. The recovered phase is of zincblende-type, due to the residual disordered arrangement between the Cu and In atoms in the cubic phase. This was also observed by Tinoco *et al* [5].

4. Conclusions

In conclusion, our studies have concentrated on high pressure structures of the ternary-compound semiconductor, CuInSe_2 . This is the first time that this material has been measured under such a high pressure. A new high pressure structure has been observed and all the tentative structure solutions have been tested. We conclude that there is an orthorhombic structure with space group $Cmcm$, based on a weak (110) reflection. Without this information, only available through a

highly sensitive area detector, the structure solution would not be fully determined. The observed structural phase transition of CuInSe₂ from the NaCl-like to *Cmcm* at the higher pressure is similar to some of their analogue binary III–V and II–VI groups, for example InP, InAs, ZnSe, CdS, CdSe, HgSe and HgTe [15, 16]. A similar transition sequence has also been reported in other ternary compounds with I–III–VI₂ and II–IV–V₂ chalcopyrite structures [17]. A fact that supports this observation is the tetrahedral bonding of these compounds at ambient pressure, for which the cohesive energy favours the high-symmetry structure of increasing coordination to the rock-salt and *Cmcm* structures in binary III–V and II–VI semiconductors and ternaries such as CuInSe₂.

Acknowledgments

We thank Roberts M A of the SRS for assistance in performing the diffraction experiments. We would also like to express our thanks to our colleagues Falconi S and Lundegard L F for their assistance with some of the data collection. This work was supported by the Thai Government Stimulus Package2 (TKK2555), under the Project for Establishment of Comprehensive Centre for Innovative Food Health Products and Agriculture, Research Funds from the Faculty of Science, Chulalongkorn University, the Asahi Glass Foundation and Thailand Research Fund contract number MRG4980031 and DBG5280002. The synchrotron powder diffraction facilities were provided by Daresbury Laboratory. TB acknowledge research grant supported by National Research Council of Thailand.

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