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A comparative study of Cu–Se and In–Se bond length distributions in $CuInSe_2$ with related In-rich compounds

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Abstract

The local atomic structure around the Cu and In atoms of $CuInSe_2$ (CIS), $Cu_2In_4Se_7$ and $CuIn_3Se_5$ was studied using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy at the Cu and In K-edges. Room and low-temperature EXAFS measurements were performed at beamline BM29 at the European Synchrotron Radiation Facility (ESRF) and collected data were analysed using the freely available IFEFFIT package. The analysis assumed a chalcopyrite structure for the $CuInSe_2$ samples while different structures (Cahlcopyrite and P-chalcopyrite) were tried for $Cu_2In_4Se_7$ and $CuIn_3Se_5$. The results show that the In–Se bond length remains constant in the $CuInSe_2$ samples within the experimental uncertainty but slight differences are observed in the Cu–Se bond lengths. These decrease with the Cu content in accordance with previous X-ray diffraction (XRD) results on the same samples. The values obtained for the Debye–Waller factors in the $CuInSe_2$ samples are lower for the In–Se bond compared to Cu–Se, which is consistent with a higher ionicity in the former bond.

Keywords: Cu–In–Se system; Chalcogens; Structural properties; X-ray absorption

1. Introduction

Ternary semiconductor compounds of Cu–III–VI_2 and their solid solutions are promising materials for high-efficiency thin film solar cells. In particular, the quantum efficiencies of $CuInSe_2$ (CIS)-based solar cells are reported to exceed 18% [1–3].

The fundamental properties of $CuInSe_2$ were studied and controlled mainly by the growing of the compound up to date. At the same time, the investigations allowed to establish that alongside with the $CuInSe_2$ phase, there can be formed a lot of ordered-positional phases of the type $CuIn_XSe_Y$, including positional vacancies [4–10]. In particular, ordered defect compounds like $CuIn_3Se_5$ form a very thin layer at the surface of CIS-based absorber material in most thin film solar cells [4]. Therefore, there has recently been an increasing interest in the In-rich ternary phases in the Cu–In–Se system.

The possible structures of these In-rich compounds have been investigated by many authors using X-ray diffraction (XRD). Tseng and Pert [11] and Xiao et al. [12] studied the $CuIn_3Se_5$ structure by transmission electron diffraction. They proposed and qualitatively explained a structural model from an ordered defect chalcopyrite, although the observed intensity data were not used quantitatively. Later, Hanada et al. [13] proposed the $I\bar{4}2m$ spatial group (S.G.) for the same compound while, following the Hönle model [14], our group refined the $CuIn_3Se_5$ structure using the $P\bar{4}2c$ S.G. [15], which seemed more reliable provided that more realistic interatomic distances could be derived from the Rietveld refinement.

The local structure of $CuInSe_2$ and $CuIn_3Se_5$ have been studied by Extended X-ray Absorption Fine Structure

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(EXAFS) spectroscopy by several authors. Chang et al. [16] found that both compounds have a well-defined local structure with the same average Cu–Se bond lengths, and the same happened for the In–Se bonds. The same type of work was performed by Lewandowska et al. [17] in $Cu_2In_4Se_7$ and $CuIn_3Se_5$ but in this case slight differences between the Cu–Se interatomic distances can be observed from their data.

To shed some light on this issue, in this work we have studied the local structure of CIS and two In-rich compounds, $Cu_2In_4Se_7$ and $CuIn_3Se_5$, at two different temperatures, room and low (35 K), using EXAFS measurements at Cu–K and In–K edges.

2. Experimental

Polycrystalline $CuInSe_2$, $Cu_2In_4Se_7$, and $CuIn_3Se_5$ were synthesised from 99.999% pure elements in vacuum-sealed quartz ampoules. Each stoichiometric mixture was gently heated above 1100 °C and slowly cooled down to 600 °C. Powder XRD and Energy Dispersive X-ray Analysis (EDAX) were used to verify the existence of single phase and to check the atomic composition in all samples respectively. Details about the sample preparation, sample labelling, composition, and structural properties can be found elsewhere [15,18,19].

The EXAFS specimens were prepared starting from the powdered samples and the amount of material was calculated to optimise the expected signal to noise ratio. The powder was diluted with BN in acetone and the solution was homogenised with ultrasounds. A ‘millipore’ filter was used to remove the acetone and the mixture was then dried in an oven at 65 °C. Finally, different pellets were sintherised in a press corresponding to several $CuInSe_2$ samples, named A1, A3, A4/B5, B4, B3, B2, and B1; one $Cu_2In_4Se_7$ sample; and one $CuIn_3Se_5$ sample.

The EXAFS measurements were performed at beamline BM29 at the European Synchrotron Radiation Facility (ESRF; Grenoble, France), using a fixed-exit Si(311) double crystal monochromator at Cu–K (8979 eV) and In–K (27940 eV) absorption edges. The energy resolution $\Delta E/E$ was estimated to be 6×10^{-5} and 7×10^{-5} at Cu and In–K edges, respectively. Two datasets were collected for each pellet in transmission mode using ionisation chambers as detectors and the average was considered for the data analysis. In addition, EXAFS measurements at In–K edge were performed at both room and low (35 K) temperature for few $CuInSe_2$ samples and the $CuIn_3Se_5$ one using a closed-cycle helium cryostat.

The different datasets were analysed using the freely available IFEFFIT package [20] for XAFS analysis, assuming a chalcopyrite structure for the $CuInSe_2$ samples and trying both chalcopyrite and P-chalcopyrite structures for the $Cu_2In_4Se_7$ and $CuIn_3Se_5$ ones.

3. Results

3.1. Cu environment

The local structure at the Cu-K edge at room temperature was studied in two CIS samples with different Cu contents determined by Rietveld refinement of powder XRD data [18], A1 and B3 with Cu

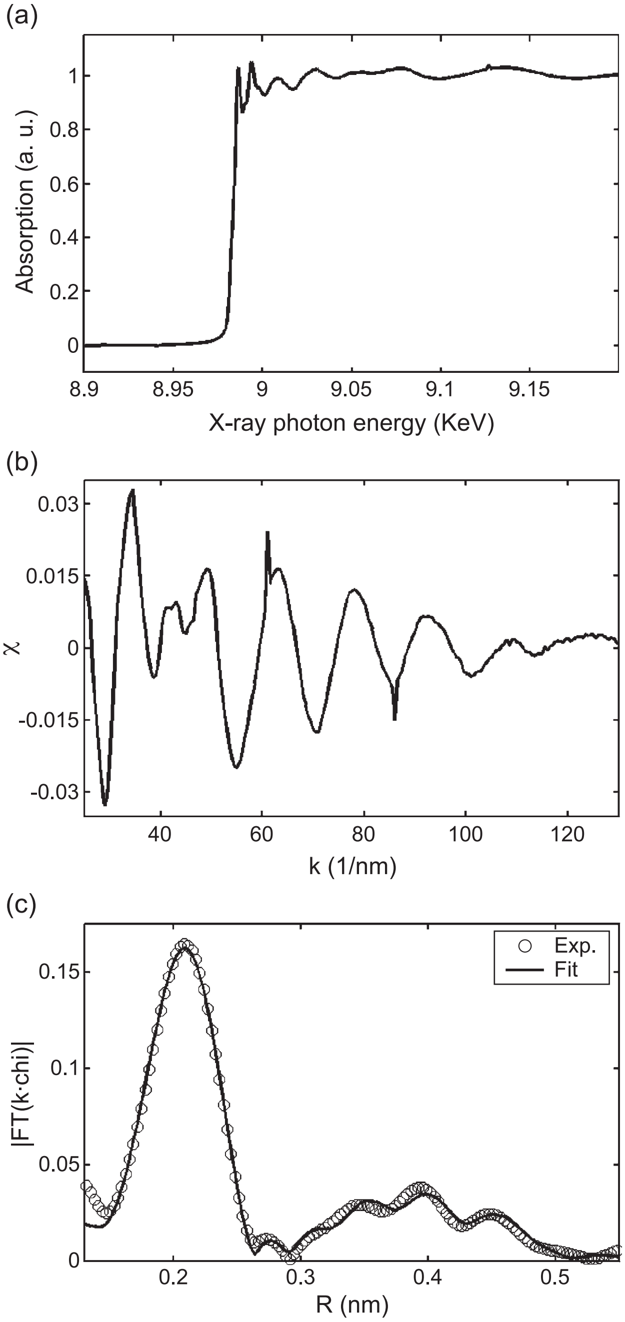

Fig. 1. Cu-K edge data for the A1 ($CuInSe_2$) sample at room temperature (N(Cu)=0.964). (a) Normalised absorption spectrum; (b) EXAFS function, $\chi(k)$; (c) Experimental (○) and fitted (—) Fourier transform in the r-space of the k-weighted $\chi(k)$ function.