

The crystal structure of kesterite type compounds: A neutron and X-ray diffraction study

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ABSTRACT

The atomic structure of the potential photovoltaic materials $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) is discussed on the basis of a structural analysis of neutron powder diffraction data refined by the Rietveld analysis. Both compounds were found to crystallize in the kesterite type structure, but with a disorder within the Cu–Zn layers at $z=1/4$ and $3/4$. The latter causes Cu_{Zn} and Zn_{Cu} anti-site defects, whose concentration depends on the sample growth conditions.

The temperature dependent structural phase transition in CZTS was studied by in-situ high temperature diffraction experiments using high energy synchrotron X-rays. The transition from the tetragonal kesterite to the cubic sphalerite type structure is discussed by means of the interplay of increasing and decreasing cation–anion–cation bond angles in the coordination tetrahedra, reflected by the shift of the anion atomic coordinates to more ideal (x and y) or non-ideal (z) values. This striking behavior may be connected with frustrations that occur due to the triangular geometry of the coordination tetrahedra.

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1. Introduction

Amongst the most promising material options for thin film solar cells are compound semiconductors. Chalcopyrite-based thin film solar cells, using $\text{Cu}(\text{In,Ga})\text{Se}_2$ as absorber, show the highest efficiencies in the laboratory (20.1% [1]) as well as in module production. However, there is a concern over the long term availability of indium, a major constituent of chalcopyrite absorbers. Indium is extremely scarce, which means that the price will continue to rise as it has almost continuously done during the last five years. In order to secure the long term development of compound semiconductor-based thin film solar cells, the search for the replacement of indium is advisable.

As some of the chalcopyrite type absorber materials are well known minerals (Roquesite— CuInS_2 , Gallite— CuGaS_2), there is a variety of stand-by chalcogenide minerals that can be used as reservoirs for the search of new, In-free materials suitable for solar cell absorbers. Recently it has come to light that the mineral kesterite ($\text{Cu}_2\text{ZnSnS}_4$) and also the selenium counterpart $\text{Cu}_2\text{ZnSnSe}_4$ might be suitable to replace the indium-containing absorber layer in thin film solar cells. These direct band gap p-type semiconductors contain only abundant and non-toxic elements. Initial attempts to fabricate photovoltaic devices with $\text{Cu}_2\text{ZnSnS}_4$ or $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin films led to promising results, with the AM 1.5 efficiencies of up to 6.7% [2] and 9.66% [3], respectively.

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2. Crystal structure of $\text{A}_2\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{X}_4^{\text{VI}}$ compounds

The mineral kesterite belongs to the $\text{A}_2\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{X}_4^{\text{VI}}$ compound family (with $\text{A}=\text{Cu}$, $\text{B}=\text{Zn}$, Fe , $\text{C}=\text{Sn}$ and $\text{X}=\text{S}$, Se). Natural kesterite often contains iron ($\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$) but the iron content varies with the locality.

For $\text{A}_2\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{X}_4^{\text{VI}}$ compounds two main tetragonal structure types are known from literature: the kesterite type structure and the stannite type structure [4]. As for the chalcopyrite type compounds, the mineral, where the structure type was determined first, gives the name of the structure. Both structures, the kesterite type and the stannite type, consist of a *ccp* array of anions, with cations occupying one half of the tetrahedral voids. Thus the structures are closely related, but assigned to different space groups due to different distributions of the cations A^+ , B^{2+} and C^{4+} (see Fig. 1). The kesterite type structure is characterized by alternating cation layers of CuSn , CuZn , CuSn and CuZn at $z=0$, $1/4$, $1/2$ and $3/4$, respectively. Thus one copper occupies the $2a$ (0,0,0) position with zinc and the remaining copper ordered at $2c$ (0,1/2,1/4) and $2d$ (0,1/2,3/4) resulting in the space group $I\bar{4}$. On the other hand, in the stannite type structure ZnSn layers alternate with Cu_2 layers. The structure is consistent with the symmetry of the space group $I\bar{4}2m$, with the divalent cation located at the origin ($2a$) and the monovalent cation at the $4d$ position (0,1/2,1/4). Sn is located at the $2b$ site (0,0,1/2) in both structures. The anion lies on the (1 1 0) mirror plane at $8i$ (x,x,z) for the stannite type and $8g$ (x,y,z) for the kesterite type structure.

Additionally tetragonal structural modifications of the kesterite type structure may be considered [5], which belong to the

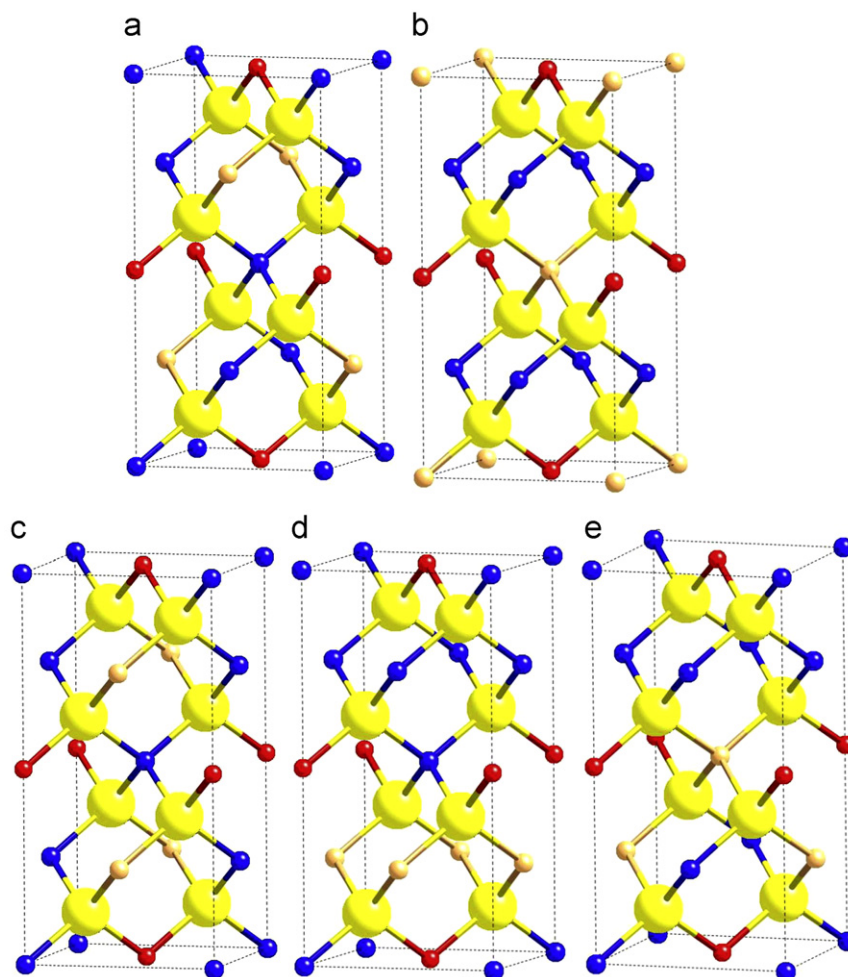


Fig. 1. Unit cell representations of the kesterite type structure (a) and stannite type structure (b); as well as for a cation distribution according to the space groups $P\bar{4}2c$, $P\bar{4}2_1m$ and $P2$. (c)–(e) The main difference is the Cu/Zn distribution (Cu—blue, Zn—orange, Sn—red). Big spheres represent the anions. Atomic sphere radii are chosen arbitrarily. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

space groups $P\bar{4}2c$, $P\bar{4}2_1c$ and $P2$. The modifications are restricted to the exchange of two ions in the cation sublattice. For the first (s.g. $P\bar{4}2c$) Cu and Zn atoms in the layer $z=1/4$ are exchanged. In the second modification (s.g. $P\bar{4}2_1m$) Cu and Zn atoms are exchanged between two layers to yield complete Zn and Cu layers at $z=1/4$ and $3/4$. The last one (s.g. $P2$) a Cu atom at $z=1/2$ is exchanged with the Zn atom at $z=3/4$. This recovers the stannite type structure at the layers $z=1/2$ and $3/4$, but maintains the kesterite type structure in the other two layers.

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) crystallizes in the kesterite type structure. Hall et al. [4] described an ordered distribution of the cations, whereas Schorr et al. [6] observed the existence of a Cu/Zn disorder on the structural sites $2c$ and $2d$. The latter structural investigations are based on neutron powder diffraction experiments. First-principles calculations for the potential photovoltaic material CZTS [5] predict the kesterite type structure with $I\bar{4}$ symmetry being the most stable one, possibly along with cation disorder within the Cu–Zn layer.

A disordered distribution of the cations may cause point defects (vacancies and anti-site defects) and hence influences the electronic properties of the material. For chalcopyrite type absorber materials a number of successful studies, especially for CuInSe_2 , have been made by absorption and photoluminescence techniques as well as deep level transient spectroscopy (DLTS) [7–9] to characterize the electronic defect levels of intrinsic point defects. Thus it can be expected that the cation distribution, especially the

Cu/Zn disorder that may cause vacancies and anti-site defects, plays a crucial role also for the kesterite type compounds.

According to literature $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) crystallizes in the stannite type structure [10], with Zn^{2+} localized on the $2a$ (0,0,0) and Cu^+ on the $4d$ position (0,1/2,1/4). But it was proposed by first principle calculations [11] that $A_2B^{II}C^{IV}X_4^{VI}$ compounds are more stable in the kesterite type structure, whereas the assumed stannite structure reported in the literature is most likely due to partial disorder in the A–B (0 0 1) layer of the kesterite structure. Hence the comparison of experimental and calculated crystal structures of $A_2B^{II}C^{IV}X_4^{VI}$ quaternary chalcogenides [11] show that there may be a long-standing misunderstanding in the crystal structure determination. Nevertheless this becomes important for the accurate characterization of the chemical and physical properties and hence their application in future optoelectronic devices.

3. Neutron diffraction investigation of $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$

The cations Cu^+ and Zn^{2+} have the identical number of electrons (28). Since the atomic scattering form factors f are proportional to the atomic number Z , the positions of the unit cell atoms of similar atomic number are not easy to be determined. Hence these cations named above are not distinguishable in the atomic structure by conventional X-ray diffraction. The problem

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