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In-situ investigation of the structural phase transition in kesterite

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A polycrystalline Cu_2ZnSnS_4 sample (kesterite) was investigated by in-situ high temperature diffraction using synchrotron X-rays, revealing for the first time a structural phase transition from the tetragonal kesterite type structure (space group $I\bar{4}2m$) to the cubic sphalerite type structure (space group $F\bar{4}3m$). Within 866–883 °C a phase transition region occurs, were a tetragonal phase and a cubic phase coexists. Outside the phase transition region, the lattice parameter of the tetragonal phase increase nearly linearly with increasing temperature, whereas the lattice parameter of the cubic phase show first a negative thermal expansion changing at ~930 °C to a further linear increase of a_{cub}. A cation anti-site occupancy can only be observed within the phase transition region. On the other hand, the anion position parameters x and z change, which starts at ~150 °C and lasts up to the phase transition region. Both atomic position parameters reach nearly the ideal value of 1/4, indicating the anion in the middle of the cation tetrahedra. Thus the structural phase transition in Cu_2ZnSnS_4 from the tetragonal kesterite type to the cubic sphalerite type structure is characterized much more by a displacive behaviour of the anion substructure then by an anti-site occupancy of the cation substructure. Because the space group $I\bar{4}2m$ is not a subgroup of $I\bar{4}2d$ and a group-subgroup relation is mandatory for displacive phase transitions, the non-existence of a $I\bar{4}2m \rightarrow I\bar{4}2d$ transition seems plausible.

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1 Introduction Kesterite (Cu_2ZnSnS_4) is not only a sulphide mineral, it is also a semiconductor compound suitable for applications in thin film photovoltaics. Highly efficient thin film solar cells based on ternary or quaternary compound semiconductors such as $Cu(In,Ga)Se_2$ as absorber material (current record efficiency of 19.9% [1]). Since the availability of indium is an object of concern regarding large scale solar cell production, its replacement with Zn and Sn is beneficial in this sense. The alternative compound Cu_2ZnSnS_4 (kesterite) shows promising characteristic optical properties: a band gap energy of about 1.5 eV and a large absorption coefficient in the order of $10^4\ cm^{-1}$ [2]. Thin film solar cells with an efficiency of $\eta = 6.7\%$ were reported in [3].

1.1 The structure of kesterite The kesterite type structure can be described as a *ccp* array of sulphur anions, with cations occupying one half of the tetrahedral voids. As first reported in [4] kesterite adopts the space group $I\bar{4}$. Concerning the ordering of the cations Cu^+ and Zn^{2+} literature describes a complete order [4] with Cu occupying the 2a Wyckoff position (0, 0, 0) as well as Zn and the remaining Cu order at the 2d (1/2, 0, 1/4) and 2c (0, 1/2, 1/4) Wyckoff position. Based on Rietveld analysis of neutron powder diffraction data, a complete disorder [5] or a partial order of Cu^+ and Zn^{2+} was reported [6]. In the complete disordered case the structure can be described using the space group $I\bar{4}2m$ with Cu^+ and Zn^{2+}occupying the 4d (1/2, 0, 1/4) Wyckoff position randomly. In the partial ordered case the structure was described using the space group $I\bar{4}$, the 2c Wyckoff position is occupied by $(0.7Cu^+ + 0.3Zn^{2+})$ and the 2d position by $(0.3Cu^+ + 0.7Zn^{2+})$ respectively. On the other hand, Sn is always located at the 2b (1/2, 1/2, 0) Wyckoff position. Which type of cation ordering is present in Cu_2ZnSnS_4 depends strongly on the sample growth conditions. The sulfur anion adopts a (x, x, z) position (s.g. $I\bar{4}2m$) or a (x, y, z) position (s.g. $I\bar{4}$) respectively.

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Kesterite belongs to the adamantines, a family of compounds their structures are based on the diamond type structure [7]. Other binary and ternary members of the adamantine family, like sphalerite (ZnS) or the chalcopyrites $CuInS_2$ and $CuInSe_2$, show temperature dependent structural phase transitions [8, 9], the latter from the tetragonal chalcopyrite type structure to the cubic sphalerite type structure. About temperature dependent structural phase transitions in Cu_2ZnSnS_4 nothing is known from literature.

In this work we present a detailed study of the structural phase transition in Cu_2ZnSnS_4 done by in-situ high temperature synchrotron radiation X-ray diffraction.

2 Experimental The Cu_2ZnSnS_4 sample used in these investigations was the same as in the neutron diffraction experiments [6], thus the cation distribution is well known. As described elsewhere [5] the sample synthesis is based on the solid state reaction technique of the pure elements in sealed evacuated silica tubes. Initially the ampoules were heated to 250 °C, 450 °C and finally to 750 °C, the temperature steps should boost the reaction of sulphur with the metals to avoid an explosion of the ampoules at higher temperatures due to the high sulphur vapour pressure. Afterwards the samples were homogenised by grinding in an agate mortar and pressed to pellets which were again annealed at 750 °C in sealed evacuated silica tubes. A further homogenisation and annealing at 750 °C the sample was cooled down to room temperature with a rate of 1 K/h.

For the synchrotron experiment the sample was encapsulated in a silica tube with ~4 mm diameter to avoid evaporation during heating. Powder diffraction experiments were performed at the High Energy beamline, ID15B, at the E.S.R.F. synchrotron radiation facility in Grenoble, France. The experimental set up was composed of a high energy monochromatic beam (88.95 keV energy), 300 × 300 μm size, a ceramic oven with two small holes at the beam height (incident and scattered beam apertures) and an on-line 2 D detector consisting of a MAR345 image plate. Sequences of 2 dimensional diffraction pattern were measured during heating the sample with a rate of 300 K/h (up to 825 °C) followed by a slower heating (38 K/h) up to the final temperature of 985 °C. The latter rate was set correspondingly to detect an image every centigrade degree (10 sec measurement + readout the 2-D detector).

An Aluminium powder reference sample was used to calibrate the beam energy ($\lambda = 0.1403676$ Å) and the sample detector distance. The 1D diffractograms were obtained by radial integration of the 2D images.

The lattice parameter, anion position, isotropic temperature factors and cation site occupancies were determined by Rietveld analysis [10] of the data using the FullProf program [11]. The modified kesterite type structure [5] (space group $I\bar{4}2m$, 2a: Cu; 4d: Cu + Zn; 2b: Sn; 8i (x, x, z): S) was used as starting model in the refinements below the phase transition temperature. Because Cu^+ and Zn^{2+} are isoelectronic it is not possible to distinguish them by X-rays due to nearly similar atomic scattering factors of the both cations (cf. [5]). Thus the structure model were Cu and Zn share the same Wyckoff position was applied. Above the phase transition temperature the sphalerite type structure (space group $F\bar{4}3m$) with Cu, Zn and Sn are disordered at the cation position 4a (0.5Cu + 0.25Zn + 0.25Sn) was applicable.

Table 1 Structure models used in the Rietveld analysis.

space group	cation positions	anion position
$I\bar{4}2m$	2a (0, 0, 0): Cu 4d (1/2, 0, 1/4): Cu + Zn 2b (1/2, 1/2, 0): Sn	S at (x, x, z)
$F\bar{4}3m$	4a (0, 0, 0): 0.5Cu + 0.25Zn + 0.25Sn	S at (1/4, 1/4, 1/4)

3 Results From a visual inspection of the 1D diffractograms the temperature range of the structural phase transition could be determined. The typical Bragg peaks of the tetragonal kesterite type structure like 002, 101, 110, 103 and others vanish at ~865 °C. Figure 1 shows a sequence of 1D diffractograms representing the solid–solid transition from the kesterite type structure to the sphalerite type structure in the temperature range 870–895 °C.

From room temperature up to 865 °C the data could be refined by Rietveld analysis using the modified kesterite type structure as structural model. R_{Bragg} values between 0.028 and 0.024 were obtained. The sphalerite type structure was applicable as model in the refinement in the temperature range 884–985 °C, obtaining R_{Bragg} values between 0.023 and 0.014. In the temperature range in between, 866–883 °C, a successful refinement was only possible assuming the existence of two phases, one with tetragonal and one with cubic structure. To support the

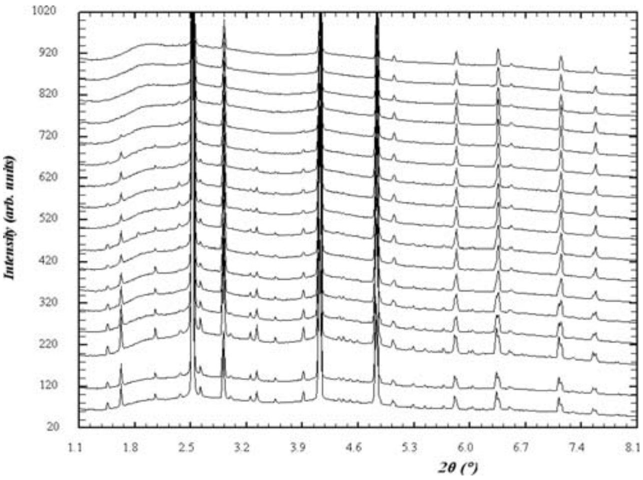

Figure 1 Temperature dependent diffraction data of kesterite (870–886 °C, from down to up). For better visibility the diffractograms are shifted by a constant amount in y-direction. The gap between 871 °C and 872 °C arises from a beam injection at the synchrotron.

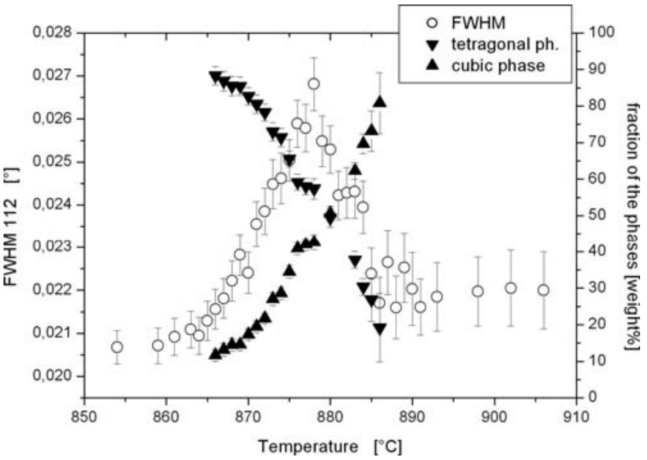

Figure 2 Line width (FWHM) of the 112 Bragg peak (open symbols) and weight fraction (closed symbols) of the tetragonal and cubic phase as determined by Rietveld analysis.

existence of the two phases, a detailed line width analysis of the Bragg reflection at $2\theta \sim 2.5°$ was performed (see Fig. 2). Although the 112 peak of the tetragonal phase and the 111 peak of the cubic phase are not visible as two separated reflections, the peak broadening shows clearly the occurrence of two phases. Moreover a quantitative analysis was possible by Rietveld refinement using two phases (see Fig. 2).

The lattice parameters a_{tetr} and c of the tetragonal phase determined by Rietveld analysis increase with increasing temperature, but with slight deviations from a linear dependence (see Fig. 3). The kink for the parameter c at about 240 °C seems remarkable. At the same temperature the occupancy of the cation 4d position shows a small kink, whereas the occupancy of the cation positions 2a and 2b remain constant. The lattice parameter a_{cub} of the cubic phase first decreases strongly with increasing temperature and shows a negative thermal expansion behaviour. It starts to increase linearly at ~930 °C.

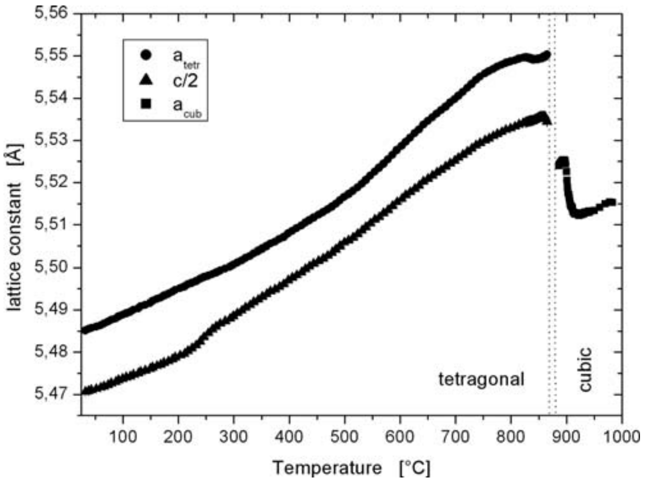

Figure 3 Lattice parameter in dependence on temperature. The phase transition region is marked by the two dotted lines.

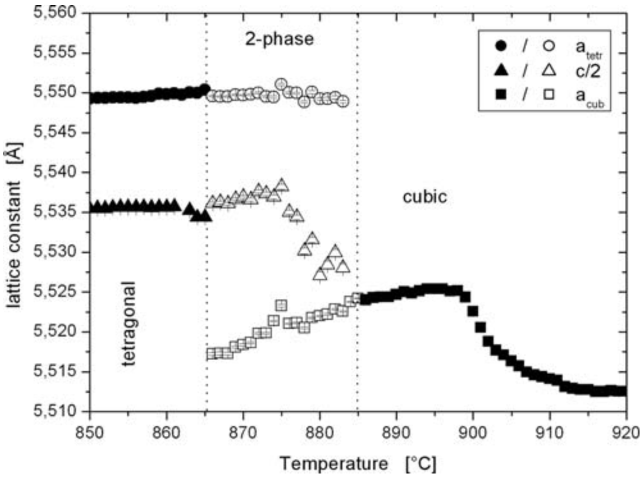

Figure 4 Lattice parameter in dependence on temperature within the 2-phase region. For better visibility the values $c/2$ are shown.

Within the temperature region, where two phases coexist, the tetragonal and cubic lattice parameter show different behaviour with temperature (Fig. 4). Whereas a_{tetr} remains constant and a_{cub} increase, the parameter c increases slightly but starts to decrease nearly in the middle of the phase transition region reaching the value of $c/2 \approx a_{\mathrm{cub}}$. On the other hand there is a large difference between a_{tetr} and a_{cub} at the high temperature end of the phase transition region.

The driving force of the structural phase transition in the chalcopyrite type compound $\mathrm{CuInS_2}$, which is an order-disorder transition, is the Cu–In anti-site occupancy [9]. Because the phase transition in kesterite is also a crossover from a (nearly) ordered cation distribution to a complete disorder (see Table 1), a similar driving force as in the chalcopyrites could be assumed. Examine carefully the cation site occupancy parameters determined by Rietveld analysis, a slight decrease with increasing temperature can be obtained for the Sn site, but only within the phase transition region. This decrease is due to the starting $\mathrm{Cu_{Sn}}$ and $\mathrm{Zn_{Sn}}$ anti-site occupancy.

These anti-site occupancies are much better visible taking into account the isotropic temperature factors (B_{iso}) of the cation sites (Fig. 5), which describes the magnitude of the temperture vibrations of the atoms. It is known from $\mathrm{CuInS_2}$ [9], that $B_{\mathrm{iso}}(\mathrm{Cu})$ can reach values up to 8 Å^2. Moreover copper is the more mobile cation in comparison to zinc. Very high B_{iso} values can be obtained for the 2a and 4d sites of the tetragonal phase. Taking into account that only the 2a site is fully occupied by Cu whereas the 4d site is occupied by (1/2Cu + 1/2Zn), the relation $B_{\mathrm{iso}}(2\mathrm{a}) > B_{\mathrm{iso}}(4\mathrm{d})$ seems plausible. The isotropic temperature factor of Sn as well as of the anion show much smaller values. Within the phase transition region a strong decrease of the $B_{\mathrm{iso}}(2\mathrm{a})$ and $B_{\mathrm{iso}}(4\mathrm{d})$ of the tetragonal phase can be obtained, even reaching the B_{iso} value of the cation site of the cubic phase. On the other hand, the B_{iso} of the tetragonal site 2b (occupied by Sn) increases slightly. This behav-

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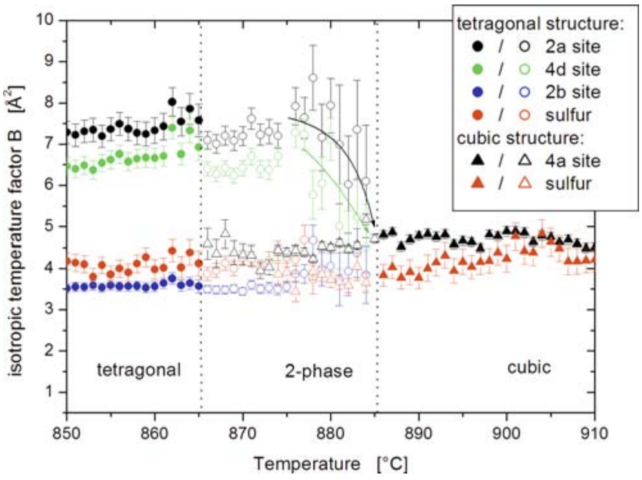

Figure 5 (online colour at: www.pss-a.com) Isotropic temperature factor (B_{iso}) near and within the phase transition region.

iour shows the Cu_{Sn} and Zn_{Sn} as well as Sn_{Cu} and Sn_{Zn} anti-site occupancy. It becomes also obvious, that the anti-site occupancy starts within the phase transition region, there is no evidence for a cation anti-site occupancy as long as a single kesterite phase exists.

Taking into account the atomic position parameters x and z of the anion, a displacive behaviour can be obtained over the whole temperature range (Fig. 6). With increasing temperature, the x value decreases linearly reaching nearly the ideal value of 1/4 at the begin of the phase transition region at 865 °C. The z parameter remains first constant, then increases and remains constant again. Only a few degree before the phase transition region the z parameter drops down reaching nearly the ideal position too.

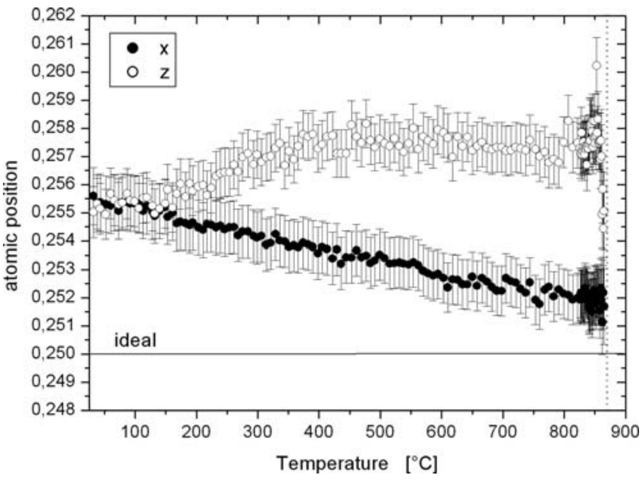

Figure 6 Anion atomic position parameters x and z in dependence on temperature. For better visibility, the atomic position parameters as determined by Rietveld analysis were modified according to $x - 1/2$ and $(1-z)/2$. The solid line gives the value of the ideal anion position as in the sphalerite type structure.

Thus it became clear, that the solid–solid structural phase transition in kesterite is much more determined by the displacive behaviour of the anion substructure, than by an order–disorder of the cation substructure. This mechanism is very different from the cation anti-site occupancy driven phase transition in the Cu–In–VI_2 chalcopyrite compounds [8, 9].

There is no hint for the existence of a phase with chalcopyrite type structure (space group $I\bar{4}2d$) and thus a phase transition $I\bar{4}2m \rightarrow I\bar{4}2d \rightarrow F\bar{4}3m$ does not exist. This is due to the fact that the space group $I\bar{4}2m$ is not a subgroup of $I\bar{4}2d$. As known from [12] in solid-state phase transitions there often exists a group-subgroup relation between the symmetry groups of the two phases. According to Landau theory, this is in fact mandatory for displacive phase transitions.

4 Conclusion

In-situ diffraction experiments using high energy synchrotron X-rays revealed for the first time the existence of a structural phase transition in Cu_2ZnSnS_4 from the tetragonal kesterite type to the cubic sphalerite type structure. The transition occurs between 866–883 °C, where a tetragonal and a cubic phase coexists.

Outside the phase transition region, the lattice parameter of the tetragonal phase increase nearly linearly with increasing temperature, whereas the lattice parameter of the cubic phase show first a negative thermal expansion changing at ~930 °C to an linear increase of a_{cub}. A cation anti-site occupancy can only be observed within the phase transition region. On the other hand, the atomic position parameter of the anion changes, which starts at ~150 °C and lasts up to the phase transition region. Both parameter x and z reach nearly the ideal value of 1/4, indicating the anion in the middle of the cation tetrahedra.

Thus we conclude, that in Cu_2ZnSnS_4 the structural phase transition from the tetragonal kesterite type to the cubic sphalerite type structure is characterized much more by a displacive behaviour of the anion substructure then by an anti-site occupancy within the cation substructure.

Because the space group $I\bar{4}2m$ is not a subgroup of $I\bar{4}2d$ and a group–subgroup relation is mandatory for displacive phase transitions, the non-existence of a $I\bar{4}2m \rightarrow I\bar{4}2d$ transition seems plausible.

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