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Cu_2ZnSnS_4 thin films characterization by XRD

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Cu_2ZnSnS_4 THIN FILMS CHARACTERIZATION BY XRD

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Introduction

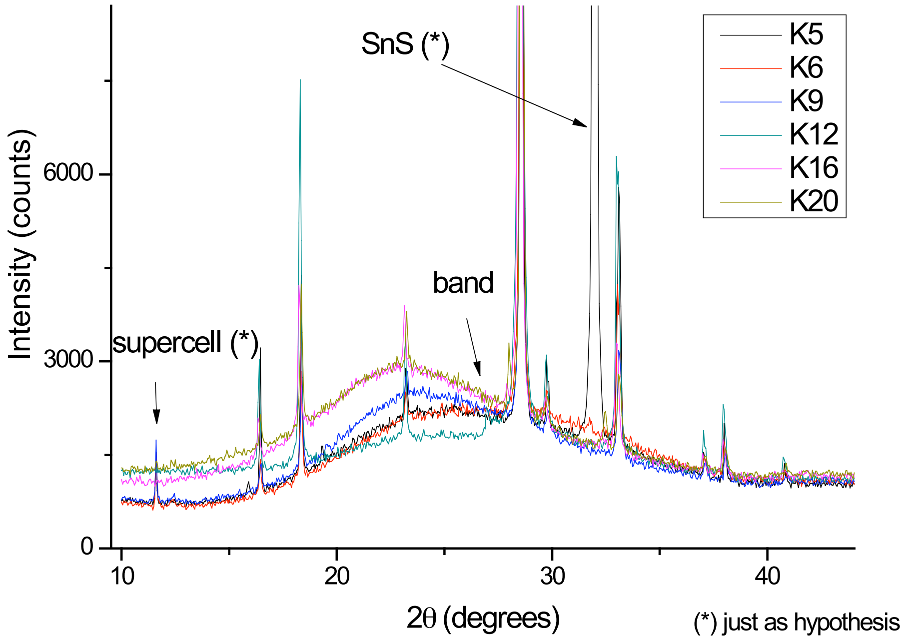
Cu_2ZnSnS_4, (CZTS) is a promising material for low cost thin-film solar cells owing to the suitable optical band-gap energy of about 1.45 eV. This semiconductor can be obtained by replacing in chalcopyrite CuInS half of the indium (In) with zinc (Zn) and the other half with tin (Sn). All constituents of this CZTS film are abundant, low cost and non-toxic.

The CZTS samples examined in this work were grown by a two-step process. A precursors is deposited by sequential evaporation of three layers of ZnS, Sn and Cu. The CZTS films is then obtained by the sulfurization of the precursor in a quartz glass tube furnace in an atmosphere of N_2 containing sulphur vapour. The stability region of CZTS is not large and small errors in the stoichiometry can produce the precipitation of spurious phases with detrimental effects on the optoelectronic film properties.

In addition to the investigation of spurious phases formation, XRD can be used to give information on film stress, defectivity and domain size.

XRD characterization of CZTS samples

We have performed a detailed examination of six CZTS samples. All studied films seem to be mainly composed of kesterite.



Extra peaks are however present in the diffraction patterns. In particular, we can divide the specimens in four main categories:

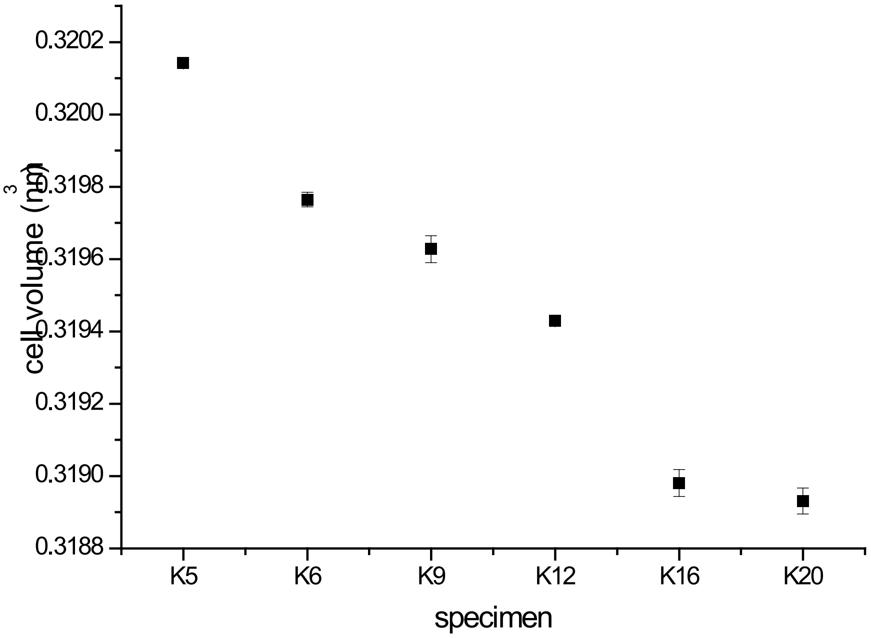
K12 the specimen seems made of kesterite only. The phase seems not textured: preferred orientation, if present, is weak. Two additional small peaks, more resembling 2D diffraction bands, are present near the (112) most intense peak. This is a possible indication of the presence of stacking faults in the structure.

K6, K9 some small extra peak is observed, with a line width compatible with that of the kesterite reflections. The peak at low angle is compatible with a 2ax2axc kesterite supercell, although this might just be a coincidence. The powder diffraction information from a thin film is not sufficient for a structural determination: it would

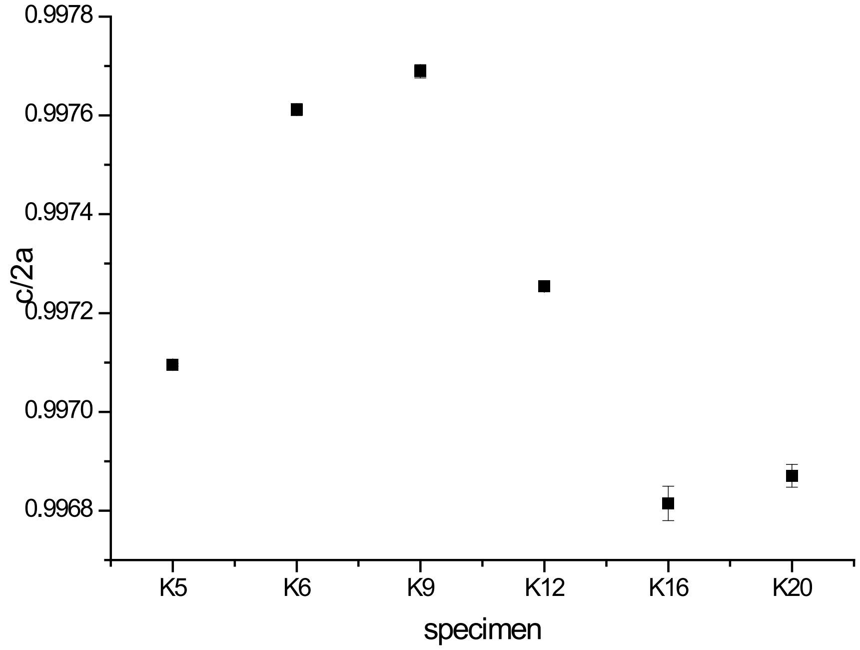
	therefore be interesting to be able to synthesize some more material and to perform a detailed diffraction analysis. The position is not compatible with any possible known sulfide of the reacting species.
K5	two major extra peaks are present in the diffraction pattern of kesterite. The broadening is larger so we can assume that those peaks belong to a second phase. The presence of just two reflections, multiple orders of the same diffraction signal, witness a possible strong texture (presumably of fiber type) of this second phase. Data are not enough for drawing any conclusions based on the present measurements alone, but peak positions are compatible with those of SnS ((*h 3k* 0) reflections of Orthorhombic SnS), a phase also observed by Raman Spectroscopy
K16, K20	A set of extra reflections is present in the pattern. A unique attribution is not possible, but peak positions are compatible with those of a copper sulfide close to (but not exactly equal to) the composition Cu_2S (Cu_9S_5)

A possible occurrence of extra phases, mainly pure or mixed copper sulphides in the production of kesterite films, has already been reported in the literature [1][2]. Different temperatures tend to stabilize different phases.

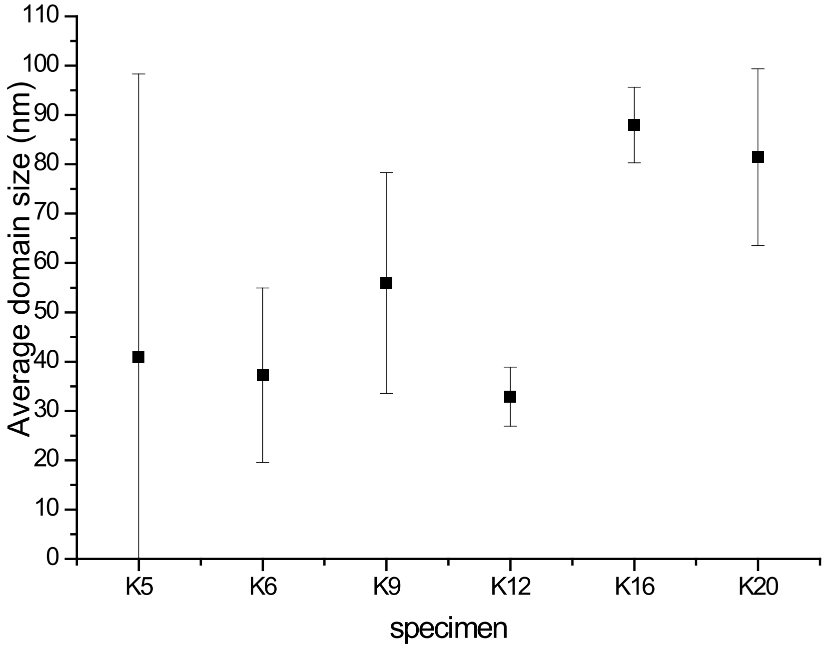
It is possible to observe a certain correlation between cell volume and specimen number. This, in practice, should be correlated with the extra phases observed in the diffraction pattern and the actual stoichiometry of kesterite. The typical cell volume of kesterite is observed for the K5 and K6 specimens, those not presenting co-existence of extra phases. Further investigation is necessary to fully understand whether the volume contraction can be attributed to the presence of defects in the kesterite structure, or to the action of compressive residual stresses (created also by the presence of the extra phases).



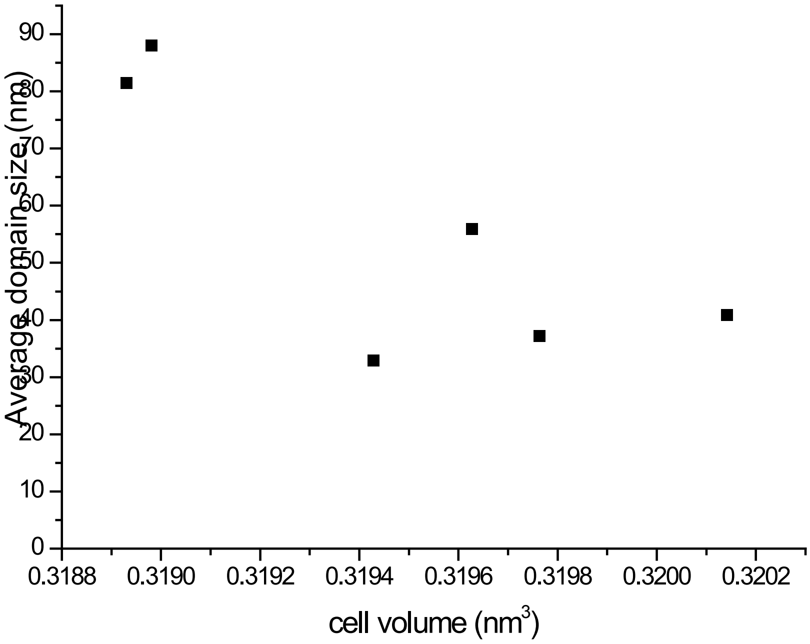
The trend in the volume seems not matched by the trend in the cell parameter ratio c/2a or, correspondingly, in the tetragonal deformation Δ (=1-c/2a) [1]. The maximum deformation is again obtained in the specimens characterized by the presence of the extra phases, and in particular of CuS. It is therefore possible that part of the available copper forms the extra sulfide and therefore copper vacancies are created in kesterite, with the primary consequence of effectively reducing the cell volume and the c/2a ratio.



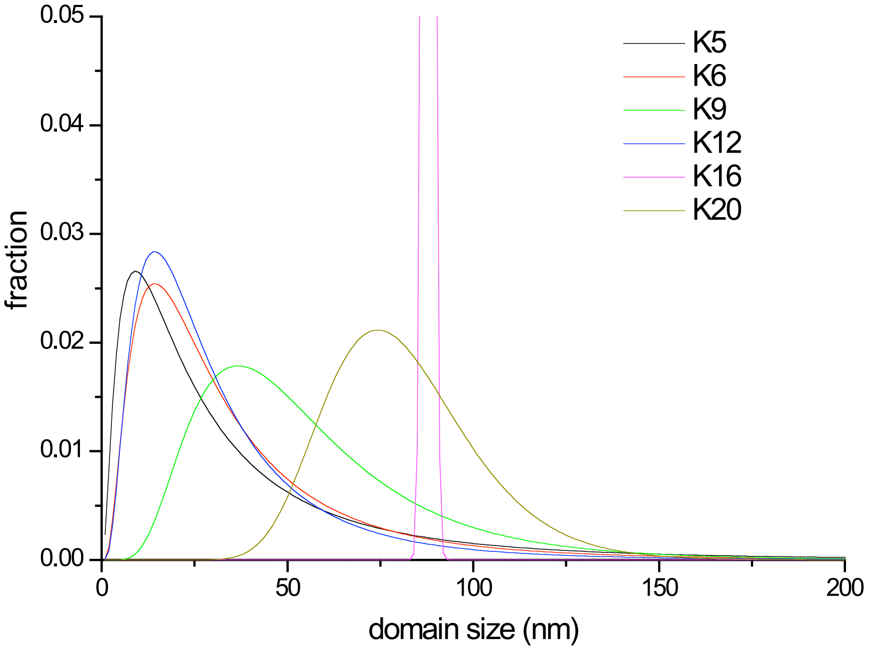
Some considerations can be made also on the size of the domains evaluated by means of the WPPM method [3]. The average domain size seems to cluster in two main groups. Specimens with a relatively small domain (around 40 nm in diameter) and specimens with a larger size (around 80 nm). The larger domains occur in the specimens showing the presence of the extra phase (K16 and K20):



From this point of view, there seems to be a tendency of more stressed specimens (those with a larger cell distortion) to grow to larger sizes



The trend of the domain size distribution is quite peculiar. There is a tendency to a large spread in the domain size distribution for almost all specimens. The size distributions are quite stable, i.e. calculation starting from different parameters lead basically to the same result. Specimen K16 seems the only one to show a very narrow distribution.



The same tendency is preserved independently of the starting set of parameters employed for the modeling. Apparently there is no correlation between the shape of the distribution and the characteristics of the films.

References

[1] Schorr et al. Thin Solid Films 517 (2009) 2461–2464
[2] Chen et al., Applied Physics Letters 96 (2010) 021902
[3] Scardi & Leoni, Acta Cryst. A 58 (2002) 190-200