Experimental report

09/02/2018

Proposal: 5-11-422 **Council:** 10/2016

Title: Definitive copper-zinc distributions in the photovoltaic Cu2ZnSnS4

Research area: Materials

This proposal is a new proposal

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Samples: Copper zinc tin sulfide

Instrument	Requested days	Allocated days	From	To
D9	9	9	25/01/2017	03/02/2017

Abstract:

Copper zinc tin sulfide (CZTS, Cu2ZnSnS4)) is of great interest in respect of applications in solar cells. A major problem with practical CZTS solar cells is processing to control the cation distribution at the atomic level of the main kesterite phase. Disorder between a pair of Zn and Cu sites is believed to provide centres for electron/hole recombination. Raman spectroscopy may be used to qualitatively investigate this disorder but no definitive structure determination has been achieved. This is because of the isoelectronic nature of Cu/Zn (negating X-ray methods) and peak overlap in the tetragonal unit cell (negating powder methods). Single crystal neutron diffraction data will allow us to determine definitively the Zn/Cu distribution in CZTS phases and we will study crystals that have been annealed at different processing temperatures to produce ordered and partly ordered materials. This will allow the qualitative Raman data on the same crystals to be mapped onto the exact Zn/Cu distributions determined in this study. This in turn will be crucial in allowing rapid Raman measurements to be used during industrial processing of CZTS films.

Outline of the Proposal

Copper zinc tin sulfide (CZTS, Cu_2ZnSnS_4)) has received increasing interest in the last decade in respect of applications in solar cells (1-8). CZTS has favourable optical and electronic properties, similar to CIGS (copper indium gallium selenide), making it well suited for use as a thin-film solar cell absorber layer, but unlike CIGS (or other thin films such as CdTe), CZTS is composed of only abundant and non-toxic elements. A major problem with CZTS is the control of cation distribution at the atomic level of the main kesterite phase. See Figure 1. Imperfect ordering of the metal atoms across the cubic ZnS type structure acts in a similar manner to the bulk phase defects in providing centres for recombination. Therefore knowledge of the distribution of the Cu, Sn and Zn over the sites in CZTS as a function of exact processing condition (particularly annealing temperature) is central to the optimisation of commercial routes for the large scale deployment of this material. In this experiment we requested and were awarded beam time to study CZTS single crystals as a function of annealing conditions as this is known to control cation distribution and PV properties.

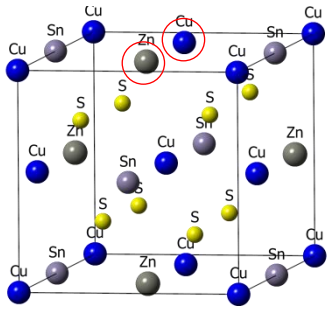

Figure 1. The kesterite structure; the key 2c and 2d sites are circled

Experiment

The initial aim of the experiment was to collect diffraction data from plate and needle forms of CZTS annealed under various temperature conditions to extract the Cu/Zn disorder parameter definitively. Crystals were initially evaluate on Orient Express – all plate-type crystals were found to be of sufficient size and quality to permit further study on D9. However for the needle-shaped crystals the quality of the diffraction meant that these were not studied further on D9. Data were collected on D9 from 6 plate-type crystals with varying experimental periods to reflect crystal size.

During the experiment, no intensity was observed for the (0 1 1) reflection in all samples, even when an extended acquisition time was used (30 seconds); the (0 1 1) reflection was expected to be the strongest odd l reflection in CZTS. A good signal to noise ratio was achieved for even l reflections using an acquisition time per detector position of only 4 seconds. Using these data the initial structure refinement was carried out using fully ordered kesterite, fully disordered kesterite and cubic zinc-blende models. However no significant difference between the *R*F2*w* factors of the cubic model and the disordered kesterite models was found for all samples studied. It was only realised later an error had been made during the initial indexing of all the samples. Since the lattice parameter *a* in CZTS is almost equal to *c*/2, the h,k,l reflections had been mistakenly indexed as h,l/2,k or l/2,k,h. This explains why no allowed l=odd reflections were observed, and the refinement yielded better *R*F2 factor in the simpler cubic space group which is an adequate descriptor for the collected data.

For the 300 °C sample it was possible to partially re-measure (with thanks to Oscar Fabelo Rosa) the diffraction data, using the correct crystal orientation, before the neutron facility shut down. The new neutron diffraction data, together with the transformed old neutron diffraction data and single crystal X-ray diffraction (SXD) data were refined simultaneously using JANA2006. The

refinement was carried out using four models: (i) an ordered kesterite model with S = 1; (ii) a disordered kesterite model with S = 0; (iii) the occupancy factors in 2c and 2d sites were refined; and (iv) the occupancy factors in 2a, 2c and 2d sites were refined (Table 1). Constraints were applied for models (iii) and (iv) so that the occupancy factor per site is equal to one, and the occupancy factor of Cu in 2c site equals to that of Zn in 2d site. If these constraints were not applied, the occupancy factors of these sites yielded unreasonable numbers, and a warning about strong correlations between the occupancy factors of 2c and 2d sites was notified. Többens *et al.* also highlighted the same problem with regards to the strong correlations. It is thought that the strong correlations between the occupancy factors in the different sites is due to the pseudosymmetry of the kesterite structure. The *R*-factors from the old neutron data and SXD data for all the models are similar, while the *R*-factors from the new neutron data clearly confirms the crystal is disordered. This is expected as the information about the Cu/Zn disorder is contained in the odd l reflections as demonstrated in simulations.

Table 1. Comparison of the combined neutron diffraction and SXD refinement results with different occupancy factors on the 2a, 2c and 2d Wyckoff positions of CZTS single crystal deliberately disordered by annealing at 300 °C.

Model	**Ordered kesterite**	**Disordered kesterite**	**Occupancy factors refined with constraint**	
Space group		I -4		
a / Å		5.4332(4)		
c / Å		10.8432(7)		
Occupancy				
Cu 2a	1	1	1	0.94(3)
Zn 2a				0.06(3)
Cu 2c	1	0.5	0.55(3)	0.56(3)
Zn 2c		0.5	0.45(3)	0.44(3)
Cu 2d		0.5	0.45(3)	0.44(3)
Zn 2d	1	0.5	0.55(3)	0.56(3)
***wR* (obs/all)**				
New neutron data (with l odd reflections)	6.83 / 7.76	4.24 / 4.48	4.21 / 4.44	4.21 / 4.43
Old neutron data (no l odd reflections)	2.72 / 3.42	2.80 / 3.50	2.80 / 3.50	2.82 / 3.47
SXD data	5.69 / 5.69	5.59 / 5.60	5.59 / 5.60	5.59 / 5.59
Overall	**5.26 / 5.56**	**4.77 / 4.93**	**4.77 / 4.93**	**4.77 / 4.92**

The site occupancy parameter for Cu/Zn has an error bar of 0.03 (on 0.45). Consideration of the raw reflection data, shows that the intensity of reflection 0 1 1 is 35 ± 4 counts per second (cps), in contrast, the intensity of reflection 1 1 2 is 6646 ± 50 cps. A longer acquisition time that was used in the rapid re-measurement would allow this to be reduced to a more acceptable 0.01 - 0.02

Conclusions

The plate-shaped crystals are of good quality and sufficient size to allow the collection of the required data and quality in approximately 1 day. However due to the error in indexing the data will need partial recollection focussing on l=odd reflections to determine the level of disorder in each of the various annealed samples.