Project no. 316488

Project Acronym: **KESTCELLS**

Project title: Training for suitable low cost PV technologies: development of kesterite based efficient solar cells.

Industry-Academia Partnerships and Pathways

Start date of project: 01/09/2012

Duration: 48 months

Project coordinator: Dr. Edgardo Saucedo

Project coordinator organization name: IREC

Project website address: www.kestcells.eu

D 1.1 cations distributions in dependence of growth processes

Delivery date: October 2015

Dissemination Level	PU
PU	Public
PP	Restricted to other programme participants (including the Commission Services)
RE	Restricted to a group specified by the consortium (including the Commission Services)
CO	Confidential, only for members of the consortium (including the Commission Services)

Document details:	
Workpackage	WP1: Fundamental properties of Kesterites
Partners	FUB
Authors	S.Schorr, G.Gurieva, L.E. Valle-Rios, K.Neldner
Document ID	
Release Date	

Neutron powder diffraction: experiments and data analysis

Off-stoichiometric CZTS and CZTSe powder samples have been synthesized by solid state reaction (milestone 1.2). Details about the growth procedure can be found in the paper *Existence of off-stoichiometric single phase kesterite* (L. E. Valle Rios, K. Neldner, G. Gurieva, S. Schorr, Jornal of Alloys and Compounds (2015), doi:10.1016/j.jallcom.2015.09.198
The phase content and chemical composition of the phases has been determined by WDX (wavelength dispersive X-ray spectroscopy) using an electron microprobe system. These measurements proved the presence of CZTS or CZTSe with an off-stoichiometric composition as main phase in all synthesized samples (table 1 and 3).

Neutron powder diffraction experiments have been performed at the Spallation Neutron Source (SNS, Oak Ridge/US) at the Powgen instrument as well as at the Berlin Research Reactor BERII (HZB, Germany) at the fine resolution neutron powder diffractometer (E9). The neutron scattering length, which determines the interaction between the neutrons and the nuclei, of Cu and Zn is different, therefore is possible to distinguish between the electronic similar elements Cu and Zn site occupation in the crystal structure.

The neutron diffraction pattern have been analysized by a Rietveld refinement using the FullProf software. The kesterite type structure was introduced as structural model in the refinement. Structural parameters, like lattice constants, site occupancy parameters and thermal displacement parameters have been determined by the Rietveld analysis.

The average neutron scattering length analysis method was applied to determine the distribution of the cations Cu^{+}, Zn^{2+} and Sn^{4+} on the four structural sites *2a, 2b, 2c* and *2d* of the kesterite type structure. Hereafter the Cu/Zn disorder at the 2*c* and 2*d* sites and other point defects, like vacancies, anti-sites and interstitials, have been identified. The deduced point defects are related to the off-stoichiometry type (A, B, C, D, F or mixtures between two types) of the present kesterite type phase. It should be noticed, that the off-stoichiometry type of the kesterite type phase was determined by the compositional ratios Cu/(Zn+Sn) and Zn/Sn (milestone 1.2).

According to the fractional amounts, based on the unit cell) of the defects, the point defect concentrations per cm^3 have been calculated (table 2 and 4).

Table 1: off-stoichiometric CZTS

Sample	Cu/(Zn+Sn)	Zn/Sn	Type fraction %				secondary phases	*a* [Å]	*c*[Å]
A0125	1.008	0.974	C	75%	E	25%	CuS (9.60%); $Zn_{0.96}(Cu_{0.03}Sn_{0.01})S$	5.426	10.866
A0100	1.094	0.864	D	14%	C	86%	CuS (29.91%)	5.424	10.864
A0050	1.220	0.735	D	22%	C	78%	CuS (12.68%); $Cu_{1.99}S$	5.418	10.846
A0025	1.305	0.659	D	24%	C	76%	CuS (4.51%)	5.417	10.822
A0000	1.303	0.635	D	18%	C	82%	CuS (12.58%); Cu_2S; $Zn_{0.99}(Cu_{0.01})S$	5.415	10.831
A5010	0.965	1.055	A	16%	B	84%	-	5.436	10.835
A3010	0.967	1.067	A	1%	B	99%	-	5.434	10.833
A3020	0.955	1.073	A	14%	B	86%	-	5.433	10.830
B1010	0.959	1.096	B	95%	F	5%	$Zn_{0.92}(Cu_{0.05}Sn_{0.02})S$ (1 grain)	5.435	10.837
B1020	0.944	1.131	B	95%	F	5%	$Zn_{0.95}(Cu_{0.04}Sn_{0.01})S$	5.435	10.840
A2000	0.941	1.152	B	91%	F	9%	$Zn_{0.95}(Cu_{0.04}Sn_{0.02})S$; $Sn_{0.97}(Cu_{0.02}Zn_{0.01})S$; $Cu_{1.99}S$	5.426	10.875
B2000	0.997	1.049	B	57%	F	43%	-	5.434	10.834
B2010	0.976	1.086	B	79%	F	21%	-	5.436	10.839
B1000	0.995	1.054	B	59%	F	41%	-	5.435	10.836
D0010	1.009	1.034	B	24%	F	76%	-	5.434	10.835
D0040	1.044	1.006	F	29%	D	71%	CuS	5.424	10.865
D0050	1.051	0.990	F	17%	D	83%	CuS,SnS	5.424	10.868
D0020R	0.996	1.088	B	54%	F	46%	CuS, SnS	5.426	10.876

Table 2: CZTS defect concentrations (x10^{20}cm^{-3})

Sample	V_{Cu}	Zn_{Cu}	Cu_{Zn}	Zn_{Sn}	Sn_{Zn}	Cu_i	Cu-Zn disorder
A0125	0	0	0.311	0	0.261	0	5.980
A0100	0	0	2.501	0	0.946	0.617	1.251
A0050	0	0	5.300	0	1.736	0.183	1.718
A0025	0	0	7.057	0	2.226	2.603	4.642
A0000	0	0	7.241	0	2.600	2.041	6.280
A5010	0.275	0.983	0	0.354	0	0	1.028
A3010	0	1.041	0	0.510	0	0	5.298
A3020	0.320	1.290	0	0.485	0	0	4.851
B1010	0	1.426	0	0.744	0	0.616	6.884
B1020	0	1.893	0	1.049	0	0.203	5.532
A2000	0	2.086	0	1.236	0	0.386	2.482
B2010	0	1.041	0	0.792	0	0.543	4.278
B1000	0	0.494	0	0.580	0	0.665	5.124
D0010	0	0.1307	0	0.465	0	0.800	5.227
D0040	0	0	0.638	0.389	0	1.416	9.004
D0050	0	0	0.866	0.267	0	1.400	3.316
D0020R	0	0.665	0	0.966	0	1.267	4.516

Table 3: off-stoichiometric CZTSe

Sample	Cu/(Zn+Sn)	Zn/Sn	Type fraction %				secondary phases	*a* [Å]	*c*[Å]
A0025-6	0.9500	1.0990	B	97%	A	3%	$Cu0_{.998}(Sn_{0.002})Se$	5.697	11.348
A0050-6	0.9197	1.1131	B	75%	A	25%	$Zn_{0.792}(Cu_{0.140}Sn_{0.068})Se$;$Sn_{0.919}(Cu_{0.333}Zn_{0.028})Se_2$	5.695	11.341
A0075-3	0.9587	1.1200	F	14%	B	86%	$Cu_{0.990}(Zn_{0.009}Sn_{0.001})Se$;$Zn_{0.795}(Cu_{0.151}Sn_{0.053})Se$; $Cu_{1.991}(Zn_{0.008}Sn_{0.001})Se$	5.694	11.347
B0050-5	0.8458	1.1924	B	62%	A	38%	$Zn_{0.744}(Cu_{0.144}Sn_{0.082})Se$; $Sn_{0.935}(Cu_{0.038}Zn_{0.027})Se_2$	5.697	11.352
B0075-5	0.9393	1.2137	F	19%	B	81%	$Cu_{0.991}(Zn_{0.008}Sn_{0.001})Se$;$Zn_{0.774}(Cu_{0.157}Sn_{0.069})Se$	5.692	11.347
C0075-7	1.1739	0.7766	C	81%	D	19%	$Cu_{0.99}(Zn_{0.01})Se$	5.694	11.356
D0100-9	1.1003	0.9614	D	91%	F	9%	$Cu_{1.989}(Zn_{0.010}Sn_{0.002})Se$; $Cu_{0.989}(Zn_{0.010}Sn_{0.002})Se$	5.691	11.341
B0075-4	1.0001	1.0456	F	50%	B	50%	$Zn_{0.950}(Cu_{0.039}Sn_{0.011})Se$; $Cu_{0.976}(Zn_{0.021}Sn_{0.003})Se$	5.694	11.349
A0025-3	0.9669	1.0449	B	75%	A	25%	-	5.695	11.352
A0050-1	0.9113	1.1273	B	76%	A	24%	-	5.696	11.339
A1000-6	0.9452	1.1487	F	10%	B	90%	-	5.692	11.330
A0075-6	0.8902	1.1341	B	63%	A	37%	$Zn_{0.910}(Cu_{0.071}Sn_{0.019})Se$	5.693	11.331
A0125-1	0.8155	1.1475	B	16%	A	84%	$Sn_{0.92}(Cu_{0.05}Zn_{0.03})Se_2$	5.693	11.331
C0025-5	1.0084	1.1002	F	59%	B	41%	$Cu_{0.982}(Zn_{0.012}Sn_{0.005})Se$	5.690	11.345

Table 4: CZTSe defect concentrations per unit cell ($x10^{20}cm^{-3}$)

Sample	V_{Cu}	Zn_{Cu}	Cu_{Zn}	Zn_{Sn}	Sn_{Zn}	Cu_i	Cu-Zn disorder
A0025-6	0	1.357	0	0.624	0	0	10.420
A0050-6	0.788	1.875	0	0.571	0	0	2.718
A0075-3	0	1.359	0	0.897	0	0.408	6.795
B0050-5	2.008	3.500	0	0.787	0	0	3.283
B0075-5	0	2.257	0	1.605	0	0.979	3.182
C0075-7	0	0	3.747	0	1.303	1.167	4.073
D0100-9	0	0	1.606	0.245	0	2.096	3.837
B0075-4	0	0.299	0	0.462	0	0.598	5.135
A0025-3	0.299	0.760	0	0.217	0	0	2.769
A0050-1	0.815	2.120	0	0.625	0	0	2.717
A1000-6	0	1.770	0	1.062	0	0.408	8.442
A0075-6	1.361	2.478	0	0.545	0	0	4.084
A0125-1	3.404	3.676	0	0.163	0	0	1.361
C0025-5	0	0.544	0	1.034	0	1.524	4.899