

...to grind or not to grind?

Cu/Zn disorder in $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ monograins

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Kesterite-type based thin film solar cell technologies are mainly based on polycrystalline absorber layers, which makes it quite difficult to correlate the crystallographic structure and the structural disorder of the kesterite-type absorber (determined by neutron diffraction for which a large sample volume is needed) to the photovoltaic performance of the device. A promising low cost alternative PV technology uses kesterite-type $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) monograins (single crystals of 50-100 μm size) which are fixed in a polymer matrix to form a flexible solar cell [1]. In this way the monograins offer the unique possibility to correlate structural disorder in kesterite-type absorbers with device performance parameters.

Structural disorder, like the Cu/Zn disorder, influences the optoelectronic properties of the kesterite-type semiconductor critically. The experimental determination of the order parameter Q , a quantitative measure of the degree of Cu/Zn disorder in CZTSSe [2], requires a differentiation between the isoelectronic cations Cu^+ and Zn^{2+} . An in-depth analysis of neutron diffraction data provides information on the cation distribution in the crystal structure allowing the determination of type and concentration of intrinsic point defects including a distinction between Cu and Zn [3].

In our previous study [4] we confirmed a correlation between the order parameter Q determined by neutron diffraction and a thermal treatment of CZTSSe monograins (quenching or slow annealing procedures, so-called order-disorder procedure) as well as the influence of very small changes in their chemical composition. In this and all the previous studies the monograins were ground before the diffraction measurement. In this study we tackle the influence of grinding on the stoichiometry deviation, the Cu/Zn disorder as well as the intrinsic point defects and optoelectronic properties of CZTSSe monograins. In order to achieve this goal, one homogenous CZTSSe monograin sample (15 gram) was first divided in two parts. One of them was kept "as grown", and the second half was ground. In the following each of the 7.5 gram powder was divided in three parts and processed the same way as described in [3,4]. In this way 2 groups of as grown, quenched and slowly annealed monograin samples were formed. The grinding was not repeated at any stage of the experiment.

We will present detailed structural investigations of the obtained CZTSSe monograins based on neutron powder diffraction experiments. The obtained results show the influence of grinding on the Cu/Zn disorder and point defect scenario. A further investigation of the effect of the disordering procedure (quenching) and ordering procedure (long time annealing at a temperature below the order-disorder transition) on the Cu/Zn disorder and optical properties of the CZTSSe monograins will be presented as well.

[1] www.crystalsol.com

[2] Toebbens et al. Phys. Stat. Sol. B 253 (2016) 1890

[3] G. Gurieva et. al., J Appl Phys 2018; 123: 161519/1-12

[4] G. Gurieva et. al., in preparation

This research has been partially supported by the CUSTOM-ART Project, funded from the European Union's Horizon 2020 Research and Innovation Programme under the grant agreement No 952982. A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.