



# Chemically and morphologically distinct grain boundaries in Ge-doped $\text{Cu}_2\text{ZnSnSe}_4$ solar cells revealed with STEM-EELS



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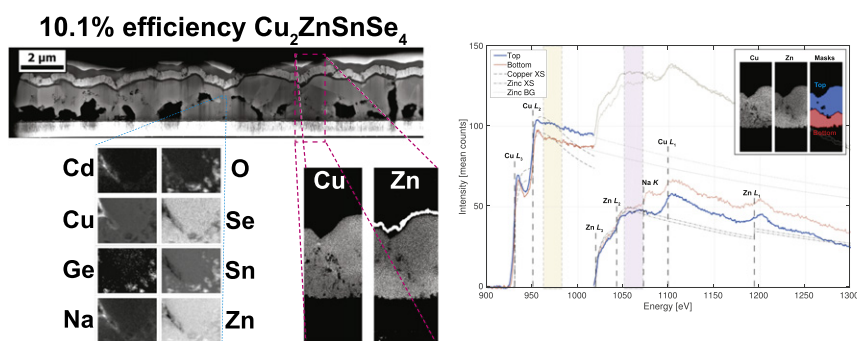
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## HIGHLIGHTS

- Advanced analytical STEM investigation of a Ge-doped CZTSe film with 10.1% efficiency performed
- Two types of grain boundaries identified
- Chemical segregation of absorber layer into two stoichiometrically-distinct layers observed
- Lower grain boundaries are poorly connected, propagate parallel to the back contact, and have SnO nanoinclusions
- Well-connected, straight grain boundaries are Cu-rich and appear in the upper half of the film

## GRAPHICAL ABSTRACT



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## ABSTRACT

Critical to the future development of  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) materials is a comprehensive understanding of the underlying nanoscale mechanisms responsible for reduced performance. Investigating these mechanisms is challenging since they arise on the nanoscale, yet manifest themselves over macroscopic regions. Here, we present an analytical study combining Scanning Transmission Electron Microscopy (STEM), sample preparation, and hyperspectral Electron Energy Loss Spectroscopy (EELS) mapping techniques to meet this challenge. We apply our method to a Ge-doped CZTSe sample with a measured efficiency of 10.1%, revealing that its microstructure is dominated by two distinct types of grain boundaries. The first type appears in the upper half of the absorber separating large grains. These are Cu-enriched, Se-poor, and have varying amounts of O. The second type of grain boundary is largely parallel to the substrate and appears predominately in the lower half of the absorber where the Cu/Zn ratio of the kesterite material is slightly lower. These grain boundaries contain voids and Sn oxide nanoparticles, exhibit high concentrations of Na, Cd, and S, and Cu assumes a higher valence state. We conclude with a discussion on the nature of and possible technological implications of these grain boundaries in this system.

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## 1. Introduction

Recent progress in solar cells based on earth abundant kesterite absorbers ( $\text{Cu}_2\text{ZnSnSe}_4$  – CZTSe or  $\text{Cu}_2\text{ZnSnS}_4$  – CZTS as well as their solid solutions), has been mainly driven by the optimization of the current density and the fill factor of the devices [1]. The currently published record devices evidence that the low open circuit voltage is the main

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obstacle impeding competitive efficiency levels in comparison to more mature chalcogenide technologies, like CdTe and Cu(In,Ga)Se<sub>2</sub> (CIGS) [2–4]. The most commonly cited causes for this deficit are Cu/Zn order-disorder [5,6] compositional/electrostatic/band-gap fluctuations [5,7], and grain boundary characteristics [8,9]. Studying these effects directly is challenging due to the complexity of the CZTSe absorber, which consists of an intricate interplay with the heterojunction [10–12], grain boundaries [9,10,12–14], and the back contact interface [15,16].

The grain boundaries in particular have been extensively studied in recent years, as their pervasiveness and complex chemistry is believed to have an enormous impact on overall efficiency. Yin et al. used first-principle density functional calculations to propose that some defects types such as Zn<sub>Sn</sub>, Na<sup>+</sup><sub>i</sub> and O<sub>Se</sub> located at the grain boundaries, could be beneficial for the device efficiency, as they might eliminate deep gap states and create hole barriers and electron sinks at the grain boundaries [13]. Kim et al. used atomic scale observation to demonstrate that partial substitution of Se by O at the grain boundaries efficiently inhibits electron-hole recombination and, in consequence, blocks hole transport [9]. Sardashti et al., proposed a grain boundary passivation mechanism by correlating photovoltaic devices with high performance and the presence of Cu-depleted and SnO<sub>x</sub> rich grain boundaries [12]. Xin et al. proposed that the presence of alkaline atoms at the grain boundaries (in this case Li), can invert the polarity of the electric field in this region, repelling the minority carrier electrons through the compensation of copper vacancies (Li<sub>Cu</sub> defects) and the reduction of Zn<sub>Cu</sub> donors [14]. Xu et al. used spatially mapped Raman spectroscopy and scanning probe microscopy to reveal that deviations in Cu stoichiometry can be found in the grain boundaries [17]. They also observed horizontal grain boundaries, and, although their chemical nature was not studied, they proposed that these grain boundaries could act as barriers against the transportation of minority carriers. Finally, Schwarz et al. reported a complete nanoscale characterization of grain and grain boundaries using atomic probe microscopy [18]. They observe that either Cu-enriched or Cu-poor grains can exist in kesterites depending on the thermal history of the sample. ZnSe was also detected in the vicinity of these grain boundaries and is dissolved after an annealing at 500 °C, together with the diffusion of Na and K towards the interfaces.

All of these works underscore the complexity of grain boundaries in kesterites, suggesting that a deeper understanding will require investigating the nanoscale compositional fluctuations and applying the results to the grain boundary networks observed on the absorber layer macroscale. Experimentally, this is a daunting task, as it requires the combination of techniques having a nanoscale spatial resolution with a field of view that is at least on the micron scale. For these reasons, many previous investigations on high efficiency systems have limited the field of view [19] or use a sampling rate that precludes the identification of nanoscale fluctuations [20]. Consequently, despite the considerable progress represented by these studies, the exact nature and chemistry of the grain boundaries in kesterites remains an open question.

In this report, we address this challenge by presenting a refined methodological approach for analytical Scanning Transmission Electron Microscopy (STEM) analysis of thin film solar cells in the kesterite family. The methodology first uses the sample preparation of a large sample area with the Focused Ion Beam (FIB) to classify the observed grain boundaries in terms of their morphology. The chemistry of these different grain boundaries is then studied in detail using Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-ray Spectroscopy (EDX). In all cases, we acquire analytical datasets with a wide field of view to guide further experiments with a higher resolution.

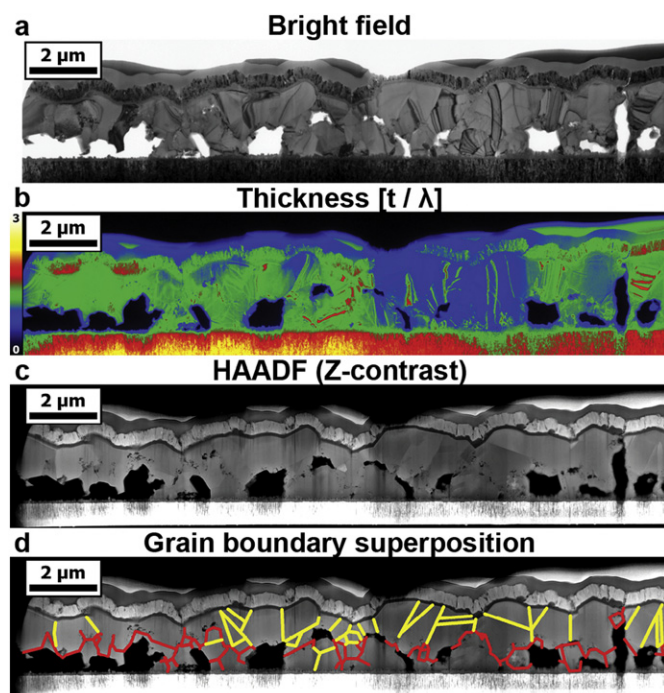
Using this methodology, we report a detailed analysis of structural, morphological, and compositional trends in a Ge-doped CZTSe sample with an efficiency of 10.1% (among the state-of-the-art efficiencies for this fabrication route). Our findings reveal that there are at least two morphologically and distinct types of grain boundaries present in this

system. These are concentrated in the upper and lower portions of the absorber layer, and the subsequent analytical STEM investigation reveals that they have very different chemical compositions. The more detailed EELS analysis of the lower grain boundaries shows that they contain large amounts of tin oxide and that copper assumes a higher valence state, whereas the upper grain boundaries are slightly Cu-enriched and contain trace amounts of oxygen. We can also link the extent of these grain boundaries to a change in the overall composition of the absorber layer, which appears to have different stoichiometries in the upper and lower halves. Finally, the potential impact of both types of grain boundaries on the device performance and fabrication is discussed.

## 2. Results

### 2.1. Overview of Cu<sub>2</sub>ZnSnSe<sub>4</sub> solar cell: revealing the grain structure

The subject of this investigation is a Ge-doped CZTSe solar cell with an efficiency of 10.1%. The main optoelectronic characteristics such as IV-curves and external quantum efficiency as well as a cross-sectional scanning electron micrograph of the solar cell can be found in Giraldo et al. [19], where this specific solar cell is denoted as Ge10. An overview of the full TEM lamella is presented in Fig. 1. In Fig. 1a, a series of bright field (BF) TEM images are stitched together. The contrast generation mechanism for this image is primarily diffraction contrast, and it reveals that the absorber layer is polycrystalline with an average grain diameter on the order of hundreds of nanometers. The lamella is suspended in a vacuum, which appears bright in this image, clearly demonstrating a number of pores which appear in proximity to the Mo back contact layer (at the bottom of the image). The through-thickness of the lamella is presented in Fig. 1b. Here, a series of energy filtered BF images were used to separate out the elastic and inelastic contributions to scattering, allowing for a measurement of the number of inelastic scattering events



**Fig. 1.** In (a), the bright field panorama of the Ge10 sample is presented. In (b), the thickness map of the entire lamella is shown in values of  $t/\lambda$ , as denoted on the color bar at left. In (c), the HAADF overview is presented, showing a strong Z-contrast. Finally, (d) shows an estimation of the propagation of the two types of grain boundaries discussed in this work. The upper grain boundaries are yellow while the lower grain boundaries are red.

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