DTU Energy
Department of Energy Conversion and Storage

Multigrain crystallography: Indexing algorithms for multiphase polycrystalline Cu_2ZnSnS_4 solar cells

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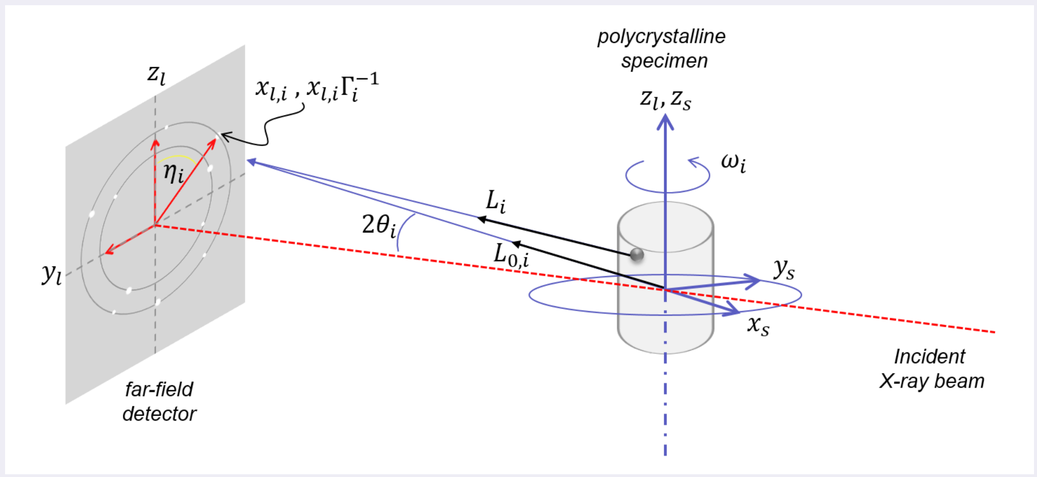
Introduction

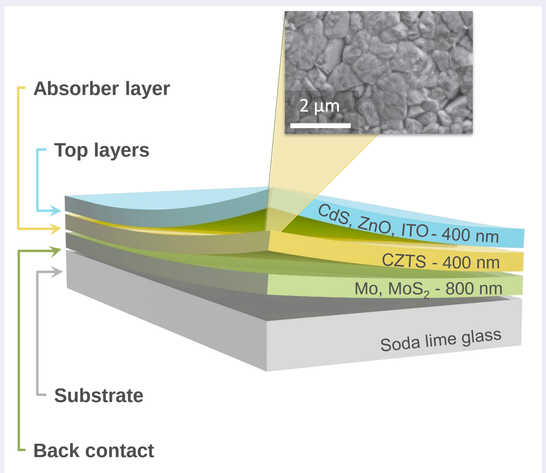
Photovoltaic technology aims to develop alternative materials that fulfill the triple challenge: sustainability, low energy payback time and scalability. Copper Zinc Tin Sulfide (CZTS) is a promising candidate, as it comprises non-toxic and earth abundant elements. It possesses a high absorption coefficient and a direct band gap, allowing an efficient collection of photons in micrometer thin films. However, the road for this material to achieve a higher efficiency is still long to go…



Experimental setup. The parameters shown in the diagram are used by the indexing algorithm to calculate the scattering vector G in the sample reference system and the forward projection into the reciprocal space: laboratory and sample reference system expressed as (x_l, y_l, z_l), and (x_s, y_s, z_s) respectively, $z_{(l,s)}$ - rotation axis, Γ - rotation matrix, x_s - position of a grain in the sample, $x_{l,i}$; $x_{l,i}$, Γ_i^{-1} position of a recorded diffraction spot in the laboratory reference system, and sample reference system, Li - direction of the diffracted ray in the sample reference system.

Objective

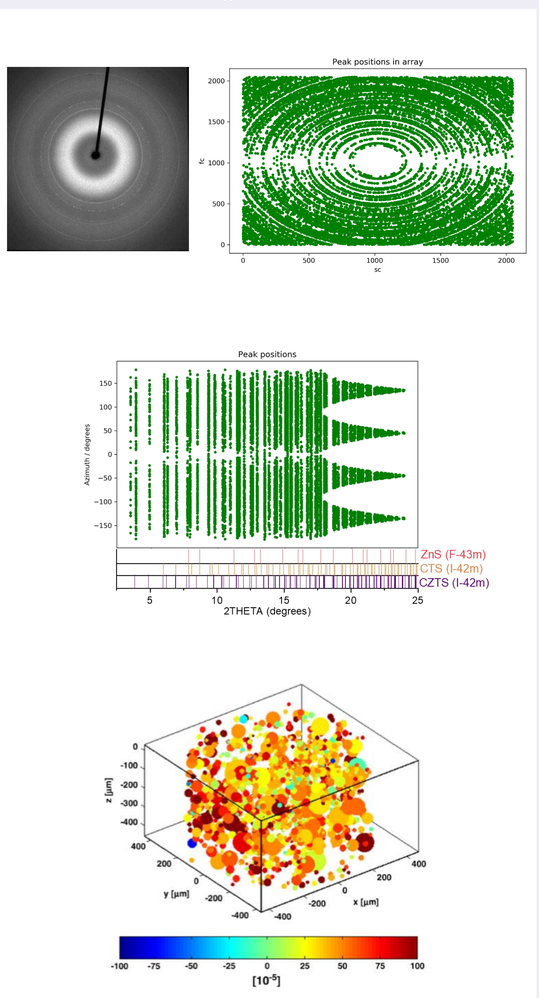
Simultaneous structural characterization of the absorber layer of the CZTS solar cells by implementing the latest indexing algorithms of multigrain crystallography to identify CZTS and the secondary phases, and to create 3D maps of the volumes, positions, orientations and stress-tensors of the grains.



The material. The absorber layer of kesterite solar cells is composed of CZTS and secondary phases: ZnS and Cu_2SnS_3, Cu_2S, SnS_2.

Phase	Space group	Lattice parameters	Reduced Unit cell lattice parameters
Cu_2ZnSnS_4	I-42m (tetragonal)	a,b=5.43344; c=10.8421 α,β,γ=90°	a,b=5.433; c=6.644 α,β=114.13 γ=90°
Cu_2SnS_3	I-42m (tetragonal)	a,b=5.413 c=10.824 α,β,γ=90°	a,b=5.413; c=6.629 α,β=114.1° γ=90°
ZnS	F-43m (cubic)	a,b,c=5.433 α,β,γ=90°	a,b,c=3.842 α,β,γ=60°

Crystallographic structures of most common phases. The unit cell of CZTS, ZnS and Cu_2SnS_3 are very similar. Conventional XRD cannot distinguish among these phases.



Top left: Diffraction pattern showing powder rings with spots known as reflections. Top right: Filtered reflections of the full set of diffraction images. Middle: Azimuthal projection of the diffraction spots and the position of the reflections of the unit cells. Bottom: 3D map of the position, volume (given by size of the sphere) and axial strain of 1118 grains of Cu. (Oddershede et al. 2011)

Methology

A monochromatic beam illuminates the sample on a rotary table in transmission geometry and a 2D far field detector records the diffraction images. A series of diffraction images are acquired covering an interval of the rotation angle ω. A key step in the analysis of such data is a multigrain indexing program.

Simulation

Diffraction patterns of 30 grains of CZTS, Cu2SnS3, and ZnS were created by the program PolyXSim, (Sørensen, 2006).

Parameters	Value
Distance to detector	160 mm
Detector	Channel size: 50 x 50 µm No. channels: 2048 x 2048
ω range [ω_{min} ; ω_{max}]	[0°; 180°]
ω step	0.5°
Wavelength	0.32628 Å
Grain size	50 µm

Indexing algorithms

- Peak search/ reduction of data

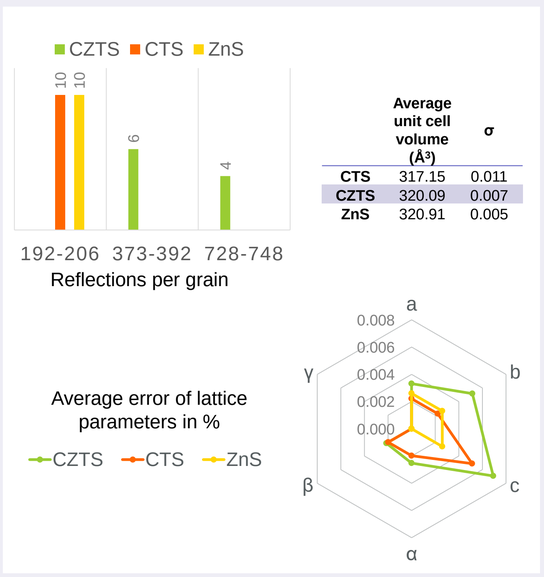
The diffraction images are composed of bright spots which are identified by applying a threshold. All pixels above the threshold are collected into connected objects.
The output file contains all the information for indexing the grains.

- GrainSpotter

Identify grains by finding vertices in orientation space and optimize the position and orientation of the identified grains.
It requires the previous knowledge of the phase. Thus, for a multiphase material, the algorithm is applied once for each phase.

- Multigrain crystallography

The candidate grains are found by searching for crystallographic planes, using a Dirac comb convoluted with box function as filter. Next, the candidate grains are validated and the unit cell is optimized. No a priori crystallographic knowledge is required.



	Average unit cell volume (Å³)	σ
CTS	317.15	0.011
CZTS	320.09	0.007
ZnS	320.91	0.005

Top: GrainSpotter identified 30 grains fitted to CZTS. Completeness of the grains (observed/expected reflections) for ZnS and 60% of CZTS is above 90%, whereas and for CTS is around 25%. The volume of each phase corresponds to the unit cell of the phases. Bottom right: Average error among lattice parameters of the unit cells of the identified grains.

Preliminary analysis

GrainSpotter: kesterite, tetragonal CTS and cubic ZnS are discerned by fitting them all to the tetragonal structure of kesterite. Moreover, unit cell volume, and the number of reflections per grain can help to identify the phase of the grain.

Multigrain Indexing algorithm fully extracted 30 grains and phases could be assigned accordingly the proposed lattice parameters with less than 0.008% average error in lattice parameters. The lattice parameters of the proposed unit cell are correlated to those of the actual phases.

Future work

Characterize quantitatively the phases in CZTS films and provide the volume fraction of each phase within a illuminated area.
Apply multigrain indexing algorithm to retrieve a larger number of grains.
Structural refinement of the individual grains and its dynamics within the bulk.
Multigrain crystallography approach has the potential to be an integral part of solar cell research.
Ideally, it can differentiate between CZTS and its secondary phases as these have different space groups that can be resolved in 3D reciprocal space.

Aknowledgements

Xnovotech, Nanna Wahlberg

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