Understanding the structural disorder of $(Ag_xCu_{1-x})_2ZnSnSe_4$ based kesterite semiconductor by neutron diffraction study

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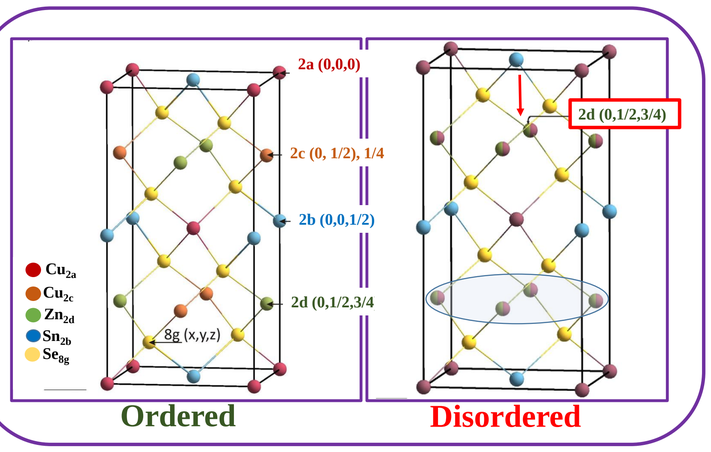
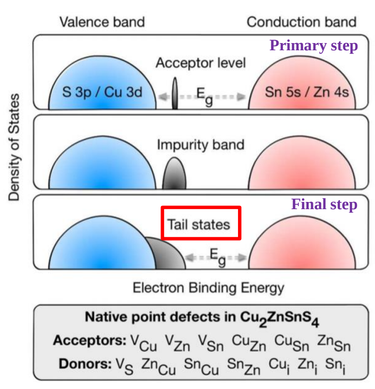
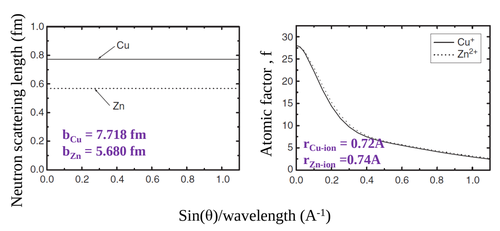
The quaternary semiconductor Cu2ZnSnSe4 (CZTSe) is a promising environment-friendly and low-cost material as a solar cell absorber layer with a power conversion efficiency of 11.6%[1]. Its photovoltaic performance is currently limited due to its disorder between the Copper & Zinc lattice sites, which creates band tailing and creates voltage deficit. By replacing Cu in CZTSe with isovalent Ag, whose ionic radius is larger than that of Cu and Zn, the density of I–II antisite defects could be suppressed. This work has been done to quantify the cation disorders on all cation symmetry sites and the effect of substitution of Ag in the CZTSe crystal structure. $(Ag_xCu_{1-x})_2ZnSnSe_4$ (A/CZTSe) samples with different compositions were synthesized by a solid-state reaction of the pure element in an evacuated quartz tube. Structural analysis of stoichiometric & off- stoichiometric samples were performed using Raman and synchrotron powder diffraction including Rietveld refinement. A neutron diffraction experiment is performed to fully understand the cation distribution analysis in A/CZTSe powder sample as Cu^+ and Zn^{2+} are not distinguishable using conventional X-ray diffraction method due to their isoelectronic character but there is a significant difference in their neutron scattering length (b_{Cu} = 7.718 fm, b_{Zn} = 5.680 fm)[2,3]. It is found that powder A/CZTSe adopts the kesterite type structure with a partial disorder of copper and zinc on the two Wyckoff position 2c and 2d. Sn has been found on Wyckoff position 2b (0, 0, ½), whereas Cu/Zn is located on 2a (0, 0, 0), 2c (0, ½ , 1/4) and 2d (0, ½ , ¾) sites. There is a presence of copper vacancies (V_{Cu}), various cation anti-site defects (Cu_{Zn}, Zn_{Cu}, Zn_{Sn}, and Sn_{Zn}) have been found for different compositions. This work will also answer the effectiveness of Ag as a substitution of Cu in kesterite based CZTSe, to suppress anti-site disorder.

Our goal --- to quantify structural defects by neutron diffraction experiment







$$F = \sum b_n \exp[(2\pi i)(hx_n + ky_n + lz_n)]$$

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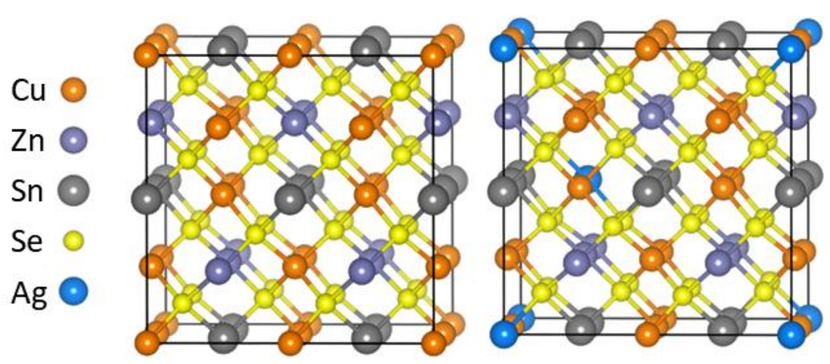
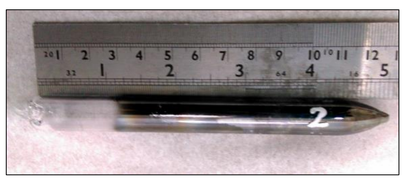


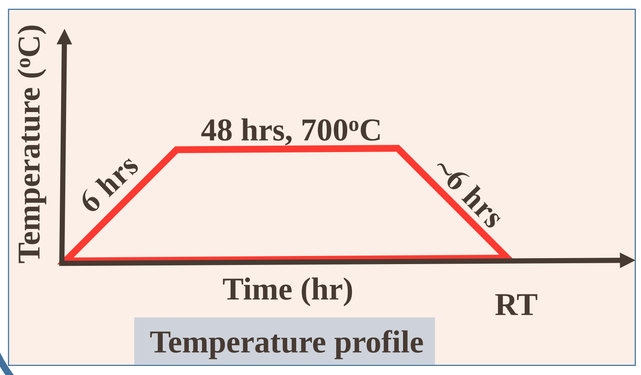
Experimental method

A/CZTSe powder sample was prepared by solid state reaction

1. Ag, Cu, Zn, Sn, Se powder sealed in quartz tube



2. Heating inside the furnace~60hrs



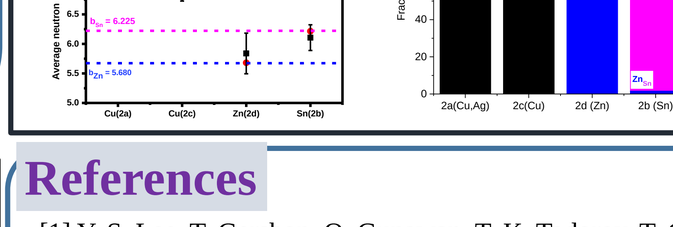
Temperature profile

3. Grinding inside mortar

4. Powder A/CZTSe

Result and discussions

I. Phase identification by synchrotron XRD and Raman



II. Average neutron scattering length analysis[4]

Experimental average neutron scattering length ⟺ **Calculated average neutron scattering length**

$\bar{b}_{2a}$ (exp) = SOF_{2a}. b_{Cu}

$\bar{b}_{2c}$ (exp) = SOF_{2c}. b_{Cu}

$\bar{b}_{2d}$ (exp) = SOF_{2d}. b_{Zn}

$\bar{b}_{2b}$ (exp) = SOF_{2b}. b_{Sn}

From refinement

$\bar{b}_j$ (calc) = $\sum_{k=Cu,Zn}^{Sn} SOF_j . bk$

From chemical composition

III. Neutron powder diffraction by ECHIDNA

IV. Quantification of defects

	V_{cu} (cm^{-3})	Zn_{Sn} (cm^{-3})	Zn_{Cu} (cm^{-3})
2a	8.30 X 10^{19}		1.5 X 10^{20}
2c			2.37 X 10^{20}
2b		1.58 X 10^{20}	

- 2c plane is mostly affected by Zn_{Cu}
- The highest defect density for Zn_{Cu} @ 2a & 2c

	V_{cu} (cm^{-3})	Zn_{Sn} (cm^{-3})	Zn_{Cu} (cm^{-3})
2a	3.0 X 10^{19}		1.2X10^{20}
2c	1.6 X 10^{20}		1.27X10^{20}
2b		5.22 X 10^{19}	

- Ag prefers to occupy in 2a plane
- Defect density decreased for Zn_{Sn} after Ag-alloying

Summary

- The samples have been structurally characterized with neutron diffraction technique with joint Rietveld refinement.
- Ag- is an effective substitute to replace Cu, to suppress disorder i.e. V_{Cu} Zn_{Sn}, Zn_{Cu} antisites.
- As a main outcome, different types and concentrations of intrinsic point defects and the Cu and related disorder have been determined.

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References

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