Experimental report

29/08/2024

Proposal: 5-23-801 **Council:** 4/2023

Title: Crystal structure and structural disorder in Ge-containing quaternarychalcogenide semiconductors for photovoltaic applications

Research area: Materials

This proposal is a new proposal

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Samples: Cu2MnGe(Se1-xSx)4
Cu2Zn(GeySn1-y)Se0.8S3.2

Instrument	Requested days	Allocated days	From	To
D2B	5	2	08/09/2023	10/09/2023

Abstract:

Kesterite-type based thin films solar cell technologies are mainly based on polycrystalline absorber layers. A promising low cost alternative technology uses Cu2ZnSn(S,Se)4 (CZTSSe) monograins (single crystals of 50-100 ¿m size) which are fixed in a polymer matrix to form a flexible solar cell. It is agreed in literature that large band tailing observed in Cu-based quaternary chalcogenide semiconductors causes voltage losses limiting the efficiency of the devices. The Cu/Zn disorder is discussed as a possible reason for this band tailing. The experimental determination of the order parameter Q which is a quantitative measure of the degree of Cu/Zn disorder requires a differentiation between the isoelectronic cations Cu+ and Zn2+. Introducing Ge and/or Mn, could be a way to avoid this disorder. We will perform a detailed structural investigation of Cu2Zn(GeySn1-y)(Se0.2S0.8)4 and Cu2MnGe(Se1-xSx)4 solid solutions, showing how structural properties and PV device performance parameters are correlated. These findings will pave the way to advanced band gap engineering methodology by cation and anion mutation.

Experimental report

Crystal structure and structural disorder in Ge-containing quaternary chalcogenide semiconductors for photovoltaic applications: $Cu_2MnGe(Se_{1-x}S_x)_4$ and $Cu_2Zn(Ge_ySn_{1-y})Se_{0.8}S_{3.2}$

Due to the reduction of the number of requested days from 5 to 3, the title of the experiment was modified to accommodate for the change and resulted in:

Crystal structure and structural disorder in Ge-containing quaternary chalcogenide semiconductors for photovoltaic applications: $Cu_2MnGe(Se_{1-x}S_x)_4$

In this study, we conducted a detailed structural investigation of a sets of chalcogenide absorbers in which a full cation substitution of Zn by Mn and Sn by Ge was applied in CZTSSe resulting in $Cu_2MnGe(Se_{1-x}S_x)_4$ (11 powder samples with x=0-1; 3g each). In the set the S/(S+Se) ratio varied systematically. Neutron powder diffraction experiments at ambient temperature were performed at D2B for 10 CMGSSe samples. Structural parameters and cation site occupancies were obtained by Rietveld analysis (FullProf) [1] of the data using the wurz-stannite structure as the starting model of refinement (e.g. Fig. 1).

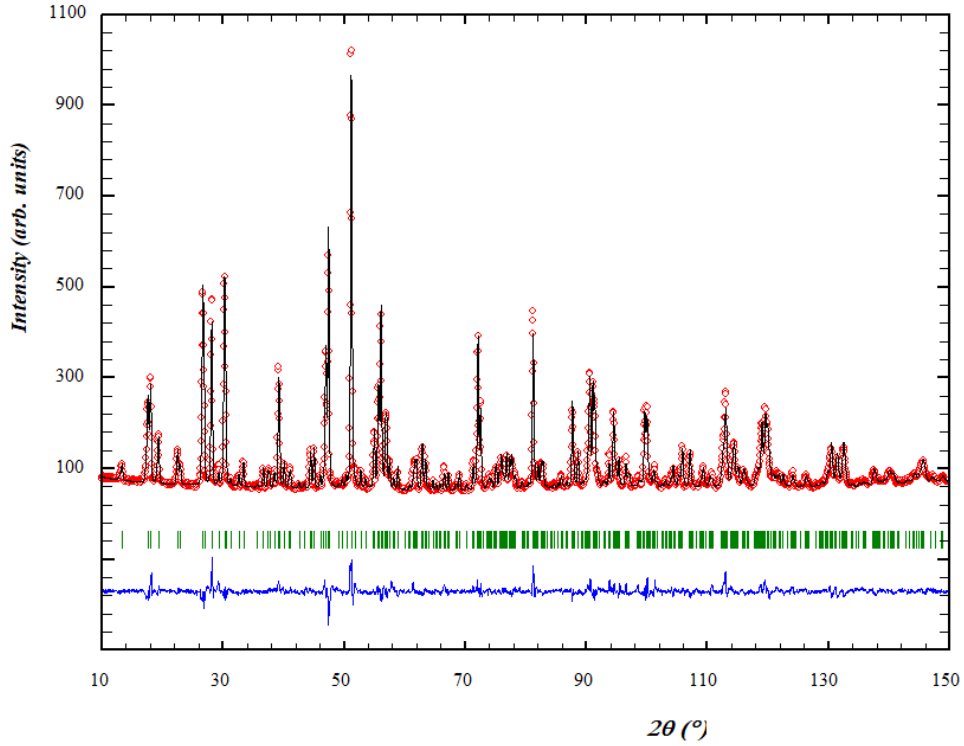

Fig.1 Rietveld analysis of neutron diffraction data for $Cu_2MnGeSe_4$.

The method of the average neutron scattering length analysis [2] was applied to determine the distribution of the cations Cu^{+}, Mn^{2+} and Ge^{4+} on the structural cation sites of the wurz-stannite type structure. The experimental average neutron scattering lengths of the four cation sites 2*a*, 2*a*, 4*b* and 2*a* were calculated as described earlier [2,3,4]. The resulting cation distribution is presented in Fig.2

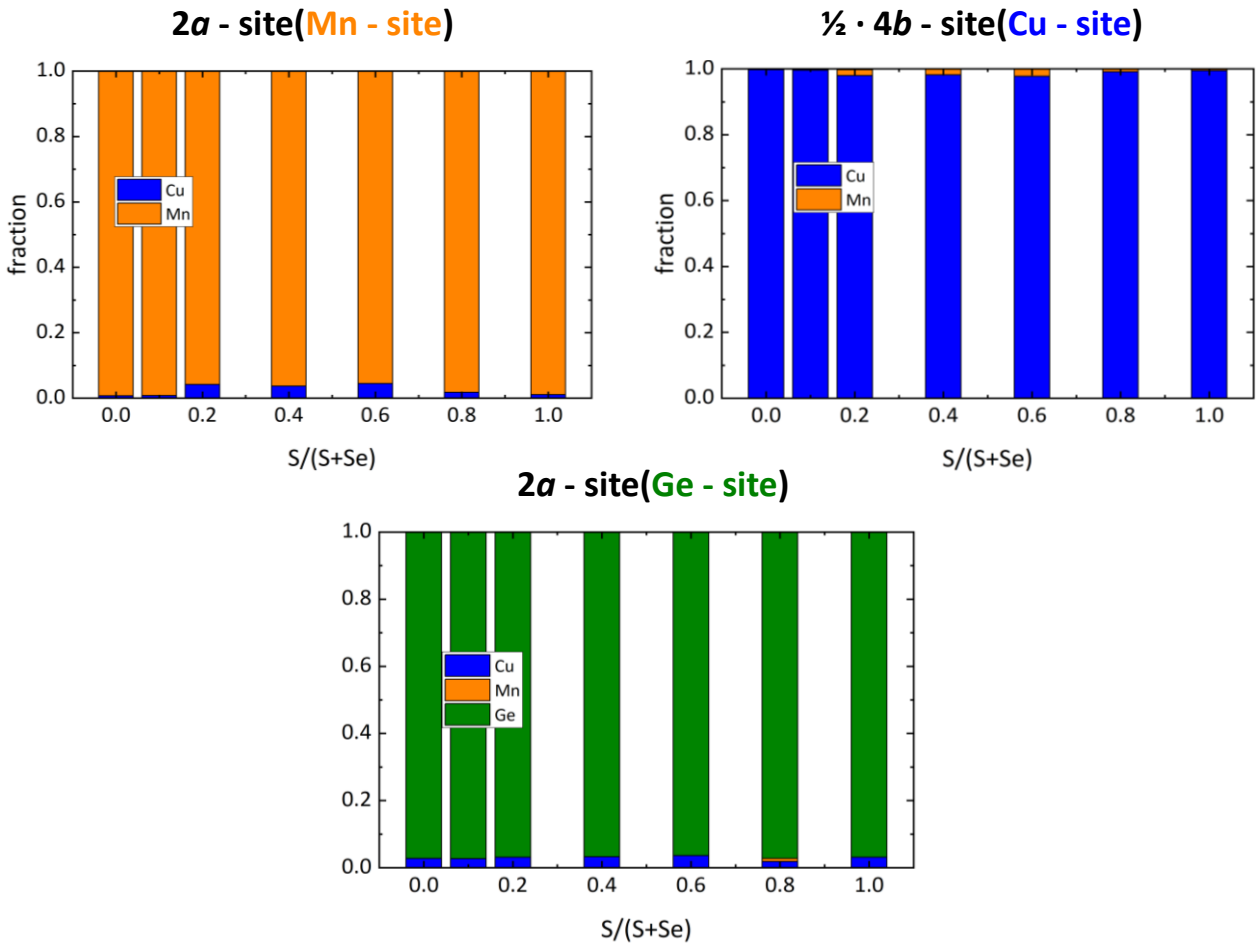

Fig.2 Resulting cation distribution of the structural sites 2a, 4b and 2a for $Cu_2MnGe(Se_{1-x}S_x)_4$ solid solution, obtained from in-depth analysis of neutron diffraction data by the average neutron scattering length analysis method.

The following conclusions were made based on the performed analysis: formation of intrinsic point defects according to the off-stoichiometry type was confirmed, additional Cu_{Mn} and Mn_{Cu} anti-site defects in amounts corresponding to Cu/Mn swapping were found. The Cu/Mn swapping was increasing with increasing anion mixing.

[1] Juan Rodriguez-Carvajal and Thierry Roisnel, www.ill.eu/sites/fullprof

[2] S. Schorr, *X-Ray and Neutron Diffraction on Materials for Thin-Film Solar Cells*, in *Advanced Characterization Techniques for Thin Film Solar Cells*, T.K.a.U.R. D. Abou-Ras, Editor. 2011, Wiley-VCH Verlag GmbH & Co. KGaA. 347.

[3] G. Gurieva, L. E. Valle Rios, A. Franz, P. Whitfield, S. Schorr, *Journal of applied physics* 123, 161519 (2018)

[4] G. Gurieva, M. Dimitrievska, S. Zander, A. Pérez-Rodríguez, V. Izquierdo-Roca, S. Schorr, physica status solidi (c), **12(6),** 588, (2015)