

## Cation order determination in kesterite-type quaternary semiconductors by Multiple Edge Anomalous Diffraction (MEAD)

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The quaternary chalcogenide semiconductors  $\text{Cu}_2\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{X}_4$  ( $\text{B}^{\text{II}} = \text{Zn, Fe}$ ;  $\text{C}^{\text{IV}} = \text{Sn, Ge, Si}$ ;  $\text{X} = \text{S, Se}$ ) have drawn wide attention for their potential applications in many fields [1]. Depending on their band gaps these materials are interesting for thin film solar cells, high-temperature thermoelectric materials, and nonlinear optics. Solid solutions of both cations and anions allow fine tuning of physical properties. It is well established that the cation arrangement in the respective structure is crucial for the electronic properties. However, often the cations involved are isoelectronic or nearly so and cannot be distinguished by routine laboratory X-ray diffraction. Neutron and anomalous X-ray diffraction have been used to overcome this problem. A variant of the later, Multiple Edge Anomalous Diffraction (MEAD) [2] was found by us to work particularly well. This method calls for measuring the energy dependency of the intensity of individual Bragg peaks around the X-ray absorption edge of a chemical element (Figure 1).

The compounds listed above crystallize in structure types derived by cation ordering from the cubic sphalerite type or the hexagonal wurtzite type crystal structure. The particular cation arrangement results either in kesterite or wurtz-kesterite structures, which are characterized by the presence of  $\text{Cu}^{\text{I}}\text{-B}^{\text{II}}$  and  $\text{Cu}^{\text{I}}\text{-C}^{\text{IV}}$  layers (perpendicular to the longest crystallographic axis). Alternatively, stannite or wurtz-stannite structures are formed, with cations arranged in  $\text{B}^{\text{II}}\text{-C}^{\text{IV}}$  and pure  $\text{Cu}^{\text{I}}$  layers. The actual type is often hard to establish and literature structures are sometimes just based on assumptions. MEAD was used to confirm the cation structure type of  $\text{Cu}_2\text{FeSnS}_4$ ,  $\text{Cu}_2\text{GaGeS}_4$ ,  $\text{Cu}_2\text{ZnSnSe}_4$ ,  $\text{Cu}_2\text{ZnSiSe}_4$  and  $\text{Cu}_2\text{ZnGeSe}_4$ . Materials crystallizing in the kesterite structure in particular are prone to cation disorder within the  $\text{Cu}^{\text{I}}\text{-B}^{\text{II}}$  layers. Depending on the compound, the degree of cation disorder can change heavily with off-stoichiometry or thermal treatment. In these cases, MEAD spectra supply a robust way of quantification. This works particularly well for compounds where all cations are isoelectronic, like  $\text{Cu}_2\text{ZnGeSe}_4$ . Joint Rietveld refinement at multiple energies also profits from prior MEAD analysis limiting the range of potential options.

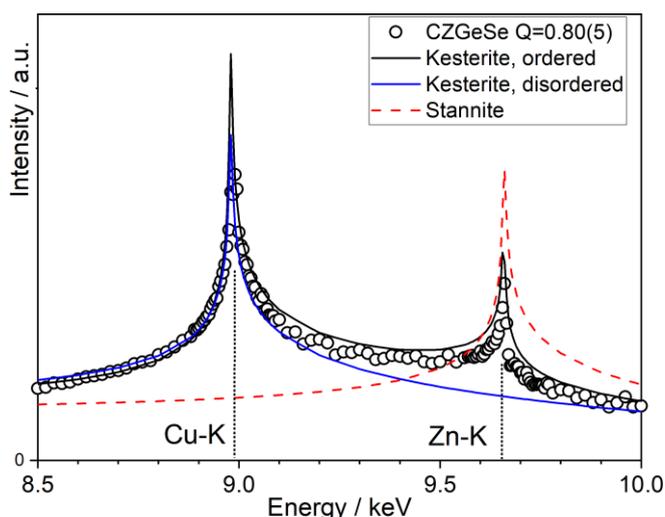


Fig. 1 Observed and simulated MEAD spectra of  $\text{Cu}_2\text{ZnGeSe}_4$  for Miller index 011

- [1] Schorr, S. and G. Gurieva, Energy band gap variations in chalcogenide compound semiconductors: influence of crystal structure, structural disorder, and compositional variations, in *Crystallography in Materials Science: From Structure-Property Relationships to Engineering*, S. Schorr and C. Weidenthaler, Editors. 2021, Walter de Gruyter GmbH & Co KG: Berlin, Boston. p. 123 - 138.
- [2] Többens, D.M., et al., Cation distribution in  $\text{Cu}_2\text{ZnSnSe}_4$ ,  $\text{Cu}_2\text{FeSnS}_4$  and  $\text{Cu}_2\text{ZnSiSe}_4$  by multiple-edge anomalous diffraction. *Acta Crystallographica Section B-Structural Science Crystal Engineering and Materials*, 2020. 76: p. 1027-1035.