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## An Anomalous Diffraction study of $\text{Cu}_2\text{Zn}(\text{Ge,Si})\text{Se}_4$

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While the silicon-rich members of the series  $\text{Cu}_{2-x}\text{Zn}_x(\text{Ge,Si})\text{Se}_4$  crystallize in wurtzite type structure [1], germanium-rich samples adopt a tetrahedral structure of the kesterite type [2]. Identification of the silicon site is straightforward from regular X-ray diffraction, as  $\text{Si}^{4+}$  is a light element and has less electrons than the other cations. However,  $\text{Cu}^{1+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ge}^{4+}$  are all isoelectronic and have very similar form factors. The kesterite type of the cation distribution has been established by neutron diffraction [2].

We now applied anomalous X-ray diffraction to this system, using Rietveld refinement and Multiple Edge Anomalous Diffraction (MEAD) [1] with data taken at the K-absorption edges of Cu, Zn, and Ge. These energies are accessible at beamline KMC-2, BESSY II, Berlin [3]. In contrast to previous studies, where  $\text{Sn}^{4+}$  was the M(IV) species in the structure [1], in  $\text{Cu}_2\text{ZnGeSe}_4$  all cations have very similar scattering power under normal conditions. This results in superstructure peaks (with respect to the cubic ZnS parent structure) that are very weak. For Rietveld analysis this is a drawback, as the optimization will be dominated by the main peaks of the parent structure. In MEAD, however, it increases the effect of the changing scattering power close the absorption edges. As a result, not only are Kesterite and Stannite types clearly distinguishable at the Cu-K edge (figure 1), also the Cu/Zn ordering within the Kesterite structure is clearly detectable and quantifiable at the Zn-K edge. The structure of the MEAD spectrum at the Ge-K edge was found to be very sensitive to the presence of vacancies at the Ge 2b site of the structure at the Si-free composition. Within the compositional range,  $\text{Si}^{4+}$  has very similar influence.

[1] D. M. Töbrens *et al.*, Cation distribution in  $\text{Cu}_2\text{ZnSnSe}_4$ ,  $\text{Cu}_2\text{FeSnSe}_4$  and  $\text{Cu}_2\text{ZnSiSe}_4$  by multiple-edge anomalous diffraction. *Acta Crystallographica* B76, 1027-1035 (2020)

[2] G. Gurieva *et al.*, Cu-Zn disorder in  $\text{Cu}_2\text{ZnGeSe}_4$ . A complementary neutron diffraction and Raman spectroscopy study. *Journal of Physics and Chemistry of Solids* 99, 100-104 (2016)

[3] Helmholtz-Zentrum Berlin für Materialien und Energie, KMC-2: an X-ray beamline with dedicated diffraction and XAS endstations at BESSY II. *Journal of large-scale research facilities*, 2, A49 (2016)

Figure 1: Observed and simulated MEAD spectra of Bragg peak 011 of  $\text{Cu}_{2.03}\text{Zn}_{1.060}\text{Ge}_{0.947}\text{Se}_4$ . The structure is highly ordered Kesterite. The peak at the Ge-edge indicates  $\leq 10\%$  vacancies at the Ge 2b site.

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