An anomalous diffraction study of $Cu_2Zn(Ge,Si)Se_4$

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While the silicon-rich members of the series $Cu_2Zn(Ge,Si)Se_4$ crystallize in wurtz-kesterite type structure [1], germanium-rich samples adopt a tetrahedral structure of the kesterite type [2] (figure 1). Identification of the silicon site is straightforward from regular X-ray diffraction, as Si^{4+} is a light element and has less electrons than the other cations. However, Cu^{1+}, Zn^{2+}, and Ge^{4+} are all isoelectronic and have very similar form factors. The kesterite type of the cation distribution of $Cu_2ZnGeSe_4$ has been established by neutron diffraction [2], which can distinguish these elements.

We now applied anomalous X-ray diffraction to this system, using Rietveld refinement and Multiple Edge Anomalous Diffraction (MEAD) [3] with data taken at the K-absorption edges of Cu, Zn, and Ge. These energies are accessible at beamline KMC-2, BESSY II, Berlin [4]. The Si-rich end member $Cu_2ZnSiSe_4$ has previously shown to be wurtz-kesterite by MEAD [1]. With the correct structure type, the degree of Cu/Zn disorder (see caption figure 1) within the Si-rich region of the series could be determined reliably from multiple-energy Rietveld refinement. For the Ge-rich, tetragonal structures, MEAD was found to be the method of choice. In contrast to previous studies, where Sn^{4+} was the M(IV) species in the structure [1], in $Cu_2ZnGeSe_4$ 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 2), also the Cu/Zn ordering within the Kesterite structure is clearly detectable and quantifiable at the Zn-K edge.

The degree of Cu/Zn order for the full series could thus be compared to other structural and physical parameters within the $Cu_2Zn(Ge,Si)Se_4$ solid solution series.

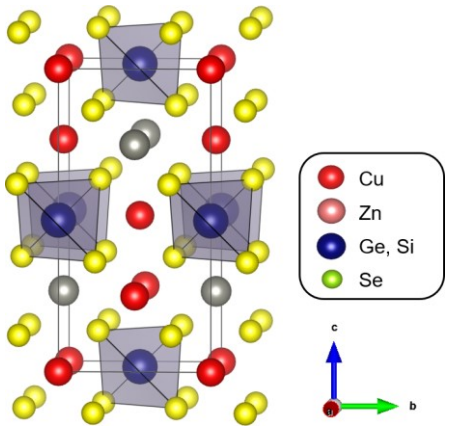

Figure 1. Kesterite structure with fully ordered Cu/Zn layers. Disorder affects cation distribution in Cu/Zn layers. Stannite type would have pure Cu layers and Zn/(Ge,Si) layers. Wurtz-kesterite type structure is comparable in this regard.

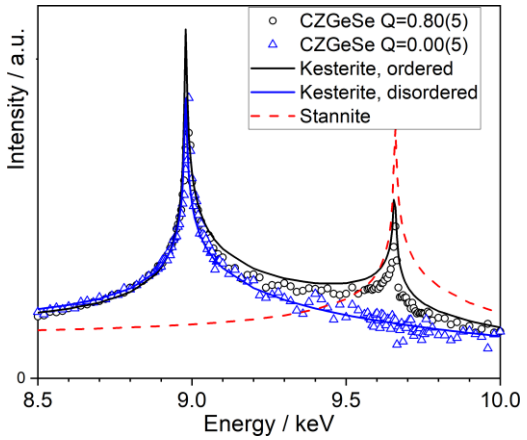

Figure 2. Observed and simulated MEAD spectra of Bragg peak 011. Samples are Kesterite type with high degree of Cu/Zn order ($Cu_{2.06}Zn_{0.99}Ge_{0.99}Se_4$) and disordered ($Cu_{2.28}Zn_{0.95}Ge_{0.96}Se_4$), respectively.

[1] Többens, D. M., Gurieva, G., Niedenzu, S., Schuck, G., Schorr, S. (2020) *Acta Cryst. B* **76**, 1027.

[2] Gurieva, G., Többens, D. M., Valakh, M. Y., Schorr, S. (2016) *J. Phys. Chem. Solids* **99**, 100.

[3] Collins, B. A., Chu, Y. S., He, L., Haskel, D. & Tsui, F. (2015). *Phys. Rev. B* **92**, 224108.

[4] Helmholtz-Zentrum Berlin für Materialien und Energie (2016) *J. Large-Scale Res. Facilities* **2**, A49

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