Electronic Supplementary Information

Structural characterization of off-stoichiometric kesterite-type Cu$_2$ZnGeSe$_4$ compound semiconductors: From cation distribution to intrinsic point defect density

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Figure S1: Averaged cation ratios obtained from WDX line scans for different grains of a C-type CZGSe sample. C-type samples heavily tend to form several kesterite phases after only one homogenization step (left panel). In some cases the repetition of homogenization step successfully led to the formation of a single kesterite phase (right panel).

The calculation of the sum formulae and the off-stoichiometry type fraction is exemplarily shown for A/B-type composition:

\[
\begin{align*}
\frac{Zn}{Ge} &= \frac{(1 + a)}{1}, \text{ solving for } a \text{ delivers } a_x = \frac{Zn}{Ge} - 1 \\
\frac{Cu}{(Zn + Ge)} &= \frac{(2 - 2a)}{(1 + a + 1)}, \text{ solving for } a \text{ delivers } a_x = \frac{Zn}{Ge} - 1 \\
\frac{Zn}{Ge} &= \frac{(1 + 3b)}{(1 - b)}, \text{ solving for } b \text{ delivers } b_y = \frac{Zn}{Ge} + 3 \\
\frac{Cu}{(Zn + Ge)} &= \frac{(2 - 2b)}{(1 + 3b + 1 - b)}, \text{ solving for } b \text{ delivers } b_x = \frac{Zn}{Ge} - 1 \\
\end{align*}
\]

(A-type)

\[
\begin{align*}
\frac{Zn}{Ge} &= \frac{(1 + 3b)}{(1 - b)}, \text{ solving for } b \text{ delivers } b_y = \frac{Zn}{Ge} + 3 \\
\frac{Cu}{(Zn + Ge)} &= \frac{(2 - 2b)}{(1 + 3b + 1 - b)}, \text{ solving for } b \text{ delivers } b_x = \frac{Zn}{Ge} - 1.
\end{align*}
\]

(B-type)

The type fraction is determined by linear interpolation between the two type lines adjoining the composition of a sample:

\[
\begin{align*}
A \text{ [\%]} &= \left(\frac{b_x - \frac{Cu}{(Zn + Ge)}}{b_x - a_x}\right) \cdot 100 \quad \text{(S5)}
\end{align*}
\]

\[
\begin{align*}
B \text{ [\%]} &= \left(\frac{\frac{Cu}{(Zn + Ge)} - a_x}{b_x - a_x}\right) \cdot 100 \quad \text{(S6)}
\end{align*}
\]
Figure S2 Refined XRD pattern of an off-stoichiometric G-F-type CZGSe sample containing ZnSe as secondary phase.

Figure S3 Unit cell volumes of off-stoichiometric CZGSe powder samples versus Cu/(Zn+Ge).
Figure S4 Refined neutron diffraction pattern of an off-stoichiometric, single-phase F-I-type CZGSe sample.

Figure S5 Overall point defect concentration in off-stoichiometric kesterite-type CZGSe powder samples in dependence of cation ratios (Cu/Zn disorder excluded; dashed lines are given as guides to the eyes).
Figure S6 Evolution of the stoichiometric coefficients $\nu$ of Cu, Zn, and Ge with changing Cu/(Zn+Ge).

Figure S7 Tauc plot of the diffuse reflectance data to deduce bandgap energies of CZGSe with different compositions.