

The effects of anion and cation substitution on the crystal structure of Cu-based quaternary chalcogenides

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The research of quaternary Cu-based chalcogenide semiconductors has caught a large interest for photovoltaic applications, as these materials consist of non-toxic and earth abundant elements. While being environmentally friendly and low cost and stable under environmental conditions, materials like $\text{Cu}_2\text{MnSnS}_4$ or $\text{Cu}_2\text{MnGeS}_4$ are very promising candidates for use as top cell absorbers in tandem solar cells, because they can cover a wide bandgap range of 1.52-1.72 eV (Beraich et al. 2020; Ramasamy et al. 2018). Compounds like $\text{Cu}_2\text{MnSnSe}_4$ could even be considered for the application in single junction solar cell with a band gap energy of 1.21 eV (Gurieva et al. 2022). This study presents new insight into the structural transformation mechanisms within the $\text{Cu}_2\text{Mn}(\text{Ge},\text{Sn})(\text{S},\text{Se})_4$ solid solution series via neutron powder diffraction.

Since Cu^+ and Ge^{4+} are isoelectronic cations and Mn^{2+} is electronic similar to Cu^+ and Ge^{4+} , they cannot be differentiated in a structural analysis based on X-ray powder diffraction data alone. However, their neutron scattering lengths are considerably different, that is why we apply neutron diffraction to analyze the crystal structure of $\text{Cu}_2\text{Mn}(\text{Ge},\text{Sn})(\text{S},\text{Se})_4$ mixed crystals. Moreover, the basis of our investigations is a careful determination of the chemical composition of the mixed crystals by WDX spectroscopy.

The endmembers of the $\text{Cu}_2\text{Mn}(\text{Ge},\text{Sn})(\text{S},\text{Se})_4$ solid solution series crystallize in different structure types: $\text{Cu}_2\text{MnSnS}_4$ and $\text{Cu}_2\text{MnSnSe}_4$ crystallize in the tetragonal stannite-type structure (space group $I4_2m$), whereas $\text{Cu}_2\text{MnGeS}_4$ and $\text{Cu}_2\text{MnGeSe}_4$ adopt the orthorhombic wurtz-stannite structure (space group $Pmn2_1$). Thus, within the solid solution series with mixed cations a structural transition from the tetragonal to the orthorhombic crystal structure can be expected.

For the presented study the compounds were synthesized by solid state reaction of pure elements in evacuated silica tubes at temperatures of 730 °C (Se-only compounds), 740-780 °C (mixed anion compounds) and 800 °C (S-only compounds). The chemical composition and homogeneity of the synthesized polycrystalline powder materials were investigated by WDX spectroscopy using an electron microprobe system. It was revealed that the synthesized powders contained the desired phase as a chemically single, homogeneous quaternary phase with slight shifts in the stoichiometric composition as well known in this type of materials (Schorr et al. 2020). LeBail refinement of the powder X-ray diffraction data was used to determine the lattice parameters of the mixed crystals. The cation distribution in the unit cell was defined by applying the average neutron scattering length analysis method (Schorr 2011) which is based on the site occupancy factors determined by Rietveld refinement of the neutron diffraction data. The derived cation distribution model is the basis to conclude on the crystal structure and structural disorder as well as to elucidate the mechanism of structural phase transition.

It will be shown that Sn-rich mixed crystals adopt the stannite type structure, whereas Ge-rich mixed crystals of the mixed cation solid solution series adopt the wurtz-stannite type structure. Within the intermediate range, two chemically identical but structurally different quaternary phases coexist, adopting the tetragonal and the orthorhombic structure respectively. It will also be shown that the respective anions influence the concentration of intrinsic point defects differently and independent to the off-stoichiometric composition.

The results of the chemical composition study in combination with structural characterization and optical bandgap evaluation from diffuse reflectance of $\text{Cu}_2\text{Mn}(\text{Ge},\text{Sn})(\text{S},\text{Se})_4$ mixed crystals will be presented. These investigations enabled us not only to determine the type and concentration of intrinsic point defects, but to show as well the structure type transformation from the stannite- to the wurtz-stannite-type structure.

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