Faraday Discussions

Cite this: *Faraday Discuss.*, 2022, **239**, 51

ROYAL SOCIETY OF CHEMISTRY

PAPER

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The kesterite–stannite structural transition as a way to avoid Cu/Zn disorder in kesterites: the exemplary case of the $Cu_2(Zn,Mn)SnSe_4$

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Received 14th February 2022, Accepted 14th April 2022
DOI: 10.1039/d2fd00042c

The solid solution series between $Cu_2ZnSnSe_4$, crystallizing in the kesterite type structure, and $Cu_2MnSnSe_4$, adopting the stannite type structure, *i.e.* $Cu_2(Zn_{1-x}Mn_x)SnSe_4$, was studied by a combination of neutron and X-ray powder diffraction. Powder samples with $0 \leq x \leq 1$ were synthesized by the solid state reaction of the pure elements and it was confirmed by wavelength-dispersive X-ray spectroscopy that each contained a homogeneous, off-stoichiometric quaternary phase. The lattice parameters and cation site occupancy factors were determined simultaneously by the Rietveld analysis of the neutron and X-ray powder diffraction data. The refined site occupancy factors were used to determine the average neutron scattering length of the cation sites in the crystal structure of the $Cu_2(Zn_{1-x}Mn_x)SnSe_4$ mixed crystals, from which a cation distribution model was derived. For the end member $Cu_2ZnSnSe_4$, the disordered kesterite structure was confirmed and for $Cu_2MnSnSe_4$, the stannite structure was confirmed. The cross-over from the kesterite to stannite type structure by $Zn^{2+} \leftrightarrow Mn^{2+}$ substitution in the $Cu_2Zn_{1-x}Mn_xSnSe_4$ solid solution can be seen as a cation re-distribution process among the positions (0, 0, 0), (0, $\frac{1}{2}$, $\frac{1}{4}$) and (0, $\frac{1}{4}$, $\frac{3}{4}$), including Cu^+, Zn^{2+} and Mn^{2+}. The Sn^{4+} cation does not take part in this process and remains on the 2b site. Moreover, the cross-over is also visible in the ratio of the lattice parameters *c*/(2*a*), showing a characteristic dependence on the chemical composition. The order parameter *Q*, the quantitative measure of Cu/B^{II} disorder (B^{II} = Zn and Mn), shows a distinct dependence on the Mn/(Mn + Zn) ratio. In Zn-rich $Cu_2(Zn_{1-x}Mn_x)SnSe_4$ mixed crystals, the order parameter $Q \sim 0.7$ and drops to $Q \sim 0$ (complete Cu/B^{II} disorder) in the compositional region $0.3 \geq x \geq 0.7$. In Mn-rich $Cu_2(Zn_{1-x}Mn_x)SnSe_4$ mixed crystals, adopting the stannite type structure, the order parameter reaches almost $Q \sim 1$ (order). Thus, it can be concluded that only Mn-rich $Cu_2(Zn_{1-x}Mn_x)SnSe_4$ mixed crystals do not

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