

MS20-P3 Structural characterisation of $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ by neutron diffraction.

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$\text{Cu}_2\text{ZnGeSe}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ are quaternary semiconductors belonging to the adamantine compound family, contain only abundant elements, which makes these materials promising candidates for engineering on their base of different high-efficient and low-cost devices [1]. $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ solar cells with Ge alloying recently reached efficiency of 8.4% [2]. CZTSe crystallizes in the kesterite type structure (space group) [3]. X-ray diffraction used for structural characterization of CZGSe was reported in the literature, and it suggests that it shows the stannite type structure (space group) [4]. In contrast to these findings recent first principal calculation predicts the kesterite type phase (space group) to be the ground state structure for this material [5]. A differentiation between the isoelectronic cations Cu^+ , Zn^{2+} and Ge^{4+} and consequently kesterite and stannite is not possible using X-ray diffraction due to their similar scattering power. But neutrons diffraction can solve this problem; the coherent scattering lengths are sufficiently different [6]. By this method our group could show that both $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnGeSe}_4$ occur in the kesterite structure. [3, 7]. A detailed structural analysis of Zn rich off-stoichiometric (B-F and F-D type mixtures) $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ powder samples, grown by solid state reaction, was performed by neutron diffraction at the fine resolution neutron powder diffractometer E9 at BER II ($\lambda = 1.7986 \text{ \AA}$, RT). Rietveld refinement of diffraction data using the FullProf suite software [8] lead to accurate values of *a* and *c* lattice constants and site occupancy factors. The latter have given insights into the cation distribution within the crystal structure of $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ solid solutions with different *x* values. The correlated information about changes in lattice parameters and cation site occupancies, details on the existing intrinsic point defects and their concentrations will be discussed.

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MS20-P4 Luminescent copper(I) complexes with chelating N^N and P^P ligands and application in light-emitting electrochemical cells (LECs)

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New lighting devices such as LECs (Light-Emitting Electrochemical Cells) and OLEDs (Organic Light-Emitting Diodes) promise considerable savings in terms of both energy and resources, due their generation of visible light as main product instead of heat with light only as a by-product. We here present light-emitting copper(I) complexes, which are a low-priced alternative to materials based on less abundant elements such as ruthenium or iridium. Encouraging results have been obtained by coordinating copper(I) with P^P chelating bisphosphanes such as POP (bis[(2-diphenylphosphino)phenyl] ether) and xantphos (4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene), in combination with 2,2'-bipyridines, 2,2':6',2''-terpyridines and other chelating N^N-donors. The copper(I) systems are very susceptible to the steric demand of the ligands. In order to stabilize the d^{10} state of Cu(I) and protect it from being oxidized, the ligands should be coordinated in a tetrahedral geometry. While smaller ligands fail to prevent the tetrahedral complex structure from flattening, sterically too challenging ligands can lead to mixtures of heteroleptic $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ with homoleptic $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ and $[\text{Cu}(\text{P}^{\wedge}\text{P})_2]^+$ complexes. Especially substitution at the 6-position of the bipyridine has considerable impact on the stability and structural features of the heteroleptic $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ complexes. Interesting complex structures were obtained by attaching various alkyl and CF_3 -groups, halogens, pyridine and aryl groups to the bipyridine. Depending on the steric demand and electronic properties of the bipyridine, the dihedral angle between the ligands as well as the torsion and tilting of the bipyridine rings (see angles I, II, III in Fig. 1 a)) vary. Furthermore, the coordinating bisphosphanes can adapt different conformers (see Fig. 1 b)), which is confirmed by crystal structures and supported by low-temperature NMR studies. For N^N = 2,2':6',2''-terpyridine, a fourfold as well as a rarely found fivefold coordination of the copper(I) center is present in the crystal structure. Further alteration of the ligands will provide much needed insights into the correlation between structural features of the complexes and important properties such as electroluminescence, lifetime of the excited state, quantum yield and ion mobility.