

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

Galina Gurieva¹, Alexandra Franz¹, Susan Schorr^{1,2}

1. Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany
 2. Free University Berlin, Institute of Geological Sciences, Malteserstr. 74-100, Berlin, Germany

email: galina.gurieva@helmholtz-berlin.de

$\text{Cu}_2\text{ZnGeSe}_4$ 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.

[1] K. Tanaka et. al., Sol. Energy Mater. Solar Cells 91 (2007) 1199

[2] Q. Guo et al., Sol. Energy Mater. Sol. Cells, 105 (2012)132.

[3] S. Schorr, Solar Energy Materials and Solar Cells, 95 (2011)1482.

[4] O.V. Parasyuk et. al., J. Alloys Comp. 329 (2001) 202–207.

[5] S. Chen et.al., Phys. Rev. B, 82 (2010), p. 195203 (8pp.)

[6] V.F. Sears, Neutron News 3 (3), 26–37, (1992).

[7] G. Gurieva, D.M.Töbrens, M. Valakh, S.Schorr, Phys and Chem of Solids. Submitted.

[8] Juan Rodriguez-Carvajal and Thierry Roisnel, www.ill.eu/sites/fullprof

Keywords: CZTGeSe, neutron diffraction

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

Sarah Keller¹, Alessandro Prescimone¹, Fabian Brunner¹, Edwin C. Constable¹, Catherine E. Housecroft¹

I. Department of Chemistry, University of Basel

email: sa.keller@unibas.ch

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 [Cu(N[^]N)(P[^]P)]⁺ with homoleptic [Cu(N[^]N)₂]⁺ and [Cu(P[^]P)₂]⁺ complexes. Especially substitution at the 6-position of the bipyridine has considerable impact on the stability and structural features of the heteroleptic [Cu(N[^]N)(P[^]P)]⁺ complexes. Interesting complex structures were obtained by attaching various alkyl and CF₃-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.

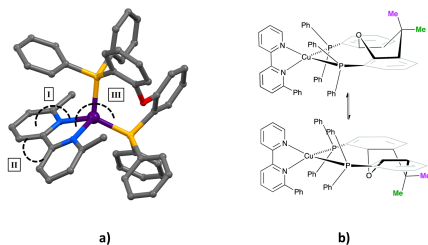


Figure 1. a) Characterizing angles of a typical Cu(POP)(bipyridine)[†] cation. b) Proposed conformers of [Cu(xantphos)(Phbp)][†] and interconversion pathway through inversion of the xanthene unit.

Keywords: Copper(I), Luminescence, Light-emitting electrochemical cells, LECs, bipyridine, bisphosphanes, conformers

MS20-P5 Structure and magnetocaloric properties of Gadolinium borohydrides

Pascal Schouwink¹, Emilie Didelot¹, Yong-Su Lee², Thomas Mazet³, Radovan Cerny[†]

1. University of Geneva
2. Korea Institute of Science and Technology
3. Université de Lorraine

email: pascal.schouwink@gmail.com

Recently, a thorough understanding of the building principles underlying inorganic metal borohydrides has promoted the search for functional materials outside the well-known field of hydrogen storage.¹ In particular, we can follow very simple design strategies based on a close structural relationship to metal oxides and halides. The low molecular mass per unit of the borohydride anion can be seen as a useful property for energy-related applications in general, where light and dense materials are often favoured. Here, we have explored if borohydrides may be potential magnetic coolers. We begin our investigations on these applications with the exploration of Gd-compounds, Gadolinium being the active magnetic ion in many benchmark cryogenic coolers. The results show that, as assumed from previous studies on Mn(BH₄)₂, the exchange interaction is very low across the BH₄ linker, and these materials can hence be considered paramagnetic salts down to very low temperatures. We present an illustrative and purposeful series of novel double-cation metal borohydride salts with a high spin density per unit mass, K_jGd(BH₄)_{4+j} (j = 0, 1, 2, 3), where the molar magnetic entropy change increases with j, while the number of Gd-Gd nearest neighbours decreases simultaneously, from 6 in Gd(BH₄)₃ to 0 in the double perovskites K₃Gd(BH₄)₆, Cs₂Gd(BH₄)₆ as well as in the novel structure type K₂Gd(BH₄)₅. For j = 0,1,3 the coordination polyhedron around Gd is an octahedron, whereas the 5-fold coordination is reported in two different geometries for j = 2 in K₂Gd(BH₄)₅, which results in a remarkable magnetic entropy change $-\Delta S_m$ of 54.6 J kg⁻¹K⁻¹ (9T). The differences in j lead to different dimensionalities of the Gd-BH₄ substructure, which comprises 2D and 3D networks as well as isolated polyanions, and are reflected in magnetization measurements. In the currently investigated compounds Potassium is used as a second counter-cation in order to build the double cation salts. There is room to improve the gravimetric magnetic entropy change by substituting K⁺ for molecules lighter in weight such as NH₄⁺. Such cationic substitutions are known to occur readily in complex hydrides¹ and a perspective will be presented on the synthesis and the potential behaviour of such materials.

Keywords: Borohydride, Magnetocaloric effect, Powder Diffraction, DFT