MS15-P22 Synthesis and structural characterization of off-stoichiometric $Cu_2ZnSnSe_4$

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$Cu_2ZnSnSe_4$ is a low cost alternative absorber material for solar cells. Record efficiency of 12.6% was reported for a CZTSSe based thin film solar cell [1]. The polycrystalline absorber layer exhibits an off-stoichiometric composition which causes intrinsic point defects (vacancies, anti-sites, interstitials) which determine the electronic properties of the material significantly.

This work focuses on the synthesis and characterization of off-stoichiometric CZTSe. In literature [2] off-stoichiometric types have been suggested, amongst them; A-type Cu-poor/Zn-rich; B-type Cu-poor/Sn-poor. We have synthesized powder samples by solid state reaction from pure elements in sealed evacuated silica tubes. The first reaction took place at 750°C with several temperature steps in between. After reaction samples were ground, pressed in pellets and annealed again.

To determine phase content and chemical composition of the obtained samples, an electron microprobe system equipped with wavelength dispersive X-ray analysis was used. The measurements proved the presence of CZTSe as main phase within all the different off-stoichiometric synthesized samples. The lattice parameters of the CZTSe main phase were determined by Rietveld analysis from XRD data. Refinements were performed by FullProf [3] with the kesterite structure model, because stoichiometric CZTSe crystallizes in the kesterite type structure [4].

Moreover, neutron powder diffraction experiments were performed at the Spallation Neutron Source in Oak Ridge/US as well as at the Berlin Research Reactor BERII in HZB/Germany. The neutron scattering length of Cu and Zn is different, therefore is possible to distinguish between Cu^+ and Zn^{2+} site occupation in the crystal structure. Further Rietveld refinements of neutron diffraction data additionally with the average neutron scattering length analysis method lead the determination of cation distribution, the Cu/Zn order-disorder in the 2*c* and 2*d* site and the formation of intrinsic point defects related to the according off-stoichiometric cation substitution type.

A study of the cation distribution and point defects formation in the crystal structure of the CZTSe phase concerning the different off-stoichiometry types will be presented.

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Keywords: kesterite, crystal structure

MS15-P23 Intermolecular interactions and second-harmonic generation properties of 1,5-diarylpentenynones

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The chalcone family (e.g. 1,3-diarylprop-2-en-1-ones) is well known to exhibit second-harmonic generation (SHG) properties [1] being crystallized in acentric crystals. To reveal factors responsible for crystallization of their quasi-planar derivatives in acentric space groups and the effect of –C≡C– bond on SHG properties, fourteen quasi-planar 1,5-diarylpentenynones were synthesized and their crystal structures were investigated. Seven of these compounds crystallize in acentric and chiral space groups. Intermolecular bonding was studied by means of periodic DFT calculations followed by the topological analysis of charge density within framework of the quantum theory of 'Atoms in Molecules' [2]. The role of the C–H···O interactions as driving force for supramolecular synthon formation has been demonstrated. Three types of C–H···O bonded synthons were revealed for this family (Figure). Those synthons are in accord with the charge distribution along the conjugated system that allows direct synthesis of acentric crystals of 1,5-diarylpentenynones. SHG properties for seven compounds crystallizing in chiral space groups have been investigated both theoretically and experimentally and confirmed prominent crystalline nonlinear optical susceptibility of this family. The crystal packing effects on calculated SHG properties have been estimated based on the recently proposed Charge Model. SHG measurements confirmed a validity of the Charge Model and demonstrated an efficiency of this family for potential application as materials for nonlinear optics.

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[1] *Nonlinear Optics of Organic Molecules and Polymers.* Ed. Nalwa, H. S. & Miyata, S. 1996. CRC Press, Boca Raton, Florida. [2] Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*. 1994. USA: Oxford University Press.

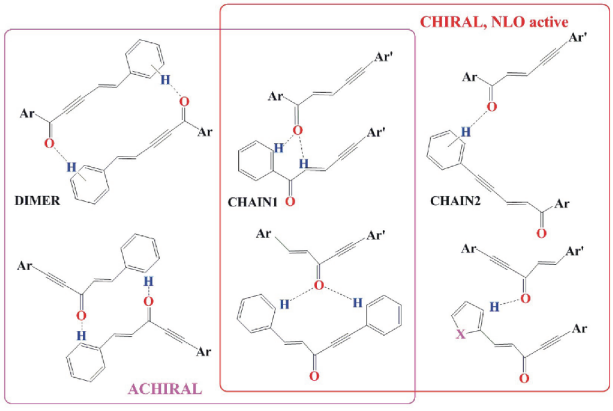

Figure 1. Schematic view of supramolecular syntons in crystals of 1,5-diarylpentenynones.

Keywords: 1,5-diarylpentenynones, second-harmonic generation properties, C–H···O interactions, charge density