Crystal structure variations and opto-electronic properties in alkali doped kesterite-type semiconductors

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Absorber layers based on kesterite-type semiconductors offer enormous potential for the fabrication of low-cost and environmentally friendly solar devices. These materials offer a direct tuneable bandgap, high absorption in the visible spectrum and rich possibilities for doping/alloying due to various anionic and cationic alloying series; p-type conductivity dominates. $Cu_2ZnSnSe_4$ (CZTSe) is investigated in this project. Advantages are the chemical composition of non-toxic elements abundant on Earth and the option of numerous synthesis routines. The main problem remains the low power efficiency of devices, mainly attributed to a high V_{OC} deficit. In particular, the influence of point defects and cation disorder is suspected. The structural flexibility can be described by the off-stoichiometriy model, where different types (A-L) can be distinguished according to the intrinsic point defects present [1], keeping the charge balance. This flexibility offers broad potential for defect engineering and the search for optimized compositions. To date the most efficient (power conversion efficiency: 12.6 % [2], 12.7 % [3]) devices are based on off-stoichiometric material (Cu-rich, Zn-poor, A-type) [2,3]; latest record (August 2021) was achieved with off-stoichiometric and Li-doped material [3]. The effects of (Li, Na, K) doping on off-stoichiometric CZTSe material are investigated in bulk powder samples. The overall objective of this work is to resolve the effects of alkali metal incorporation into off-stoichiometric bulk CZTSe and to characterise crystal structural variations as well as opto-electronic properties. Dopant incorporation is performed using two different approaches. For direct incorporation LiCl (NaCl, KCl respectively) is mixed with pure elements (5N) and annealed at 750°C for 200 hours in sealed evacuated silica tubes, yielding doped directly kesterite-type material. This procedure is compared to a post deposition treatment, in which dopants (LiCl, NaCl, KCl) are added to pre synthesised CZTSe powder and annealed at 700°C, 48 hours under analogous conditions. X-ray diffraction with subsequent Rietveld refinements is performed to obtain lattice parameters and the anion position of the alkali doped CZTSe. Phase-purity, homogeneity, and chemical composition is investigated by wavelength dispersive X-ray spectroscopy (WDX) using an electron microprobe system. The concentration as well as the distribution of dopants is determined by laser ablation inductively coupled plasma mass spectroscopy (La-ICP-MS). As a key semiconductor characteristic, bandgap energy is quantified using diffusive reflectance Fourier-transformed infrared spectroscopy.

[1] Gurieva, Galina, et al. "Intrinsic point defects in off-stoichiometric Cu2ZnSnSe4: A neutron diffraction study." Journal of applied physics 123.16 (2018): 161519.

[2] Wang, Wei, et al. "Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency." Advanced energy materials 4.7 (2014): 1301465.

[3] Zhou, Jiazheng, et al. "Regulating crystal growth via organic lithium salt additive for efficient Kesterite solar cells." Nano Energy 89 (2021): 106405.