Structural phase transitions in photovoltaic materials: an in-situ high temperature synchrotron X-ray diffraction study

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Thin film solar cells are considered the next generation of photovoltaics because of their considerable cost reduction potential based on reduced consumption of material, energy and man power. Ternary semiconductor compounds of I-III-VI_2 type and their solid solutions, as well as the quaternary compounds Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe), are promising materials for high-efficiency thin film solar cells. In particular, the quantum efficiency of $Cu(In,Ga)Se_2$ based solar cells is reported to reach 20 % [1]. The crystal structure of the ternary and quaternary compounds is closely related, but assigned to different space groups: the first crystallize in the chalcopyrite type structure (space group $I\bar{4}2d$), whereas the quaternary compound adopts the kesterite type structure (space group $I\bar{4}$).

Taking into account that the accordance of thermal expansion coefficients and structural properties of substrate and thin film materials is important for functioning of thin film devices, in-situ temperature dependent investigations are crucial. In-situ powder diffraction experiments were performed at the high enery beamline ID15B in a temperature range from room temperature to 1100°C using a furnace for 2-D diffraction and an image plate detector. The samples were encapsulated in evacuated quartz ampoules (4 mm diameter) to avoid e. g. sulfur evaporation during heating. The experiment consisted of collecting a sequence of diffraction pattern during heating the sample. The temperature gradient was choosen in such a way, that recording an image every centigrade degree is possible.

The high temperature behaviour of $CuBX_2$ chalcopyrites (B=Al, Ga, In; X=S, Se, Te) and Cu_2ZnSnS_4 was studied in detail [2-4]. Both, chalcopyrites and kesterites, show a structural phase transition from the chalcopyrite / kesterite type structure to the sphalerite type structure (space group $F\bar{4}3m$). But the character of the phase transition was found to be different. The transition in the chalcopyrites $CuInX_2$ and $CuGaTe_2$ is a fast process and characterized by an order-disorder behaviour in the cation substructure. The structural phase transition in kesterite is slow and dominated by a displacive process in the anion substructure.

The presentation will give an overview of the structural phase transitions observed in these compound semiconductors. The differences will be pointed out, concerning not only the transition temperature, but primarily the character of the phase transition, the order parameter, its critical behaviour and universality. Finally complementary neutron diffraction based investigations will be discussed.

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