

Structural flexibility of photovoltaic materials: the key to high efficient solar cells

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Photovoltaics (PV) based on crystalline silicon wafers has developed into a mature technology for the conversion of sunlight into electrical energy. Thin film PV is an emerging alternative technology because of short energy payback time and minimum use of high purity materials, addressing the urgent need for cost-competitive renewable energy technologies.

Compound semiconductors with a high absorption coefficient are the most advanced and most efficient absorber materials in thin film PV technologies. Highly efficient devices are based on absorber layers out of ternary or quaternary chalcogenides or hybrid halide perovskites.

Record efficiencies are reached with solar cells based on Cu(In,Ga)Se₂ (CIGSe) Cu₂ZnSn(S,Se)₄ (CZTSSe) and (Cs,MA,FA)Pb(I,Br)₃ absorbers (power conversion efficiency of 23.3%, 13.0% and 25.5% respectively [1]).

CIGSe crystallizes in the chalcopyrite-type structure (space group $I\bar{4}2m$) whereas CZTSSe adopts the kesterite-type structure (space group $\bar{4}$). Both compounds (and silicon as well) belong to the adamantine family [2] which is characterized by a 3D network of corner sharing tetrahedra. (Cs,MA,FA)Pb(I,Br)₃ (MA-methyl-ammonium, FA-formamidinium) crystallizes in the perovskite-type structure, characterized by a 3D network of corner sharing octahedra. In this sense these materials are based on common building blocks: an A_2B_2X -tetrahedron in ternary $A^I B^{III} X_2$ and an A_2BCX -tetrahedron in quaternary $A^I_2 B^{III} C^{IV} X_4$ chalcogenide semiconductors. The parent structure of the adamantines is the diamond-type (space group $F\bar{4}_1/d\bar{3}2/m$). In binary, ternary and quaternary adamantines the metals are ordered on defined cation sites which led to typical superstructures with lowered symmetry. The parent structure (aristotype) of ABX_3 perovskites is the cubic perovskite-type structure (space group $Pm\bar{3}m$) in which the B cations are octahedrally coordinated by the anions. Thus, the PbX_6 -octahedra are the building blocks of hybrid halide perovskites. Tilting and distortions of the octahedra led to structures with lowered symmetry (Bärnighausen tree [3]), but all these crystal structures are named perovskite structure which leads to confusion sometimes [4].

The success of CIGSe, CZTSSe and (Cs,MA,FA)Pb(I,Br)₃ as PV material has to do with their overall structural flexibility. In the tetrahedrally coordinated chalcogenides this flexibility originates from the propensity of the crystal structure to stabilize intrinsic point defects as vacancies, anti-sites, and interstitials. Deviations from the stoichiometric composition led to the formation of such intrinsic point defects without dramatic structural changes, but with significant influence on the electrical and optical properties of the material [5]. On the other hand, hybrid halide perovskites were shown to have a high defect tolerance. Here the flexibility of the crystal structure gives remarkable positional freedom of the molecular cation and ionic movement.

The presentation will give an overview of the basic building block principle of these compound semiconductors, the flexibility of the crystal structure and the resulting effect on the optoelectronic materials properties.

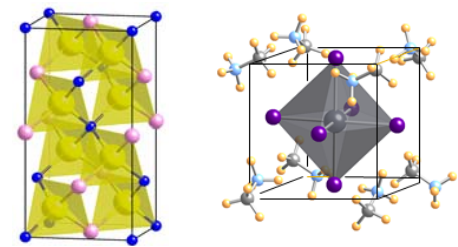


Fig.1 Chalcopyrite (left) and perovskite (right) structure showing the building block.

[1] NREL Efficiency Chart, www.nrel.gov/pv/cell-efficiency.html

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