School of Materials Science and Engineering

Seminar Topic:
Crystal Structure, Structural Disorder and Point Defects in Cu-based Quaternary Compound Semiconductors

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Abstract

Photovoltaic thin film solar cells based on kesterite Cu2ZnSn(SxSe1-x)4 compounds (CZTSSe) have reached >12% sunlight-to-electricity conversion efficiencies. The performance of these devices has been limited by a low open circuit voltage (VOC), the origin of which has been the subject of intense debate. A leading explanation is that CZTSSe suffers from extreme band tailing due to structural disorder (intrinsic point defects) accounting for a significant part of the VOC loss. The kesterite type structure (space group 4) can be described by a stacking sequence of cation layers Cu-Sn –Cu-Zn–Sn-Cu–Cu-Zn–Cu-Sn perpendicular to the crystallographic c-direction. As the most likely origin of the band tailing the disorder in the Cu-Zn plane in the kesterite structure is discussed, but also recombination of charge carriers at deep defects attributes to band tailing. Such defects are resulting from deviations from the stoichiometric composition. The best performing kesterite-based thin film solar cells were obtained with a material quite different from the stoichiometric compound, especially with a Cu-poor/Zn-rich composition. Thus besides Cu/Zn disorder, formed by CuZn and ZnCu antisites, various kind of intrinsic cationic point defects (vacancies, antisites, interstitials) occur in off-stoichiometric kesterite type semiconductors. The formation of such defects is driven thermodynamically by minimizing the Gibbs free energy of the crystal. We have developed a classification of intrinsic point defects in kesterites, named off-stoichiometry types.

Elastic coherent neutron scattering (diffraction) allows a non-destructive analysis of the crystal structure of photovoltaic absorber materials like kesterites from the surface deep into the volume of the sample. Only with the use of neutrons a differentiation between the electronic similar elements copper and zinc in the crystal structure is possible. In a systematic study based on neutron powder diffraction, applying the average neutron scattering length analysis method, we were able to evaluate experimentally the off-stoichiometry type and intrinsic point defect concentrations as well as the Cu/Zn disorder in kesterite-type semiconductors.

In our structural investigations we have demonstrated, that kesterite type CZTS/Se as well as Cu2ZnGeSe4 can self-adapt to Cu-poor and Cu-rich compositions without any structural change except the cation distribution. This ability to accept deviations from stoichiometry is correlated to the formation of intrinsic point defects. The Cu/Zn disorder, which is based on the formation of CuZn and ZnCu antisite defects in the Cu-Zn planes at z=¼ and ¾, occurs always, in stoichiometric as well as offstoichiometric kesterites. We were able to show for the first time quantitatively that the Cu/Zn disorder in kesterites causes shifts in the energy band gap giving raise to band tailing, a possible performance limiting parameter for thin-film solar cell devices based on kesterite-type absorber layers. The substitution of Cu by Ag opens a possibility to overcome these limitations. We have demonstrated, that in spite of both end members of the (Ag1-xCux)2ZnSnSe4 solid solution crystallizing in the kesterite type structure, solid solutions with x>0.1 crystallize in the stannite type structure (space group 4 2). In the latter the stacking sequence of cation layers can be described with Zn-Sn–(Cu,Ag)–Sn–Zn –(Cu,Ag)– Zn/Sn. In this way the formation of Cu/Zn disorder is completely blocked in (Ag1-xCux)2ZnSnSe4. A similar structural transition from the kesterite to the stannite type structure can be observed in the Cu2(Zn1-xCdx) SnS4 series.
Biography

Professor Susan Schorr is the Professor for Geo-Materials Research and Crystallography, Freie Universitaet Berlin and Head of the Department of Structure and Dynamics of Energy Materials at the Helmholtz-Zentrum Berlin for Materials and Energy (HZB).

Professor Schorr received her Diploma degree in crystallography from the Humboldt University, Berlin, in 1991. After she obtained her PhD degree in Physics from the Technical University Berlin in 1995, she joined the inelastic neutron scattering group at the Hahn-Meitner-Institute Berlin as a Postdoctoral Associate. She was a Visiting Scientist at the Los Alamos National Laboratory, US, from 1997 to 1998. In 2001, she started as a Research Associate at the Institute of Mineralogy, Crystallography and Materials Science on the University Leipzig, where she finished her habilitation in 2006. Back then she started to work on ternary and multinary compound semiconductors for photovoltaic applications. She developed the average neutron scattering length analysis method to evaluate the materials intrinsic point defects.

Professor Schorr went to the Hahn-Meitner-Institute Berlin (now HZB) to join the Institute of Technology in the Solar Energy Division as a group leader. In 2008 she was appointed as Professor for Geo-Materials Research at the Institute of Geological Sciences, Freie Universitaet Berlin. She became the Department Head at HZB in 2011. Since 2015, she is also the Chair of the Scientific-Technical Council of HZB.