

Solution-Phase Synthesis of Earth Abundant Semiconductors for Photovoltaic Applications

by

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Transitioning to a carbon-neutral future will require a broad portfolio of green energy generation and storage solutions. With the abundant availability of solar radiation across the Earth's surface, energy generation from photovoltaics (PVs) will be an important part of this green energy portfolio. While silicon-based solar cells currently dominate the PV market, temperatures exceeding 1000 °C are needed for purification of silicon, and batch processing of silicon wafers limits how rapidly Si-based PV can be deployed. Furthermore, silicon's indirect band gap necessitates absorber layers to exceed 100 μm thick, limiting its applications to rigid substrates.

Solution processed thin-film solar cells may allow for the realization of continuous, high-throughput manufacturing of PV modules. Thin-film absorber materials have direct band gaps, allowing them to absorb light more efficiently, and thus, they can be as thin as a few hundred nanometers and can be deposited on flexible substrates. Solution deposition of these absorber materials utilizing molecular precursor-based inks could be done in a roll-to-roll format, drastically increasing the throughput of PV manufacturing, and reducing installation costs. In this dissertation, solution processed synthesis and the characterization of two emerging direct band gap absorber materials consisting of earth abundant elements is discussed: the enargite phase of Cu_3AsS_4 and the distorted perovskite phase of BaZrS_3 .

The enargite phase of Cu_3AsS_4 (ENG) is an emerging PV material with a 1.42 eV band gap, making it an ideal single-junction absorber material for photovoltaic applications. Unfortunately, ENG-based PV devices have historically been shown to have low power conversion efficiencies, potentially due to defects in the material. A combined computational and experimental study was completed where DFT-based calculations from collaborators were used inform synthesis strategies to improve the defect properties of ENG utilizing new synthesis techniques, including silver alloying, to reduce the density of harmful defects.

Chalcogenide perovskites are viewed as a stable alternative to halide perovskites, with BaZrS_3 being the most widely studied. With a band gap of 1.8 eV, BaZrS_3 could be an excellent wide-bandgap partner for a silicon-based tandem solar cell. Historically, sputtering, and solid-state approaches have been used to synthesize chalcogenide perovskites, but these methods require

synthesis temperatures exceeding 800 °C, making them incompatible with the glass substrates and rear-contact layers required to create a PV device. In this dissertation, these high synthesis temperatures are bypassed through the development of a solution-processed deposition technique. A unique chemistry was developed to create fully soluble molecular precursor inks consisting of alkaline earth metal dithiocarboxylates and transition metal dithiocarbamates for direct-to-substrate synthesis of BaZrS₃ and BaHfS₃ at temperatures below 600 °C.

However, many challenges must be overcome before chalcogenide perovskites can be used for the creation of photovoltaic devices including oxide and Ruddlesden-Popper secondary phases, isolated grain growth, and deep level defects. Nevertheless, the development of a moderate temperature solution-based synthesis route makes chalcogenide perovskite research accessible to labs which do not have high temperature furnaces or sputtering equipment, further increasing research interest in this quickly developing absorber material.