

Exploration of Colloidal Nanocrystals for Established and Emerging Semiconductor Materials

For reliable, facile, and user-friendly, solution-based synthesis of materials, the colloidal nanocrystal route has proven to be the method of choice for so many. The tunability that this process renders its users—from the choice of precursors, solvent systems, and reaction conditions including temperature, pressure, and precursor addition order—is truly second to none. In their simplest form, these nanomaterials are usually comprised of an inorganic core of the desired material and an outer layer of surface-stabilizing molecules called ligands. These ligands provide colloidal stability and allow for the solution-processing of these materials for downstream usage in devices such as light-emitting diodes and photovoltaics, for example. In this thesis, the studies performed primarily cover the use of colloidal nanomaterials of $\text{Cu}(\text{In,Ga})\text{S}_2$ (CIGS) and $\text{II}^{\text{A}}\text{-IV}^{\text{B}}\text{-S}_3$ (including BaZrS_3 and SrZrS_3) sulfides. Additional experimental endeavors looked at exploring alkaline earth polysulfides ($\text{II}^{\text{A}}\text{S}_x$; $\text{II}^{\text{A}} = \text{Sr, Ba}$; $x = 2, 3$), and other materials like Cu_2GeS_3 and $\text{Cu}_2\text{BaSnS}_4$, for studies into the formation and colloidal stability of these materials, for example.

More specifically, an experimental protocol was developed to fabricate high-quality CIGS nanoparticles with carbonaceous residues that are substantially reduced from traditional pathways. Traditional methods for synthesizing colloidal CIGS NPs often utilize heavy, long-chain organic species to serve as surface ligands which, during annealing in a Se/Ar atmosphere, leave behind an undesirable carbonaceous residue in the film. To minimize these residues, *N*-methyl-2-pyrrolidone (NMP) was used as an alternative surface ligand. Through the use of the NMP-based synthesis, a substantial reduction in the number of carbonaceous residues was observed in selenized films. Additionally, the fine-grain layer at the bottom of the film, a common observation of solution-processed films from organic media, was observed to exhibit a larger average grain size and increased chalcopyrite character over those of traditionally prepared films, presumably as a result of the reduced carbon content, allowing for superior growth. As a result, a gallium-free $\text{CuIn}(\text{S,Se})_2$ device was shown to achieve power-conversion efficiencies of over 11% as well as possessing exceptional carrier generation capabilities with a short-circuit current density (J_{SC}) of 41.6 mA/cm^2 , which is among the highest for the CIGSSe family of devices fabricated from solution-processed methods.

The II^A-IV^B-S₃ system is just beginning to emerge as a material shown to be capable of solution-based synthesis methods. This is primarily due to the extremely high oxophilicity of the IV^B elements, Ti, Zr, and Hf, necessitating that extreme care and judicial use of inert environments be used to synthesize these materials via solution-based methods. In the II^A-IV^B-S₃ system exists some of the chalcogenide perovskites, including BaZrS₃, which are expected to have similar electronic properties to the well-known, high-performing halide perovskites, albeit much more stable, making them attractive prospects as novel semiconductor materials for optoelectronic applications. This work builds upon recent studies to show a general synthesis protocol, involving the use of carbon disulfide insertion chemistry to generate highly reactive precursors, that can be used towards the colloidal synthesis of numerous nanomaterials in the II^A-IV^B-S₃ system, including BaTiS₃, BaZrS₃, BaHfS₃, α -SrZrS₃ and α -SrHfS₃. Additionally, we establish a method to reliably and reproducibly control the formation of the BaZrS₃ perovskite, a complication seen in previous literature where BaZrS₃ appears to exist as two different phases when synthesized via colloidal methods. The utility of these nanomaterials is also assessed via the measurement of their absorption properties and in the form of highly stable colloidal inks for the fabrication of homogenous, crack-free thin films of BaZrS₃.

Finally, some discussion is also provided on the use of transmission electron microscopy (TEM) and how it was extensively used to characterize various nanoscale materials from the Cu-based chalcogenides, to chalcogenide perovskites and beyond.