SOLUTION-PROCESSED SYNTHESIS OF CHALCOGENIDE SEMICONDUCTORS FOR OPTOELECTRONIC APPLICATIONS

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The need for novel semiconductors for optical, electronic, and optoelectronic applications such as solar cells, LEDs, photodetectors, and transistors has never been greater. Organic-inorganic lead halide perovskites, belonging to one class of semiconductors, are proving to be very efficient in applications like solar cells, LEDs, lasers, flexible low-cost electronics and are challenging silicon's dominance in these areas. However, these lead halide perovskites are inherently unstable when exposed to air and moisture, so their use in real-world situations is still uncertain.

Inorganic semiconductors, on the other hand, are more stable when faced with oxygen, moisture, and heat. They have been widely studied and used for many applications. Among inorganic semiconductors, chalcogenides such as $Cu(In,Ga)Se_2$, $Cu_2ZnSnSe_4$, and transition metal dichalcogenides are becoming ever more popular and are being actively researched for different uses. This has led to increased interest in other chalcogenide compounds that may perform just as well or even better. In this work, several promising yet less-studied chalcogenide semiconductors such as chalcogenide perovskites and $AgInSe_2$ are investigated for optoelectronic applications.

Chalcogenide perovskites (ABX_3, where A = alkaline earth, B = transition metal, X = S, Se) exhibit excellent semiconducting and optical properties as well as impressive stability, but have been difficult to synthesize, which has limited their widespread adoption. In most cases, these compounds have been synthesized via solid-state reactions at temperatures above 900°C and then studied. However, to fabricate functional large-scale devices, these materials need to be synthesized at lower temperatures using simpler methods. This study identifies the factors that necessitate high-temperature synthesis and offers solutions, resulting in record-low synthesis temperatures for these compounds. Based on the hypothesis that reactive precursors, an oxygen sink, and a transport agent are required for low-temperature synthesis, this research develops several new solution-deposition methods. These methods use various metal salts, pure metals, organometallics and metal chalcogenides as metal precursors, along with different sulfur sources and various molecular precursor solutions. The study also introduces a novel oxygen sink to capture residual oxygen during synthesis, which is critical due to the high oxophilicity of early transition metals. Moreover, the study examines different transport agents to improve mass transfer

and element interaction during synthesis. Combining these efforts has led to several methods for depositing continuous thin films of chalcogenide perovskites at record-low temperatures. These low-temperature films have been characterized for their optoelectronic properties, and functional devices have been fabricated from them.

Beyond solution-based methods, this work has developed techniques to synthesize colloidal nanocrystals of various sulfide and selenide members of the hexagonal chalcogenide perovskites at temperatures below 400°C, which can easily be used to make thin films or functional devices. The study also demonstrates a new method for synthesizing thin films of chalcogenide perovskites on conductive substrates, a longstanding challenge in the literature, opening new opportunities for their widespread adoption. The research on chalcogenide perovskite concludes by identifying remaining synthesis and optoelectronic challenges that must be addressed before chalcogenide perovskites can reach their full potential.

Metal oxide and metal halide salts are commonly used to synthesize various chalcogenide semiconductors. The oxophilicity and haliphilicity of metals can help guide the choice of synthesis conditions. In this study, thermodynamic calculations were performed using the Gibbs free energy of formation for metal salts, metal oxides, and metal sulfides, resulting in the development of oxophilicity and haliphilicity scales for metals. Using these scales, Ba-based chalcogenide compounds were synthesized for the first time in the literature from metal chloride and metal iodide precursors.

$AgInSe_2$ is a promising chalcogenide semiconductor with an ideal bandgap for single-junction photovoltaic applications. However, this material has remained understudied due to the poor optoelectronic properties previously reported in the literature. This study identifies a suitable solution-based chemistry for synthesizing $AgInSe_2$ thin films and investigates selenium loss or unavailability during synthesis as a primary reason for the observed poor optoelectronic properties. By optimizing synthesis conditions, including selenium availability, the study achieves record minority carrier lifetime values for this semiconductor.