Structural Characterization of Chalcogenide Glasses During Solution Processing

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1 Background

Chalcogenide glasses are a class of amorphous materials containing one or more of the chalcogens sulfur, selenium, or tellurium with properties of interest for optoelectronics. Their high refractive indices and optically induced behaviors like photocrystallization make them well-suited for information transfer and storage devices like photonic waveguides and optical discs [1]. Their transparency in the mid-infrared, a crucial spectral region spanning two atmospheric transmission windows, enables remote sensing of many molecules [2]. Additionally, they can be doped with metallic nanoparticles to enhance these desirable traits [3].

Solution processing is commonly employed with chalcogenides, since the glasses dissolve readily in organic solvents and can then be doped, stored, or spin-coated with relative ease [3, 4]. But while this process has been well studied with regards to film and device preparation, little is known about the solution itself prior to deposition. Arsenic sulfide (As$_2$S$_3$), for instance, takes on elusive solvent-dependent structures during dissolution, leading to molecule-like clumps or polymer-like chains that can then influence film morphology [5, 6].

The first of these structures explored was in $n$-propylamine. Chern and Lauks detected amine salts in the solution—evidence of a solvent-solute reaction—despite the fact that optical properties were similar to bulk As$_2$S$_3$. They hypothesized a structure consisting of as-bulk As$_2$S$_3$ clusters with a sulfide shell bonded to the amine groups of the solvent [5]. Though yet unproven, this theory was assumed to be true by Kohoutek et al. in a later experiment that then claimed the size of the clusters increased with concentration [7].

While these studies provide a useful starting point for discussions on solution structure, their conclusions have gone largely untested. More than thirty years after the Chern and Lauks structure was proposed, there is still no direct experimental evidence to support it, no understanding of what determines its dimensions, and consequently, no way to truly forward engineer the morphological properties of films.
2 Objectives

This work aims to employ novel materials characterization techniques to fill this void in understanding. The study focuses on As$_2$S$_3$ in amine solvents, beginning with n-propylamine, and seeks direct evidence of a stable solution structure, hopefully consistent with what has been proposed in the literature. Furthermore, we seek a thermodynamically sound explanation of the structure and its dependencies that will enable researchers focused on applications to tune their solutions based on the structure they desire.

3 Research Progress

So far, progress has been made in two areas. The first is in methods development. To directly image As$_2$S$_3$ clusters, we are adapting cryo-electron microscopy (cryo-EM) for our samples. Cryo-EM is a technique from structural biology that earned its developers the 2017 Nobel Prize in Chemistry; it involves flash-freezing solutions onto grids and imaging them with low electron doses to view the solute in its dissolved state [8, 9]. Chalcogenide solutions add challenges to this already sensitive technique, as volatile organic solvents sustain much more beam damage than aqueous biological solutions. We are working to mitigate this by establishing a freezing protocol that gives optimal thickness of frozen solution and an imaging protocol that minimizes exposure.

The second area of progress is in verification of the concentration-dependent cluster size observed by Kohoutek, et al. in [7]. Using dynamic light scattering, we have observed a roughly linear size increase as the concentration of As$_2$S$_3$ in n-propylamine increases from 0.01 M to 1 M, and we are in the midst of exploring possible explanations.

4 Conclusion

The in-solution structure of chalcogenide glasses is a long overlooked question that will help understand the way these materials are processed. By combining experimental techniques with thermodynamic and chemical sensibilities, this project will take a fundamental approach to a class of materials normally looked at from an applications standpoint.

Furthermore, the novel methodological approach of this project (adapting cryo-EM for a new class of samples) stands to expand the catalog of characterization techniques available to materials scientists. Thus, with this work we not only hope to bring closure to a decades old theory in the area of chalcogenide glasses, but to equip scientists in other areas with a new way to explore their own materials of interest.
References


