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An invited talk

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PHYSICAL AND CHEMICAL AGING IN CHALCOGENIDE GLASSES

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The chalcogenide glasses are an important group of functional materials. It is known that the optical and photonic functions of chalcogenide glasses strongly depend on their chemical variations, and hence, on their microstructures. However, one crucial question has not been fully answered in literature, i.e., how do the structure and properties of chalcogenide glasses react to physical and chemical aging processes at or below the glass transition temperature (T_{o}) ? In this study, we perform systematic aging experiments on six types of chalcogeneide glasses at various temperatures at or below T_{σ} for different durations in different gases. Afterwards we determine the consequences of the aging process to the glass transition, structure and properties. The aged samples are characterized with respect to both surface and bulk properties by means of differential scanning calorimetry (DSC), thermogravimetry (TG), Vickers indentation, secondary neutral particle mass spectroscopy (SNMS) and optical spectroscopy. The T_g values, the fictive temperatures and the fragility indices of the glasses are determined by DSC, while the oxidation extents of the glasses are estimated using TG. We have found that both the aging and the sample preparation histories exert dramatic impact on the glass transition of chalcogenide glasses. After aging the samples in atmospheric air, we have observed a remarkable 'anionic' inward diffusion process, i.e., diffusion of anions (like Se²⁻ and S²⁻) from the surface to the. A concomitant enrichment of cations takes places in the surface layer. As a result, the glass surface becomes softer as the hardness of glass drops with increasing aging duration. The mechanism of the anionic inward diffusion is explained in terms of the structural topology, the liquid fragility, the jonic field strength and the kinetics. The compositional dependence of the inward diffusion is determined to understand the effect of the chemical bonding nature on the diffusion. Furthermore, we study the changes in optical properties of the samples with increasing the degree of annealing and with varying the atmospheric conditions.

Keywords: chalcogenide glasses, physical aging, glass transition, fictive temperatures, diffusion, hardness and optical properties.