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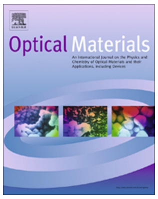

Chalcogenide glass fibers: Optical window tailoring and suitability for bio-chemical sensing

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ABSTRACT

Glassy materials based on chalcogen elements are becoming increasingly prominent in the development of advanced infrared sensors. In particular, infrared fibers constitute a desirable sensing platform due to their high sensitivity and versatile remote collection capabilities for *in-situ* detection. Tailoring the transparency window of an optical material to the vibrational signature of a target molecule is important for the design of infrared sensor, and particularly for fiber evanescent wave spectroscopy. Here we review the basic principles and recent developments in the fabrication of chalcogenide glass infrared fibers for application as bio-chemical sensors. We emphasize the challenges in designing materials that combine good rheological properties with chemical stability and sufficiently wide optical windows for bio-chemical sensing. The limitation in optical transparency due to higher order overtones of the amorphous network vibrations is established for this family of glasses. It is shown that glasses with wide optical window suffer from higher order overtone absorptions. Compositional engineering with heavy elements such as iodine is shown to widen the optical window but at the cost of lower chemical stability. The optical attenuations of various families of chalcogenide glass fibers are presented and weighed for their applications as chemical sensors. It is then shown that long-wave infrared fibers can be designed to optimize the collection of selective signal from bio-molecules such as cells and tissues. Issues of toxicity and mechanical resistance in the context of bio-sensing are also discussed.

1. Introduction

From industrial window glass to advanced telecom waveguides, amorphous solids are used in a wide range of technological applications thanks to their excellent optical transparency. This desirable property stems from their homogeneous microstructure which can be retained during elaborate fabrication processes such as blowing, drawing or molding. The unique rheological properties of glasses indeed enable the production of complex objects with superior optical quality at minimal cost. This is in contrast to crystalline solids which typically form through nucleation and growth and result in materials containing many grain boundaries causing strong light scattering and eventually leading to opacity. This can be overcome by producing single crystals with excellent optical quality, but their synthesis and subsequent shaping is prohibitively expensive for large scale applications. This is the reason why the large majority of optical elements are made of glass, in particular those designed to operate in the visible and near-infrared regime. In this range of wavelength, silicate glasses vastly dominate the optical elements market due to their superior optical transparency, their excellent glass forming ability, and high chemical durability.

In contrast, mid-infrared systems still largely rely on optical elements made of crystalline solids such as KBr, ZnSe or Ge. In particular, Ge has been the material of choice for the fabrication of advanced lenses for night vision systems such as thermal cameras. However, these lenses must be produced from large single crystals subsequently polished by diamond turning and consequently constitute one of the main source of the exceedingly high price of such devices. Nevertheless, there has recently been a shift away from crystalline infrared optics, driven by the development of novel infrared transparent glasses based on chalcogen elements. Indeed, these glasses can be easily molded with high precision to yield aspheric or diffractive lenses and are now produced industrially for a fraction of the price of that of crystalline optics [1–3]. Lenses made of chalcogenide glasses are now commercialized under different brand names and have helped reduce the price of infrared optical system. In particular, night vision cameras

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equipped with these lenses are now mounted in car bumpers and serve as driving assistance in hazardous conditions such as foggy weather or at night [1]. This type of large scale production is expected to further reduce the price of infrared optics.

But besides thermal imaging, the mid-infrared domain is of great interest for vibrational spectroscopy of chemicals and biomolecules [4–9]. Indeed, almost all molecules exhibit highly specific vibrational signatures in the 2–16 microns range which provides an effective mean of performing selective optical sensing. In particular, biomolecules and microorganisms have distinct mid-infrared signatures which can be used to identify strains or monitor metabolic processes [10–14]. Due to their broad infrared transparency, chalcogenide glasses have therefore been used to fabricate many optical elements for the design of novel infrared biosensors [15–18]. And due to their excellent rheological properties, chalcogenide glasses can be drawn into fibers for the design of remote infrared sensors [19–22]. In this paper we first investigate the source of the fundamental limitation of the optical window in a series of chalcogenide glasses and the corresponding optical fibers, and we present recent development in the production of long-wave infrared fibers suited for the study and monitoring of biomolecules as well as the trade-off between optical properties and chemical stability.

2. Experimental

2.1. Glass synthesis

The chalcogenide glasses produced in this study are composed of mixtures of Se, Te, Ge, As and I. Elements of high purity (>99.9999%) are introduced in a silica tube under high vacuum ($\sim 10^{-5}$ Torr) and pumped for several hours to remove all trace of oxygen and water. Surface oxide on Se and As are eliminated by heating the elements *in-situ* to remove the high vapor pressure oxide species. A small amount of Al (50–100 ppm) is also added to the mixture to capture remaining oxygen by forming Al_2O_3. The resulting mix is then sealed in the silica ampoule under vacuum and introduced in a rocking oven for homogenization at 800 °C for 12 h. The liquid is then quenched in water to produce a glass rod which is then introduced in a distillation tube. The glass mixture is then distilled *in-situ* to eliminate the low vapor pressure impurities such as carbon and the Al_2O_3 that has formed during the heating process. After distillation the glass is further homogenized at 800 °C for 6 h, then quenched in water and immediately introduced in an annealing oven set at ~5 °C below the glass transition temperature T_g to remove mechanical constraints and avoid cracking. The temperature is then slowly decreased to room temperature and the glass rod is recovered for processing. Further detail on the purification process can be found in Ref. [23].

2.2. Fiber preparation

Glass fibers are produced from purified glass rods by melting the tip of the rod in a narrow ring heater held at a temperature above T_g. The fiber is then rolled on a Teflon coated wheel and the fiber diameter is monitored *in-situ* during the drawing process using an optical sensor. The drawing process is performed under He flow to avoid oxidation. The fiber diameter is controlled by adjusting the fiber tension, drawing speed and rate of preform introduction into the heater.

2.3. Characterization

Optical transmission of glassy samples is measured on discs with thickness of 2 mm using a FTIR spectrometer Brucker Tensor 27 equipped with an internal DTGS (Triglycerine sulfate) detector. The fiber attenuation is measured using the FTIR spectrometer and a fiber testing attachment equipped with concave gold mirrors for light coupling in and out of the fibers and an external MCT (Mercury Cadnium Telluride) detector cooled with liquid nitrogen. The attenuation is measured using the cut-back method.

3. Limitation of the optical window in chalcogenide glasses

The optical transmission of amorphous solids is limited on the short wavelength side by electronic absorption processes (mainly controlled by the band gap energy), and on the long wavelength side by vibrational transitions which are mainly controlled by the reduced mass m^* and the force constant k of the network oscillators following Eqs. (1) and (2):

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{1}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}} \tag{2}$$

where E_n is the quantized energy of a vibrational state and ν is the vibration frequency of the oscillator. While Eq. (2) is strictly defined for a diatomic oscillator, it provides a good indication of the vibrational properties of a network. Indeed, the extent of the optical window at long wavelengths is a strong function of the mass of component elements as depicted in Fig. 1 for a series of stoichiometric As_2X_3 glasses based on arsenic combined with increasingly heavier chalcogenide elements.

Amorphous solids composed of lighter elements such as As_2O_3 exhibit strong absorption at relatively high frequency resulting in a multiphonon cut-off at short wavelength near 6–7 μm (Fig. 1). This glass would therefore be inadequate for mid-infrared applications. In addition, As_2O_3 is highly hygroscopic as shown by the OH absorption peak near 3 μm (Fig. 1) and as a consequence it degrades and becomes opaque within a few days in ambient atmosphere. Substitution of O by S to produce As_2S_3 results in better chemical stability and wider transparency up to ~10 μm which is practical for many infrared applications. Indeed As_2S_3 was one of the first glass investigated for infrared applications [24]. Finally, substitution of S by increasingly heavier chalcogens Se and Te pushes the multiphonon cut-off far into the infrared down to 18 and 25 μm respectively.

The term "multiphonon" cut-off originates from the fact that the absorption edge is limited by the broad phonon density of state

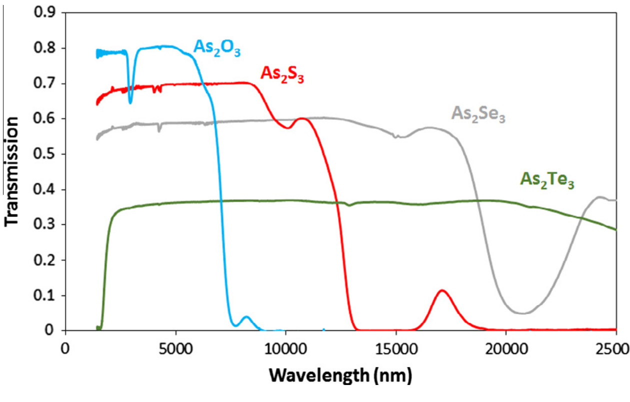

Fig. 1. Long-wave transmission window of amorphous solids composed of increasingly heavier elements. Heavier component elements result in extended transmission in the infrared region. The transmission was measured on 1–2 mm thick discs.