Journal of Optoelectronics and Advanced Materials Vol. 3, No. 3, September 2001, p. 627 - 640

# APPLICATIONS OF CHALCOGENIDE GLASS OPTICAL FIBERS AT NRL

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Chalcogenide glass fibers based on sulphide, selenide, telluride and their rare earth doped compositions are being actively pursued both at the Naval Research Laboratory (NRL) and worldwide. Great strides have been made in reducing optical losses using improved chemical purification techniques, but further improvements are needed in both purification and fiberization technology to attain the theoretical optical losses. Despite this, chalcogenide glass fibers are enabling numerous applications which include laser power delivery, chemical sensing, imaging, scanning near field microscopy/spectroscopy, IR sources/lasers, amplifiers and optical switches.

(Received July 26, 2001; accepted September 3, 2001)

*Keywords:* Chalcogenide glass, Optical fibers, Optical losses

## 1. Introduction

Chalcogenide glasses are based on the chalcogen elements S, Se and Te and the addition of other elements such as Ge, As and Sb leads to the formation of stable glasses [1]. The addition of halides leads to the formation of chalcohalide glasses [2]. Examples of stable glasses include $As_2S_3$ [1], $Ge_{20}S_{40}Br_{40}$ [2], $As_2Se_3$ [1] and $Ge_{30}As_{10}Se_{30}Te_{30}$ [3]. More recent efforts have reported on rare earth doping for active applications and consequently alternative glasses have been developed. Examples of these glass systems include Ge-Ga-S [4], Ge-As-Ga-S [5], Ga-La-S [6], Ga-Na-S [7], Ge-S-I [8] and Ge-As-Se [9].

Since the chalcogenide glasses transmit to longer wavelengths in the IR than silica and fluoride glasses (Fig. 1), there are numerous potential applications in the civil, medical and military areas. These can be essentially divided into two groups, namely “passive” and “active” applications. The passive applications utilize chalcogenide fibers as a light conduit from one location to another without changing the optical properties, other than that due to scattering, absorption and end face reflection losses associated with the fiber. Active applications of chalcogenide glass fibers are where the initial light propagating through the fiber is modified by a process other than that due to scattering, absorption and end face reflection losses associated with the fiber. Examples of these include fiber lasers, amplifiers, bright sources, gratings and non-linear effects.

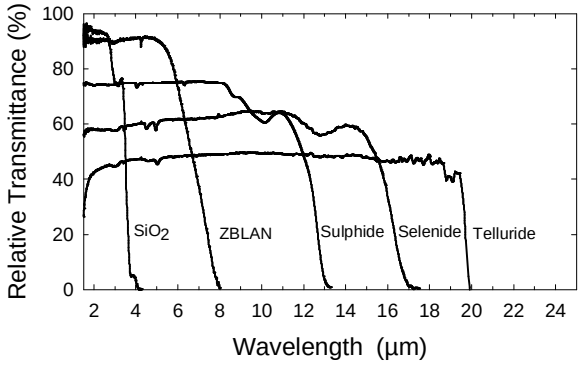


Fig. 1. Transmission spectra for several glasses (thickness of about 2-3 mm).

This paper describes some of the applications being developed in our laboratory as well as a review of the literature describing where chalcogenide fibers are being used and where they could potentially be used.

## 2. Experimental techniques for preparing fibers

Chalcogenide glasses are either melted directly in quartz ampoules or in vitreous carbon crucibles located within quartz ampoules. Typical melt temperatures range from 600°C to 1100°C, depending upon composition. The liquids are quenched and the glass rods annealed at temperatures around the appropriate softening temperatures. The optical fibers are obtained by heating preforms fabricated via rod-in-tube type processes [10,11] or by double crucible (DC) processes [11,12,13]. The cladding tubes can be obtained via an in-situ casting process, which is preferred due to less contamination and higher quality surfaces, or by core drilling from larger samples which typically leads to a rough surface quality. The preforms can also be obtained by extrusion of core and cladding glass billets [7]. The DC process enables adjustments to be made in the core/clad diameter ratio during fiber drawing by independent pressure control above each melt. Therefore both multimode and single mode fibers can be drawn with relatively fewer processing steps using the DC process.

There has been much work on determining the origin of the extrinsic scattering centers and absorption impurities and consequently numerous purification techniques based on distillation and sublimation of precursors and glasses have been developed to reduce their contribution to the total optical loss of the fiber [14,15,16].

## 3. Results and discussion

### 3.1. Properties of fibers

Table 1 lists some physical, mechanical and optical properties of two chalcogenide glasses used in making optical fibers [17]. Compared to the more traditional oxide glasses, they can be described as having lower Tg's, higher CTE's, lower hardness and higher indices of refraction [17]. From a practical viewpoint, the most important difference is their longer wavelength transmission. Figs. 2a and b show the transmission spectra of three chalcogenide fibers made in the authors' laboratory as a function of precursor quality.

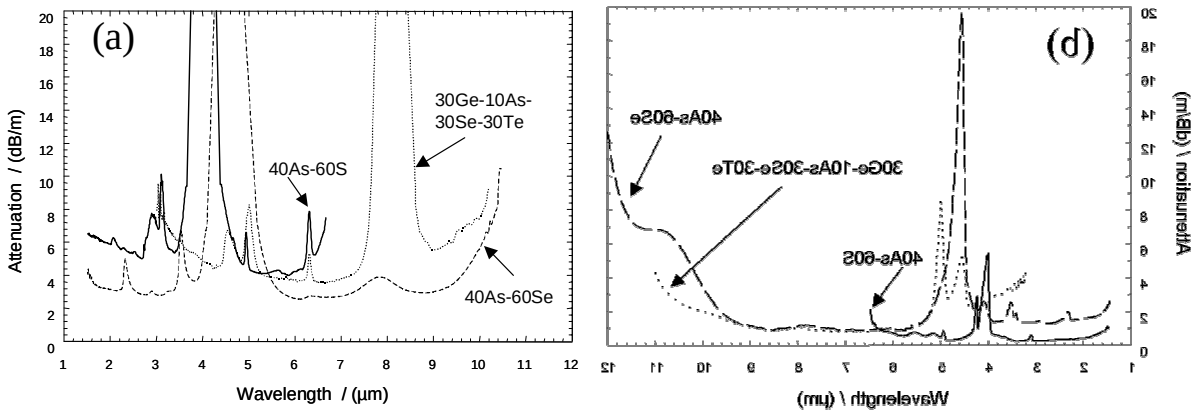


Fig. 2. Transmission loss spectra of chalcogenide glass fibers, (a) without purification of chemicals and (b) after purification of chemicals.

The fibers in Fig. 2b were made using distillation and sublimation of the precursors [16]. Depending upon composition, the sulphide, selenide and telluride based fibers transmit between about 0.8-7 μm, 1-10 μm, and 2-12 μm, respectively. Therefore, the practical applications dictate the type of fiber to be used. The As-S fibers have received the most attention to-date in our laboratory and so the loss routinely achieved is about 0.1-0.2 dB/m in fiber lengths in excess of 100 meters. Comparing Figs. 2a and b, it is apparent that both purification and composition play an important role in making low loss fibers. Fig. 3 compares the losses routinely obtained for a couple of chalcogenide glasses along with the lowest ("champion") losses reported in the literature [3,15].

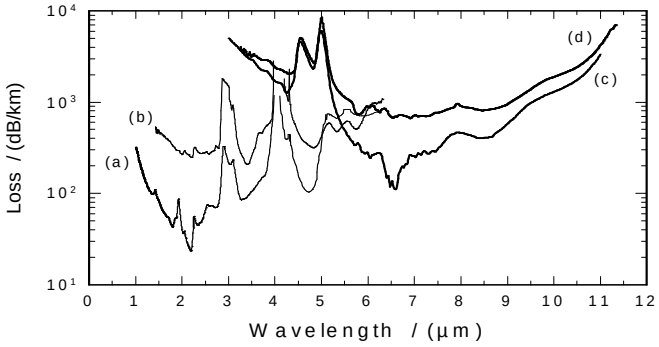


Fig. 3. Transmission loss spectra of (a) lowest loss sulphide fiber, (b) typical sulphide fiber, (c) lowest loss telluride fiber, and (d) typical telluride fiber.

Table 1. Some physical, mechanical and optical properties of chalcogenide glasses used for making optical fibers [17].

| | **$As_{40}S_{60}$** | **$Ge_{30}As_{10}Se_{30}Te_{30}$** |
|---|---|---|
| Physical Properties | | |
| $T_g$ / ($^oC$)[a] | 197 | 265 |
| CTE / ($10^{-6}/^oC$)[b] | 21.4 | 14.4 |
| Thermal Conductivity / (W/m-$^oC$) | 0.17 | ~0.2 |
| Mechanical Properties | | |
| Density / ($g/cm^3$) | 3.20 | 4.88 |
| Knoop Hardness / ($kg/mm^2$) | 109 | 205 |
| Fracture Toughness / ($MPa.m^{1/2}$) | ~0.2 | ~ 0.2 |
| Poisson's Ratio | 0.24 | ~ 0.26 |
| Youngs Modulus / (GPa) | 16.0 | 21.9 |
| Optical Properties | | |
| Refractive Index[c] | 2.415 (3.0) | 2.80 (10.6) |
| dn/dT / ($10^{-5}$ $^oC^{-1}$)[c,d] | +0.9 (5.4) | +10.0 (10.6) |
| Bulk transmission / (:m) | 0.6 - 10.0 | 1.0 - 17.0 |
| Fiber transmission / (:m) | 0.8 - 6.5 | 3.0 - 11.0 |
| Lowest Loss / (dB/km)[c] | 23 (2.3) | 110 (6.6) |
| Typical Loss / (dB/km)[c] | 100-200 (2.2-5.0) | 500-1000 (6.0-9.0) |
| Estimated minimum loss / (dB/km)[c] | 1.0 | nd |

[a] $T_g$ is the glass transition temperature.
[b] CTE is the coefficient of thermal expansion.
[c] Wavelength in μm given in parenthesis.
[d] dn/dT is the change in refractive index with temperature.
nd – not determined

The question arises as to what is the origin of the extrinsic scattering and absorption losses, and furthermore, how can these impurities be removed. The scattering centers have been previously identified as bubbles and particles of $SiO_2$ and carbon and their contribution to the scattering loss has been rigorously analyzed [14]. Despite this, the concentration of these species has not been experimentally determined. On the other hand, the absorbing species have been quantitatively characterized [16]. Table 2 lists the estimated concentration of typical absorbing impurities found in sulphide and telluride fibers [16]. Although the losses of the fibers are routinely higher than the champion values, it is worthwhile to estimate the theoretical minimum loss. This has been done for an arsenic sulphide glass [16] and the results are shown in Fig. 4.

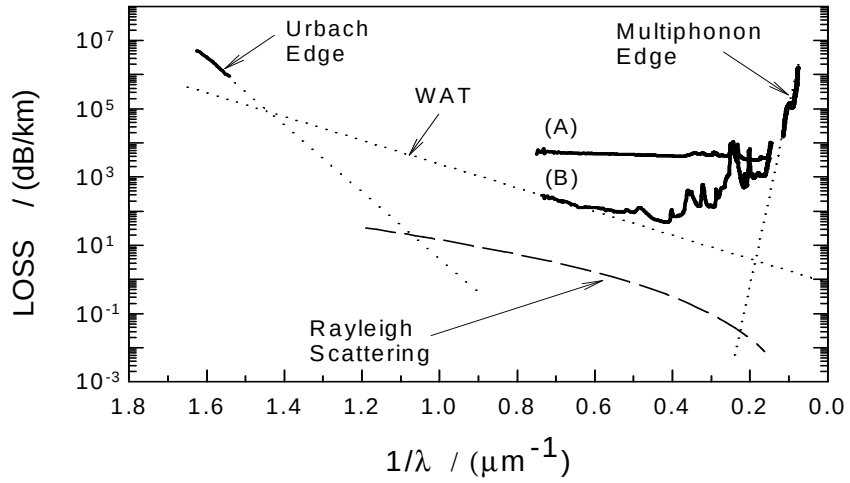


Fig. 4. Estimation of theoretical minimum loss in a sulphide fiber. A and B represent poor and high quality glasses, respectively [16].

Table 2. Estimated concentration of typical impurities in sulphide and telluride fibers [16].

| Impurity Absorption | Wavelength (μm) | Absorption Loss (dB/m) | Extinction Coefficient (dB/m/ppm) | Impurity Concentration (ppm) |
|---|---|---|---|---|
| **Sulphide Fibers** | | | | |
| H-S | 4.0 | 10 | 2.3 | 4.3 |
| O-H | 2.9 | 0.3 | 5.0 | 0.06 |
| **Telluride Fibers** | | | | |
| H-Se | 4.5 | 3.0 | 1.1 | 2.7 |
| Ge-H | 5.0 | 6.0 | --- | --- |
| $H_2O$ | 6.3 | 0.07 | 34.0 | 0.002 |
| Ge-O | 7.9 | 0.16 | 2.6 | 0.06 |

The minimum loss is estimated to be about 4 dB/km at 5.0 μm [16]. Although the losses of the sulphide fibers are routinely higher than both the "champion" and the estimated theoretical values, these fibers can, and are being used in numerous applications. Unfortunately, theoretical estimates are not available for other glass systems, but despite this, the selenide, telluride and rare earth doped glass fibers are being fabricated and utilized in numerous applications. The minimum loss obtained for a 400 ppm Dy doped unclad selenide glass fiber was 0.8 dB/m at 6.6 μm and 3 dB/m at 1.3 μm. Multimode fiber has been drawn with a loss of 6 dB/m at 1.33 μm and a minimum loss of about 3 dB/m at approximately 6 μm. The losses for Pr doped fibers are similar. Undoped samples have been fabricated into singlemode fibers (core / cladding diameters = 4 / 110 μm) with losses of 3 dB/m at 1.55 μm. In general, typical measured losses for the rare earth doped glasses are >0.5 dB/m and so improvements in purification and fiberization technology are still needed to reduce the measured optical losses.

Tables 3 and 4 list the passive and active applications of chalcogenide glass fibers, respectively, that have been demonstrated or are being investigated. These will be discussed in more detail in the next section.

Table 3. Passive applications of IR transmitting chalcogenide glass fibers.

| **Applications** | **References** |
|---|---|
| Laser Power Delivery | |
| • 5.4 μm (CO) | 18,19 |
| • 10.6 μm ($CO_2$) | 18,19 |
| • Atmospheric 2-5 μm region | 20,21 |
| • Medical Free Electron Laser (2-10 μm) | 22,28 |
| • Anti-reflection (AR) coatings | 18,20 |
| Chemical Sensing | |
| • Aqueous, non-aqueous, toxic chemicals | 24-28 |
| • Polymers, paints, pharmaceuticals | 11,27,29 |
| • Condition Based Maintenance (CBM) | 27 |
| • Cone Penetrometer System | 30 |
| • Active Coatings | 31 |
| • Bio-medical | 22,32 |
| Temperature Monitoring | |
| • Grinding ceramics | 33 |
| Thermal Imaging & Hyperspectral Imaging | |
| • Coherent fiber bundles | 34, 35,36,38 |
| Near Field Microscopy | |
| • Imaging and spectroscopy | 39-41 |
| Fiber Multiplexing | |
| • Fiber couplers | 42 |

Table 4. Active applications of IR transmitting chalcogenide glass fibers.

| **Applications** | **References** |
|---|---|
| Rare Earth Doped Fibers | |
| • Fiber Lasers - 1.08 μm (Nd) | 54 |
| • Amplifiers - 1.08 μm (Nd) | 55 |
| - 1.34 μm (Pr) | 7 |
| - 1.34 μm (Dy) | 53 |
| • Infrared Scene Simulation (IRSS) | 58 |
| • Chemical Sensing | 22 |
| • Gratings - 1.5 μm | 59 |
| Non-linear | |
| • Optical switching | 62 |
| • Second Harmonic Generation | 64 |
| • Frequency mixing | ---- |
| • Electrical Poling | ---- |

### 3.2. Passive Applications

#### *3.2.1. Laser Power Delivery*

High power CO and $CO_2$ lasers operating at 5.4 μm and 10.6 μm, respectively, are readily available and can be used for industrial welding and cutting. Transmitting the laser power through fibers enables remote operation. Small core diameter (<200 μm) fibers have demonstrated tolerance to power densities of ~125 kW/cm$^2$ at 5.4 μm and ~54 kW/cm$^2$ at 10.6 μm without damage [19] (Fig. 5). Telluride glass fiber losses at 10.6 μm lie in the range of 1.5 dB/m to 3 dB/m, depending upon composition and purity [3,18].

The arsenic sulphide fibers transmit in the atmospheric 2 to 5 μm region and can be used for transmission of laser power in this region [20]. Pulsed laser power delivery has been demonstrated (Fig. 5). The average power is about 2.69 Watts but the peak power is 26.9 kW, which corresponds to a peak power density of 1.07 GW/cm$^2$ without fiber damage for up to 1.5 x 10$^7$ pulses [21]. This remarkable threshold to damage is close to the predicted value of about 3.0 GW/cm$^2$ due to dielectric breakdown at the surface. This threshold to damage is obtained by control of fiber polishing, otherwise the fiber end face undergoes damage at relatively lower powers.

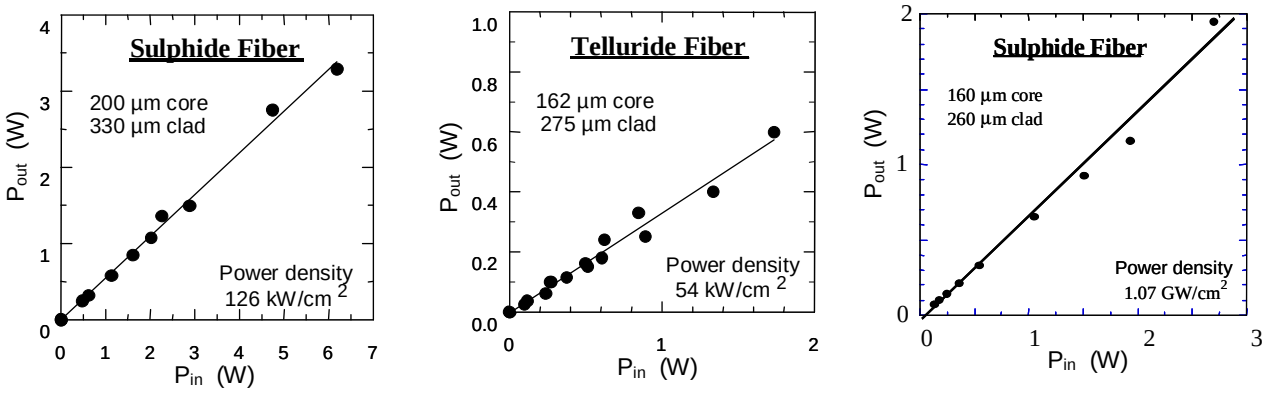


Fig. 5. (a) CO laser transmission, (b) $CO_2$ laser transmission and (c) pulsed high energy laser transmission in the 2-5 μm region.

Recent efforts have considered delivery of energy from a medical free electron laser (MFEL) operating between 2 and 10 μm through chalcogenide fiber [22]. The MFEL can emit more than 10 MW of power in a femtosecond pulse which relates to an average power of greater than 10 Watts. While not all this power is needed, it has been shown [23] that in certain cases, surgery at 6.45 μm based on cleaving of protein bonds is more efficient and leads to less denatured tissue and scarring than with conventional Er:YAG lasers at 2.94 μm based on OH absorption [23]. Current efforts are underway to perform surgery using chalcogenide fibers at 6.45 μm. Nevertheless, ophthalmic surgery requires operation at 2.94 μm, with an energy requirement of 1-2 mJ. This has been demonstrated using chalcogenide fibers. Harder tissue will require up to 30 mJ and consequently larger core diameter (900 μm) fiber is currently being developed. Output energy from an Er:YAG laser operating at 2.94 μm has been transmitted through sulfide fiber. Up to 271 kW/cm$^2$ power density has been transmitted without damage to the fiber. It is conceivable that laser power can be used for machining numerous materials and biological samples by tuning the wavelength and transmitting the laser power through the chalcogenide fibers to remote areas.

The end face reflection losses decrease the overall throughput of laser power. For example, $As_{40}S_{60}$ and $Ge_{30}As_{10}Se_{30}Te_{30}$ glasses have refractive indices of about 2.4 and 2.8, for which reflection losses are about 17% and 22% per face, respectively. Consequently, AR coatings are being developed for both discrete wavelengths as well as broad band operation [18,20]. Reflection losses have been reduced to about 1 % per face for sulphide fibers at some IR wavelengths [20].

### *3.2.2. Chemical Sensing*

Chalcogenide fibers are well suited for chemical sensing applications since practically most molecular species vibrate in the infrared region. The chalcogenide fibers can be used in fiber optic chemical sensor systems for quantitative remote detection and identification as well as detecting chemicals in mixtures. Examples of different sensing techniques include evanescent/ATR (attenuated total reflectance) [24-26], diffuse reflectance and absorption spectroscopy [27-29]. The diffuse reflectance and evanescent/ATR techniques are useful for samples that scatter or are opaque at the IR wavelengths. Numerous systems have been studied and many species have been detected including aqueous, non-aqueous and toxic liquids as well as solids [24-29]. Examples include oil, freon, soap, paints, polymer curing reactions, glucose/water, benzene and derivatives, chlorinated hydrocarbons,

alcohols, carboxylic acids, aqueous acids, perfumes and pharmaceutical products. Fig. 6 shows some representative spectra. Condition based maintenance (CBM) is becoming increasingly important and uses the approach, “if it isn’t broken, don't fix it”. For example, changes of oil in motor vehicles are routinely performed every 3000 miles or so, but are not necessarily needed and therefore the incurred costs can be quite significant. A fiber optic dipstick probe could potentially monitor the quality of the oil and consequently save large amounts of money in preventing unnecessary oil changes in the military and civil sector. For example, there is an additive package used to inhibit viscosity breakdown of engine oil. Unfortunately, the environmental breakdown of the additive package occurs and leads to viscosity breakdown of the oil.

A fiber optic dipstick can be used to monitor the by-products of degradation of the additive package (Fig. 6b). The alarm bells sound when these reach a pre-determined threshold value, signaling an oil change.

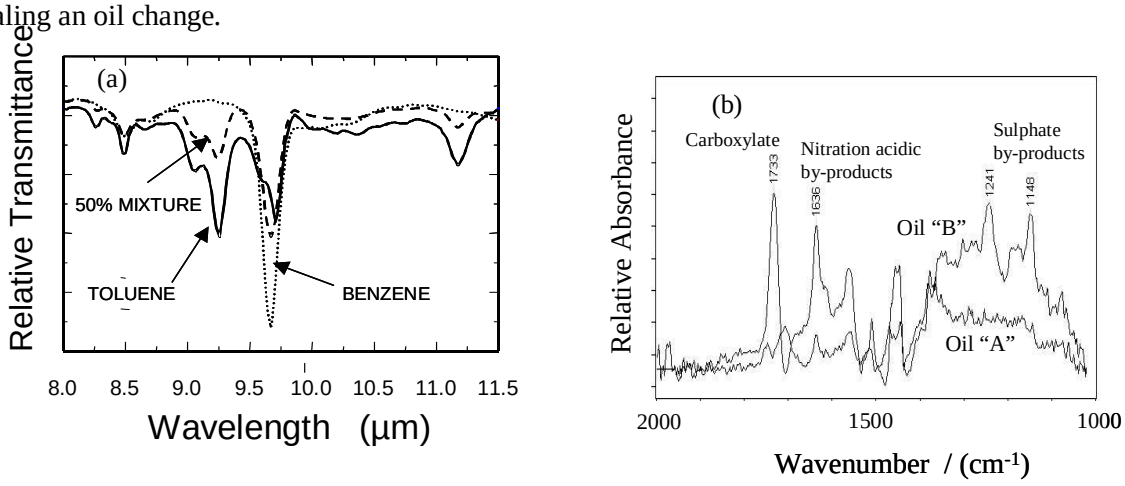


Fig. 6. Chemical sensing using IR fibers for (a) mixture of benzene and toluene and (b) difference spectra of degraded oil (after 27).

A fiber optic based reflectance probe has been used to detect contaminants in soil (Fig. 7) [30]. The detection was accomplished with the probe deployed in a cone penetrometer and tested in the field. Detection limits of 130 ppm of marine diesel fuel in sea sand have been demonstrated using a 20 meter length of cable [30].

Chalcogenide fibers with a glass cladding have been used for evanescent sensing of a few 10’s of ppm of benzene (and derivatives) and chlorinated hydrocarbons. The low detection limits were achieved by etching the cladding glass and re-covering with specific polymer coatings which preferentially enrich one phase in them near the core surface [31]. Polydimethylsiloxane (PDMS) preferentially enriched benzene (and derivatives) and low-density polyethylene enriched the chlorinated hydrocarbons on the core surface while preventing water from penetrating the coating.

Recently, a chalcogenide fiber ATR probe has been used to show the spectral differences between various tissues and organs in bio-medical samples. Fig. 8a shows the IR spectra for various organs/tissues from a dead chicken, while Fig. 8b shows the IR spectrum recorded from the liver of an anaesthetized sheep [22]. Similar IR spectra have been recorded from an anaesthetized mouse with a malignant (cancer) human breast tumor grown near the surface.

While these data were recorded using chalcogenide glass in contact with tissue, alternative IR transmitting and bio-compatible probes will most likely be needed for human testing. However, the chalcogenide fibers can be utilized to generate a bio-medical database for medical diagnostics such as tissue evaluation and early detection of cancer [32]. Currently, sections are cut out of the body, prepared into thin sections and desiccated before FTIR analysis is performed. Obviously, the flexible fiber optic approach is minimally invasive. While silica fibers are available they are inappropriate for infrared spectroscopy in the 2-10 μm region.

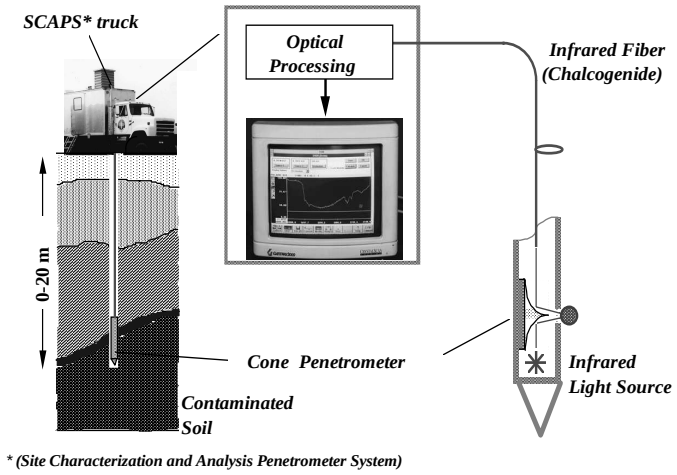


Fig. 7. The cone penetrometer system using chalcogenide fiber for detection of contaminants and water in soil.

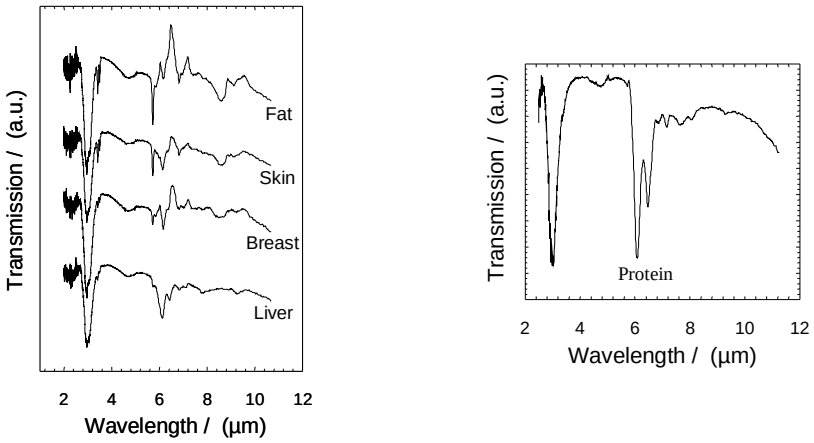


Fig. 8. Attenuated Total Reflection (ATR) spectra of (a) chicken tissue/organs and (b) liver of living sheep.

### *3.2.3. Temperature monitoring, thermal imaging and hyperspectral imaging*

Ueda et al. [33] have used As-S fibers with a Teflon cladding to measure temperature increases of up to 200$^{o}$C on the surface layer of ceramic plates during grinding.

Kapany and Simms first suggested the use of chalcogenide fibers for thermal imaging [34]. Saito et al. [35] recorded the image of an electric iron at 773 K, with some degree of coherency through a 1000 fiber bundle. Nishii et al. [36] fabricated a flexible fiber bundle containing 8400 Teflon coated fibers and recorded the thermal image of an operating integrated circuit in the 3 to 5.4 μm region using an InSb detector. Techniques are needed for the fabrication of coherent and registered fiber bundles containing small diameter fiber but with tight tolerances and high precision.

The area of hyperspectral imaging can be exploited by coupling coherent fiber bundles to focal plane array (FPA) detectors based on InSb (2-5.4 μm) or MCT (3-11 μm). The focal plane array detectors are extremely sensitive and can be used for performing both spatial and spectral analysis in the infrared [37]. In other words, one can derive an IR spectrum from each pixel thereby performing chemical spectroscopy at every pixel. FPA detectors have been used for obtaining spectral and spatial information about the environment for a number of years, but without fibers. The only report in the literature pertaining to IR fibers is a 10x10 fiber bundle of $As_2S_3$ fiber with a Teflon cladding which was reformatted to a 1x100 array and the output analyzed using a grating spectrometer [38]. The intensity contour of a Xenon lamp was recorded. Coupling to FPA's requires high precision diameter and high quality fiber bundles so that each fiber in the bundle couples to only one pixel on the

detector otherwise the images will be blurred. We are currently involved in the development of coherent and registered fiber bundles.

#### *3.2.4. Near field microscopy*

Sub-diffraction limit resolution has been demonstrated using single mode silica fibers by pulling and/or etching the fiber ends from a diameter of 125 μm to below 100 nm at the fiber tip. Preliminary results were obtained using multimode chalcogenide fiber micro-tips with about 1 μm resolution [39]. More recently, the authors have used high quality singlemode and multimode chalcogenide fibers to demonstrate about 20 nm topographic resolution and about 200 nm spectral resolution for different samples such as polycrystalline diamond [40], pancreatic cells [41], biofilms and semiconductor samples. Figs. 9 and 10 show the topographic and optical images for a polycrystalline diamond film and pancreatic cells, respectively. In our opinion, this is a promising technique for imaging and performing spectroscopy of semiconductor and biological samples with sub-micron resolution.

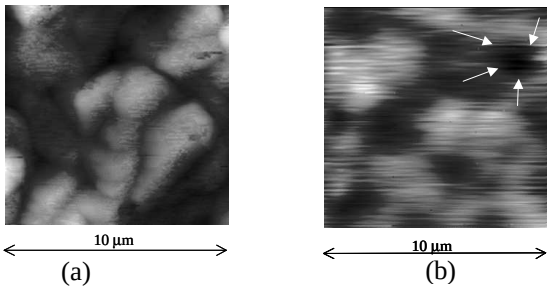


Fig. 9. The scanning near field IR microscopic (SNIM) data for a polycrystalline diamond film using a sulphide fiber micro-tip. The (a) topographic and (b) optical spectra (at λ=3.5 μm) were recorded with a resolution of about 200 nm.

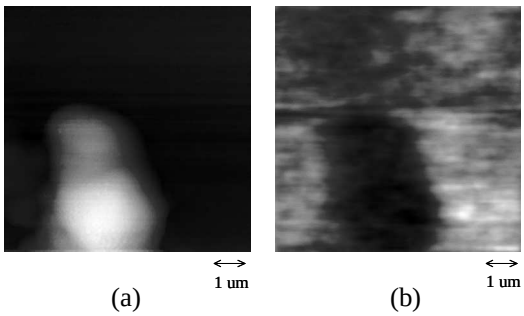


Fig. 10. The scanning near field IR microscopic (SNIM) data for pancreatic cells using a selenide fiber micro - tip. The (a) topographic and (b) optical spectra (at λ = 6.1 μm) were recorded with a resolution of about 25 nm and 200 nm, respectively.

#### *3.2.5. Fiber multiplexing*

Fused fiber couplers are important since they enable fiber multiplexing. For example, they might be used in IR fiber optic chemical sensing systems and data transmission systems. A preliminary fused taper fiber coupler has been fabricated using a multimode arsenic sulphide fiber with a coupling ratio of 3:1 at 2.65 μm [42], but it should be possible to use singlemode fibers.

### 3.3. Active applications

#### *3.3.1. Rare earth doped fibers*

Rare earth ions possess characteristic electronic energy levels which are only slightly influenced by the host matrix due to the screening effect of the d-electrons. When pumped with the

appropriate energy, the electrons are excited into upper levels from which they can subsequently decay to lower levels. Certain transitions become increasingly more efficient in longer wavelength transmitting hosts such as the chalcogenide glasses due to less multiphonon quenching and IR fluorescence emissions beyond 2 μm are only seen in chalcogenide glasses and not in silica. Table 5 lists the IR emission wavelengths found in chalcogenide glasses [43-53]. The only laser oscillation observed in chalcogenide fibers has been from Nd at 1.08 μm [54] while amplification has been demonstrated using Nd at 1.08 μm [55] and Pr at 1.34 μm [7]. These results were obtained in sulphide glass hosts. The 1.3 μm wavelength is of interest for telecommunications [56]. The gain coefficient obtained from the singlemode sulphide (Ga-Na-S) fiber at 1.34 μm was a remarkable 0.8 dB/mW and the efficiency was about 30 %. The fiber loss at 1.34 μm was about 1 dB/m [56].

Table 5. The IR emission wavelengths in chalcogenide glasses and wavelengths which have exhibited laser oscillation and amplification in chalcogenide fibers.

| Rare Earth Ion | IR Emission Wavelengths (μm) | Laser Oscillation Wavelength (μm) | Amplification Wavelength (μm) |
|---|---|---|---|
| **Nd** | 0.786, 0.919, 1.08, 1.37 [42,43] | 1.08 [54] | 1.08 [55] |
| **Er** | 0.822, 0.860, 0.987 [44,45], 1.54 [46], 2.7, 3.5, 4.5 [47] | ----- | ----- |
| **Tm** | 1.21, 1.45, 1.81, 2.35 [48] | ----- | ----- |
| **Ho** | 0.76, 0.91 [45], 1.2, 2.9, 3.9[49] | ----- | ----- |
| **Pr** | 1.3, 1.6, 2.9, 3.4, 4.5, 4.8, 4.9, 7.2* [50,51] | ----- | 1.34 [7] |
| **Dy** | 1.3, 1.8, 2.3, 4.3 [52] | ----- | ----- |
| **Tb** | 3.0, 4.8, 8.0* [47] | ----- | ----- |

* Indirect evidence
The numbers in [ ] are references.

Recent work has shown that Dy doped selenide glasses are better candidates for 1.3 μm fiber amplifiers due to the lower phonon energy of the host glass, and the larger absorption and emission cross-sections for Dy [53]. Consequently, the efficiency is expected to be about 90% and the gain coefficient approximately double the value for the best Pr doped sulphide fiber [53]. Modeling has shown that the Dy doped selenide fiber can tolerate higher losses compared with the Pr doped sulphide fibers. Therefore, device lengths will be shorter, such that a 45 cm length of doped selenide fiber with a loss of about 10 dB/m can give almost 40 dB gain at 1.34 μm. Table 6 shows some of the properties. Preliminary multimode fibers have been drawn with losses of about 6 dB/m at 1.3 μm and less than 3 dB/m at about 6 μm [57]. Unclad fibers have been fabricated with losses of about 3 dB/m at 1.3 μm and less than 1 dB/m at 6 μm. Preliminary single mode fibers have been drawn with minimum losses of about 3 dB/m [57].

Since the rare earth doped chalcogenide fibers emit in the 2 to 5 μm region [66], an array of the fibers can be used for infrared scene simulation (IRSS) for characterization of focal plane array detectors (e.g. InSb) [58]. Fig. 11 shows the emission spectrum of a Pr doped selenide glass fiber, demonstrating broad band emission between about 3 and 5 μm. Prototype bundles have been fabricated and mid-IR emission measured from the pixels [58]. Black body temperatures of up to 900 K have been simulated in single pixel pumping indicating that these fibers are capable of providing bright sources in the IR [58].

It is possible to use these fiber sources in chemical sensor systems [22]. For example, figure 12 shows the IR transmission spectrum of a thin film of toluene between two $CaF_2$ plates recorded using a Pr-doped selenide fiber (pumped at 1.064 μm) as a mid-IR source.

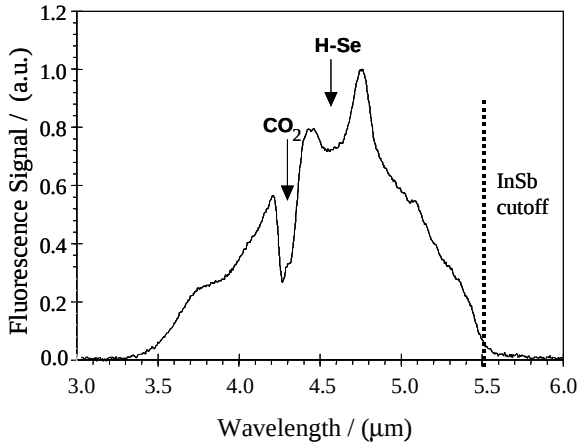


Fig. 11. The broad band mid-IR emission from a Pr doped GeAsGaSe glass fiber.

Table 6. Branching ratios (β), quantum efficiencies (βη), lifetimes (τ), emission cross-sections (σ) and gain coefficients (στ), for potential 1.3 μm fiber amplifier systems.

| Glass System | β | η (%) | βη (%) | τ (ms) | σ ($x10^{-20}$ $cm^2$) | στ ($x10^{-26}$ $cm^2s$) |
|---|---|---|---|---|---|---|
| **Pr: ZBLAN** | 0.6 | 3.4 | 2.0 | 110 | 0.35 | 38.5 |
| **Pr: GaLaS** | 0.52 | 58 | 30 | 295 | 0.84 | 250 |
| **Pr: GaNaS** | 0.52 | 58 | 30 | 370 | 1.08 | 400 |
| **Dy: GaLaS** | 0.93 | 29 | 27 | 59 | 2.8 | 165 |
| **Dy: GeAsSe*** | 0.93 | 95 | 88 | 310 | 2.7 | 837 |

* based on Ge-As-Se system

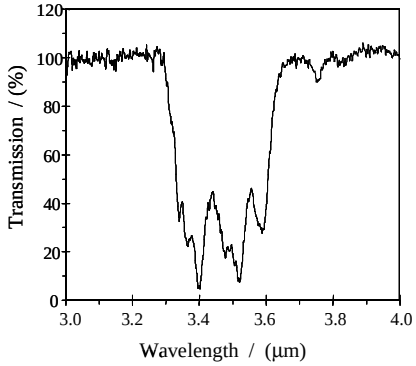


Fig. 12. Transmission spectrum of toluene using the mid-IR emission from a Pr-doped GeAsGaSe glass fiber.

The ability to write gratings in chalcogenide fibers will enable smart compact devices including lasers and dispersion compensators. Some work has been performed on writing gratings in chalcogenide glass fibers [59]. Asobe et al. [59] have fabricated an $As_2S_3$-based fiber Bragg grating for 1.55 μm wavelength operation by the transverse holographic method using a He-Ne laser. A reflectivity of > 90% was obtained with an estimated change in refractive index of about $10^{-4}$.

### *3.3.2. Non-linear effects*

Glasses possessing high third order non-linearities ($X^3$) are required for ultra-fast switching, especially for time division multiplexing (TDM) in telecommunications systems. It is well established that the values of $X^3$ for chalcogenide glasses are about two orders of magnitude larger than silica [60,61]. To our knowledge, the number of papers reporting the use of this phenomenon in actual switching applications is not extensive. M. Asobe et al. [62] demonstrated efficient optical Kerr shutter (OKS) switching operation with pico-second response time using a 1 meter length of elliptical core fiber and a 100 GHz signal operating at a wavelength of about 1.5 μm.

Since glasses lack a center of inversion symmetry and thus have no second order nonlinear succeptibility ($X^2$) then they should not exhibit second harmonic generation (SHG) [63]. However, undoped and Pr-doped GaLaS glasses have exhibited SHG [64]. This SHG may be due to crystallization or the effect of frozen-in electric fields. The latter arises from the relationship $X^2 = E_{dc}X^3$, where $E_{dc}$ is the frozen-in electric field [63]. Electric poling has been successfully used to produce SHG in silica based fiber systems [65]. It is not unreasonable to expect similar results in chalcogenide fibers. While $X^3$ is about 2 orders of magnitude larger in chalcogenides compared with silica, we expect larger SHG efficiencies in electrically poled chalcogenide glasses. However, the question arises as to whether the electric fields can be frozen-in for chalcogenide glasses. We have observed preliminary second harmonic generation using electrically poled chalcogenide glasses. At the present time the magnitude appears comparable to silica glass but the mechanism is unknown.

## 4. Conclusions

Tremendous progress has been made in reducing the optical losses of the chalcogenide glass fibers in the past several years resulting in numerous applications. We strongly believe that IR fiber optics will become increasingly more important in the future as further improvements are made to the quality of the fibers and new compositions developed. One of the most exciting developments in the future is going to be in the area of rare earth ion doping of fibers for IR fluorescence emission. The IR light sources, lasers and amplifiers developed using this phenomenon will be very useful in civil, medical and military applications. Remote IR spectroscopy and imaging using flexible fibers will be realized for medical and military applications. Other future research areas which will inevitably be explored include the gratings and non-linear optical properties of the IR glasses. The authors strongly believe that chalcogenide glass fiber optics will grow due to the numerous and potentially extensive applications. The availability of high quality, low loss and high strength singlemode and multimode fibers will undoubtedly improve the capabilities of existing technologies as well as enable new technologies. In summary, the future of chalcogenide glasses and fibers looks very bright.

**Acknowledgements**

The authors would like to acknowledge M. Druy (Sensiv Inc.), R. Waynant (FDA), Z. Bhatalwalla (Johns Hopkins U.), G. Edwards, N. Tolk, J. M. Gilligan, D. Jansen (Vanderbilt U.), M. Luce, R. Generosi, P. Perfetti, A. Cricenti (Instituto di Struttura della Materia), G. Margaritondo (Ecole Politechnique Federale) and D. Schaafsma (Tetra Tech Data Systems).

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