Recent improvements on mid-IR chalcogenide optical fibers

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ABSTRACT

Fabrication process of arsenic-sulfide (As-S) and arsenic-selenide (As-Se) optical fibers has been improved to enhance the transmission in the mid-IR region. Typical attenuation spectrum of As-S or As-Se optical fibers shows impurities bands, such as S-H, Se-H, O-H, which limit their operation and cause the increase of the attenuation loss in the mid-IR. Precursors purification methods and glass processing were improved to minimise those impurities bands. Regarding As-S fibers, the attenuation around 2.7 μm is 0.12 dB/m and S-H concentration is lower than 0.3 ppm. In the case of As-Se fibers, the minimum of attenuation located at 6 μm is 0.2 dB/m and Se-H concentration is lower than 0.5 ppm. Efforts have been also made to improve the mechanical properties which are usually affected by several parameters such as drawing conditions or heterogeneous inclusions contained in the glass. The double-crucible method gives high quality core/clad interface and consequently increases the strength of the fiber. Inclusions consist mainly of carbon and silica particles. Those impurities enter the glass from initial precursors and are also formed by interaction with the apparatus material. Thanks to the process improvement, impurities particles are minimized and tensile strengths up to 0.32 GPa and 0.41 GPa are reached for As-Se and As-S fibers respectively.

Keywords

Chalcogenide glass, Arsenic-sulfide, Arsenic-selenide, optical fibers, mid-IR

1. Introduction

Chalcogenide glasses based on As-S and As-Se systems are the most promising materials for fiber optics in the mid-IR. Such materials have high transparency between 2 -5μm and 2- 8 μm for respectively As-S and As-Se glasses. As-S system is stable against the crystallization, so As-S optical fibers can be easily made by standard fiber processing like rod-in-tube or double-crucible. On the other hand, As-Se glasses tend to crystallise [1] if the drawing process is not carefully controlled. Glass fabrication process has to be optimized to obtain low loss optical fibers. Indeed, optical losses in fibers from glasses prepared without special purification can be larger than 1 dB/m. This high attenuation is mainly due to impurities coming from the raw materials (As, S and Se) such as hydrogen/oxygen groups (S-H, Se-H, O-H) and carbon (C, C-S). Losses can be also caused by particles that create scattering centers. These particles are mostly silica particles coming from the apparatus used for the glass process [2].

2. Experiment

2.1. Glass fabrication

As-S and As-Se glasses are synthesised by the well-known dynamic melting-quenching process in evacuated silica ampoules. Targeted glass compositions are close to the stœchiometric formulas (As_2Se_3 and As_2S_3).

High purity (at least 6N) raw materials (As, S and Se) are used to synthesised As-S and As-Se glasses. All compounds are manipulated in glove box with oxygen and moisture controlled. Before glass fabrication, purification processes of raw materials are necessary to improve their purity against organic impurities (C, H and O). After these steps, raw materials are mixed in the right ratio to get the targeted core and clad compositions and then charged in silica ampoule. Hydrogen getters can be also added to minimize S-H or Se-H impurities absorption. Distillations of the melt under vacuum are generally necessary to get better glass transmission. Glass melts are then homogenized at high temperature in a rocking furnace and quenched in water. Finally glasses are annealed several hours at temperature close to the Tg and slowly cooled down to room temperature.

2.2. Optical fiber drawing

As-S and As-Se optical fibers are fabricated by the double-crucible process. After cool down, core and clad ampoules are broken. In order to remove silica residues coming from the ampoule, glass rods are cleaned in diluted HF acid in an ultrasonic bath and then rinsed with deionised water and isopropanol. After drying, glass rods are inserted in a pyrex or quartz double-crucible especially adapted to the targeted core/clad fiber diameters. Temperature control of the drawing tower is a critical parameter especially for As-Se glasses that tend to easily crystallize. Core/clad ratio and fiber diameter are monitored by adjusting temperatures, pressures and drawing speed. Optical fibers are protected by UV cured acrylate coating.

2.3. Optical fiber characterization

Chalcogenide fibers are proof-tested typically between 15 kpsi and 25 kpsi.
Tensile strength measurements are made with a MTS tensiometer. Gage length is 0.5 m. Coating effect is taken account by calculating the R factor with the following formula:

$$R = \frac{E_0 A_0}{E_0 A_0 + E_1 A_1} \qquad (1)$$

with E the young modulus and A the cross sectional area of the corresponding materials. Underscripts 0 and 1 refer to the glass and the coating respectively. In paragraph 2.1, we mention that core and clad formulas are close to the stœchiometric compositions, then we can assume that the core/clad Young modulus is similar to the stœchiometric one's. Therefore E_0 take values 15.9 GPa and 18 GPa for respectively As-S and As-Se glasses.
Failure stress with coating compensation σ_c is calculated by equation:

$$\sigma_c = R\sigma \qquad (2)$$

with σ the measured failure stress without coating compensation.
Results are presented in terms of Weibull distribution by plotting the variations of:

- the failure probability F in percent with the failure stress σ_c in GPa
- ln(-ln(1-F)) versus σ_c

ln(-ln(1-F)) = f(σ_c) is a linear function that allows to determine both tensile strength parameters :

- the Weibull modulus M or the slope of the function
- the average strength S_0 given at ln(-ln(1-F)) = 0

Background loss of the fibers is measured by the cut-back method with a FTIR spectrometer especially modified for fiber measurements. A liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector is used to improve the sensitivity of the measurements. To eliminate cladding mode, the coating is removed for a portion of the fiber (several centimeters at both ends) and liquid gallium is applied on these sections of the fiber.

Numerical aperture (NA) is determined from the measurements of the far-field optical power distribution exiting from a two-meter length of fiber. The source is an Agilent EELED at 1550nm. Liquid gallium is used as cladding mode stripper. The distance between the detector and the output of the fiber is fixed. During the measurement, the detector is angular moved and the angular intensity is monitored. Far-field distribution is obtained by plotting the variations of the normalised angular intensity with the angle. The spatial distance between the 5 percent intensity levels is noted and the sine of half the angle between the points represents the numerical aperture.

Mid-IR high-power transmission tests on As-S fibers are also made by launching a beam at 2.825 μm coming from an 10W Er: ZBLAN fiber laser. The transmitted power is monitored by increasing the launched power up to the maximum of the fiber laser output power. Thermal effects are simultaneously quantified by measuring the increase of the fiber temperature.

By taking account of the Fresnel reflection R at both ends, the transmitted power P_t is given by the following formula:

$$P_t = P_i(1-R)^2 10^{-\alpha L/10} \tag{3}$$

With:

- α (dB/m) the attenuation of the fiber at 2.825 um
- L the fiber length (m)
- R the Fresnel reflection : $R = \left(\frac{n_G - 1}{n_G + 1}\right)^2$ with n_G the refractive index of As-S glass at 2.825 um, $n_G \sim 2.41$, then, R = 0.17
- P_i and P_t the incident and transmitted powers (W)

If there is no saturation of P_t, equation (3) is a linear function with a slope:

$$\mathrm{p} = (1-R)^2 10^{-\alpha L/10} \tag{4}$$

Therefore, by measuring the slope we can calculate α and compare this value with the cut-back measurement.

3. Results

3.1. As-S fiber

3.1.1. Background loss

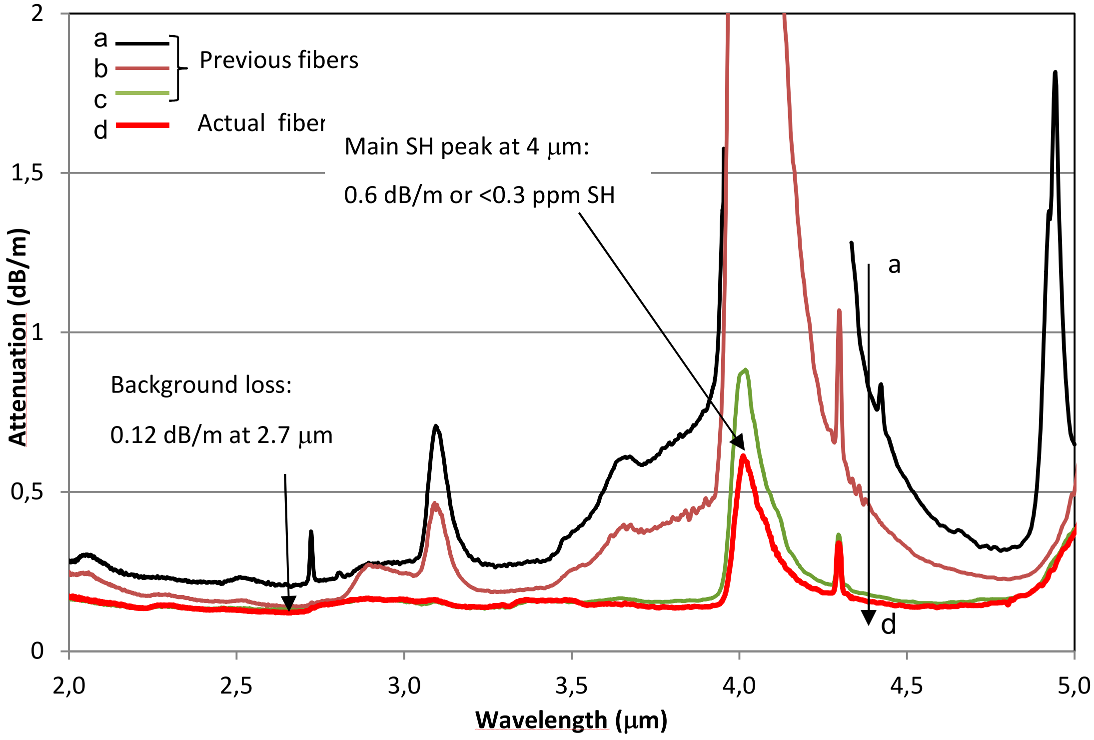

Figure 1. Attenuation spectrum of multimode As-S fibers as a function of glass processing improvements

Figure 1 shows the improvements of the transmission of multimode As-S fiber. Core and clad diameters are 100 µm and 170 µm respectively. Spectrum labelled "a" refers on glasses synthesized without specific raw materials purification and without dynamic distillation. Attenuation curve presents the typical impurities absorption bands such as H_2O at 2.7 µm, O-H at 2.9 µm, S-H first overtone at 3.1 µm, main S-H peak at 4 µm, and C at 4.9 µm. The attenuation at 4 µm is larger than 10 dB/m. By improving raw materials As and S purification and also the glass processing, the last generation of multimode As-S fiber is characterized by the attenuation curve "d". The S-H absorption band is only 0.6 dB/m at 4 µm. S-H absorption coefficient value is 2.5 dB/m/ppm at 4 µm [3]. Therefore, S-H concentration is lower than 0.3 ppm. No significant OH peak is observed. H_2O and C bands are not present. Background loss is 0.12 dB/m. Minimum attenuation is still located around 2.7 µm, but by decreasing the S-H peak, we tend to shift this minimum towards the theoretical wavelength range i.e. between 4.7 and 4.8 µm [4]. Indeed, attenuations at 2.7 µm and 4.7 µm are almost the same.

3.1.2. Numerical aperture measurement

Far field measurement at 1550nm give the following goniometric profile for a 2 m length multimode As-S fiber:

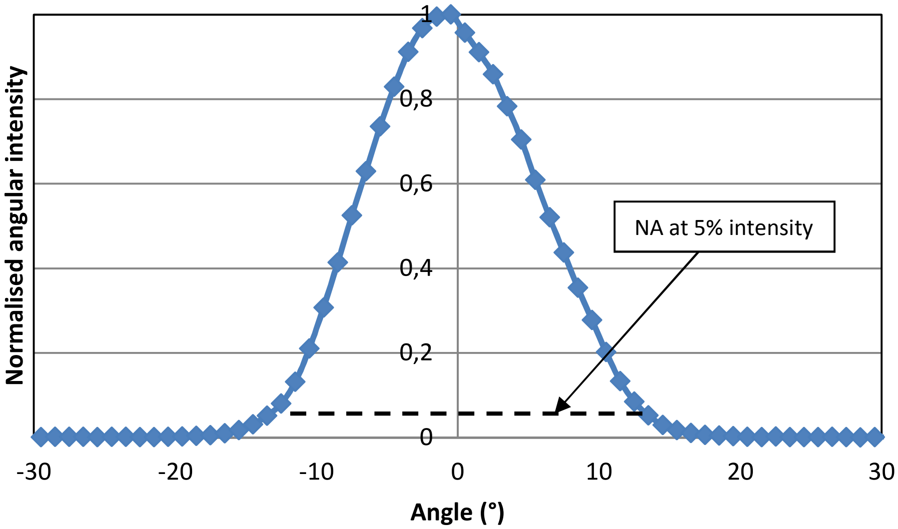

Figure 2. Goniometric profile of multimode 100/170µm As-S fiber

NA at 5% intensity is directly deduced from the profile. In this case, NA = 0.23.

3.1.3. Tensile strength measurements

Figure 3a shows the variations of the failure probability F with the failure stress σ_c in GPa and the equivalent in natural logarithm is given in figure 3b. By optimizing the fabrication process, impurities particles are minimized as well as heterogeneous inclusions like carbon and silica particles. The consequence is the increase of the average strength at ln(-ln(1-F))=0 (Failure probability = 63%) from 0.25 GPa to 0.41 GPa and a raise of the Weibull modulus from 11 to 14.

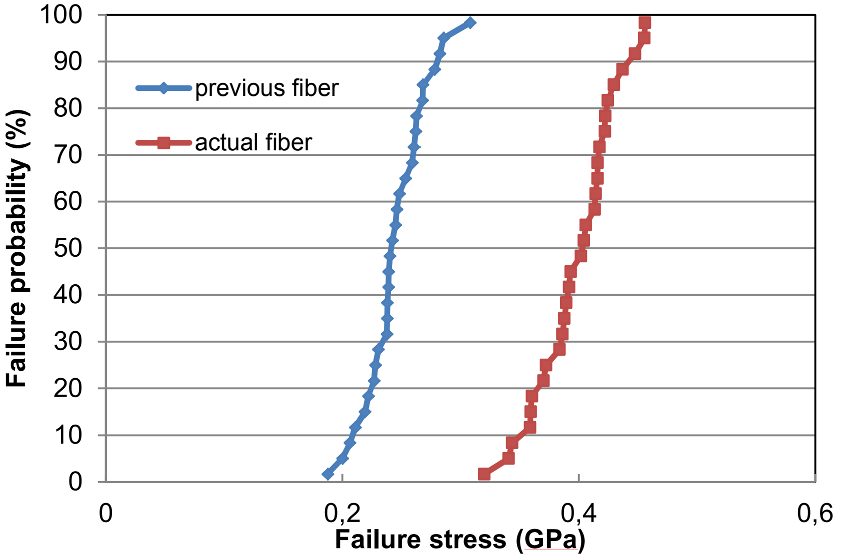

Figure 3a. Failure probability F versus the failure stress σ_c

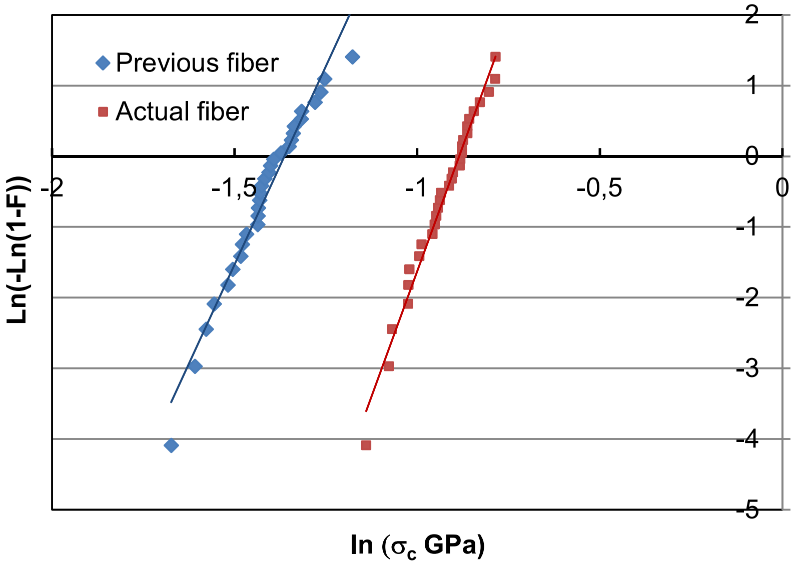

Figure 3b. ln(-ln((1-F))) versus the failure stress σ_c

3.1.4. High power transmission at 2.825um

This section relates the transmission at 2.825 µm of the last generation of multimode As-S fiber characterized by the attenuation spectrum “d” in figure 1. The experiment consists of injecting a beam from a 10W Er :ZBLAN laser at 2.825 µm in a 11m long 100/170µm As-S fiber. Liquid gallium is applied at both ends of the fiber to ensure light injection in the core and the transmitted output power is monitored as well as the raise of temperature between room temperature (TR). Results are shown in figure 4.

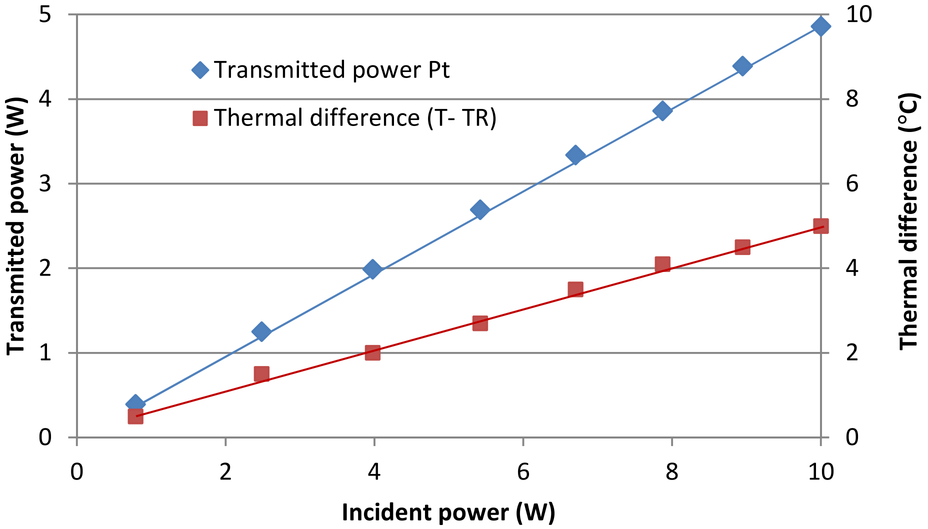

Figure 4. Transmitted power P_t and thermal difference versus the incident power

As expected, the transmitted power versus the incident power is a linear function. Therefore, P_t follows equation (3). There is no saturation at high pump power, so the fiber can support more than 10W of incident power, and the only limitation is the laser output power.

A linear fit gives p = 0.49. From equation (4), we calculate α = 0.13 dB/m. This value is consistent with the cut-back measurement (i.e. 0.12 dB/m). No degradation of the fiber is observed: the transmitted power remains constant after 20 minutes at maximum incident power.

Regarding thermal analysis, the overall increase of fiber temperature is only 5°C. Moreover, we did not see hot spots in the fiber which proves the high purity of the glass and the absence of particles.

3.2. As-Se fiber

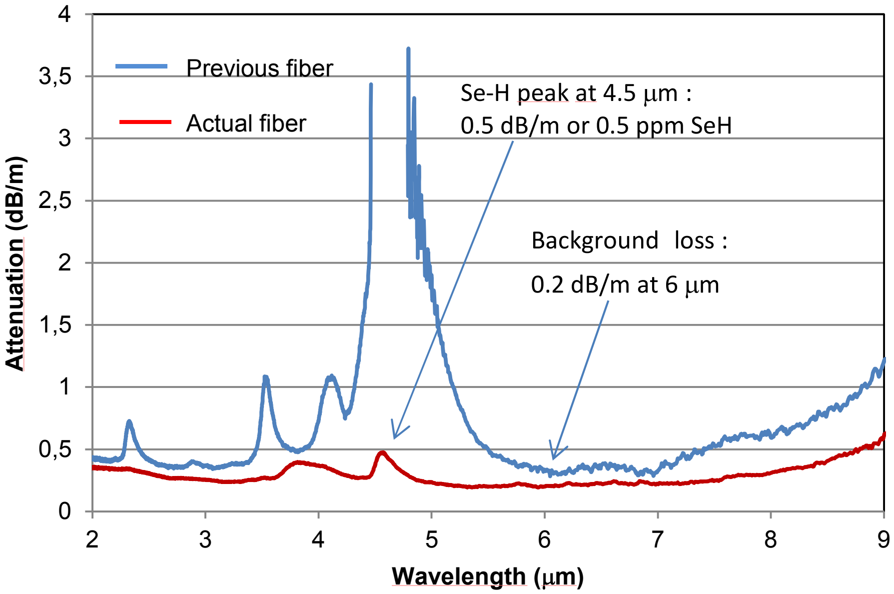

Figure 5. Attenuation spectrum of multimode As-Se fibers as a function of glass improvements

Figure 5 shows the effects of the fabrication process on the attenuation spectrum of multimode 100/170 µm As-Se fibers. The strong impurity Se-H peak centered at 4.5 mm is decreased to 0.5 dB/m. Se-H absorption coefficient value is 1.1 dB/m/ppm at 4.5 µm [3]. Therefore, Se-H concentration is lower than 0.5 ppm. Background loss is 0.2 dB/m at 6 µm. Regarding tensile strength measurements, the average strength is increased to 0.32 GPa.

4. Conclusion

This paper summarizes the fabrication and characterization of arsenic-sulfide and arsenic-selenide optical fibers. Raw materials As, S and Se are carefully purified to minimize impurities especially hydrocarbon. Glass processing was also improved. The result is a strong decrease of usual impurities bands S-H and Se-H in As-S and As-Se fibers respectively. S-H attenuation at 4 µm is only 0.6 dB/m or less than 0.3 ppm in S-H. Also, the absorption of Se-H at 4.5 µm is 0.5 dB/m or 0.5 ppm in Se-H.

Background loss and mechanical properties are also improved. The minimum attenuation of multimode As-S and As-Se fibers are 0.12 dB/m and 0.2 dB/m respectively. Tensile strength measurements give an average strength for As-S and As-Se fibers of 0.41 GPa and 0.32 GPa respectively.

5. References

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