MIR chalcogenide fiber and devices

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ABSTRACT

Ongoing efforts on the purification of chalcogenide glasses and fiber draw processes enable the production of commercial-grade mid-infrared (MIR) fibers for 1.5-10 μm transmission. Results show multimode and single-mode MIR fibers with low-loss (<0.1dB/m) and high tensile strength (>20kpsi). High-power laser transmission has been achieved in single-mode fiber (>5 MW/cm^2 CW).

Keywords: Chalcogenide, fiber, sensor, mid-infrared, sulfide, selenide, nonlinear, glass

1. INTRODUCTION

Chalcogenide glasses (glass based on S, Se and Te) are excellent candidates to develop mid-infrared fibers. A wide range of applications become possible with chalcogenide glass fibers due to the broader MIR wavelength transmission window (1.5-11 μm), higher nonlinearities[1] (approximately 1000 times that of silica) than any other infrared (IR) optical fibers, and chemical durability, making them ideal for the development of mid-infrared applications. In particular sulfide (As-S) and selenide (As-Se) chalcogenide fibers have good transmission between 1.5-6 μm and 1.5-9.5 μm respectively. Furthermore As-S fiber has low negative thermo-optical coefficient[2] ($dn/dT < -1x10^{-6}$) that enables very high-power laser transmission without self-focusing causing catastrophic failure.

Recently, much effort has been made in fabrication of high purity As-S and As-Se fibers to decrease the content of impurities as oxygen, carbon, hydrogen, silica, etc. Theses impurities induce additional absorption in the mid-infrared, as well as scattering losses due to micro inclusions. Improved purification methods during glass fabrication and treatment process have been developed. Also the fiber draw tower equipment has been optimized for the fabrication of chalcogenide fibers with excellent control on the fiber diameter and core/clad concentricity. This paper presents the results of the development on multimode and single-mode As-S and As-Se fibers with good optical and mechanical properties.

2. CHALCOGENIDE GLASS FABRICATION

Chalcogenide glasses are fabricated from highly purified precursors in controlled atmospheric environment to minimize impurities that would otherwise increase fiber loss. Raw materials (As, S, Se) commercially available at 6N (99,9999% purity) cannot be used directly for As-S and As-Se fibers fabrication. Further purification of the raw materials is necessary to remove organic impurities (H, O, C). The desired chemical compositions of sulfide (As_2S_3) and selenide (As_2Se_3) are prepared in highly controlled glove boxes (<1ppm moisture, <1ppm O_2). Chemicals are batched inside special quartz glassware. The desired chalcogenide glass chemical composition can be precisely controlled to 0.5% or better. Hydrogen getter is added to minimize S-H or Se-H impurities. Chalcogenide glass purification is performed in special furnace in a series of dynamic distillations under high vacuum (10^{-5} torr). The purified glass melt is homogenized in a rocking furnace at high temperature. The final glass melt is quenched in water and annealed several hours at a temperature close to the glass transition temperature before being cooled down slowly to room temperature. These steps are required to reduce the absorption of impurities and the introduction of extrinsic scattering centers that contribute to the total optical loss of the fiber. Chalcogenide glass rods are left in sealed quartz ampoules.

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3. CHALCOGENIDE FIBER DRAW

Chalcogenide fibers are produced by the double-crucible (DC) technique[3]. The selected chalcogenide glasses for the core and clad are removed from the sealed quartz ampoules. The chalcogenide glass rods are cleaned in HF acid to remove any silica particles on the surface. The rods are loaded in the DC glassware. Multimode and single-mode chalcogenide fibers can be drawn with special DC glassware. The DC glassware is designed with precise exit holes for specific core and clad dimensions.

The DC glassware is inserted inside the oven at the top of the fiber draw tower. The oven is inside a Plexiglas box purged with nitrogen gas. The fiber draw structure itself is inside a Class 100 cleanroom enclosure (ISO 5). The temperature is ramped up to the drawing temperature and the pressures over the core and clad melts are individually adjusted to obtain the desired core/clad diameter ratio. UV cured acrylate coating is applied on the fiber for protection. The drawing speed is automatically adjusted with the feedback signal from the fiber diameter gauge. The control system has been optimized to precisely control the fiber diameter at ±1 μm or better.

4. AS-S FIBER

4.1 Optical properties

Sulfide (As-S) fiber transmits well in the 1.5-6 μm range. Figure 1 shows the loss spectrum for a 100/170 μm core/clad diameters. The loss spectrum is measured by the cutback technique. FTIR is used with liquid nitrogen cooled HgCdTe detector. The absorption peak at 4 μm is caused by S-H bond impurities. The minimum background loss is 0.083 dB/m at 4.8 μm.

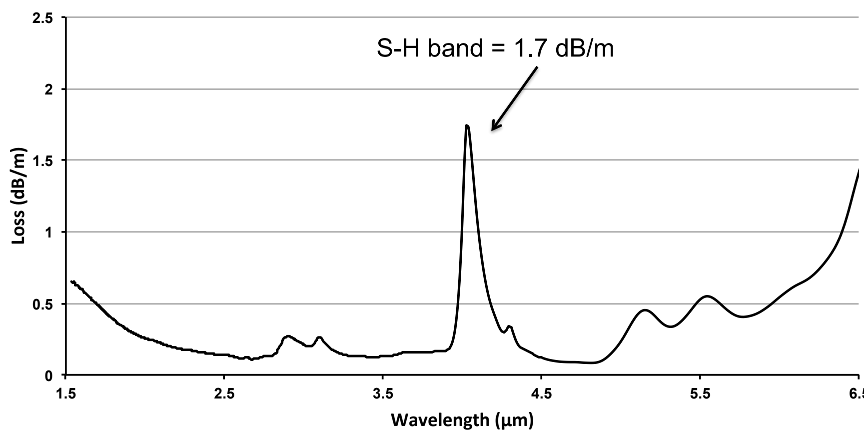

Figure 1. Loss spectrum for the 100/170 μm core/clad As-S fiber.

Multimode and single-mode As-S fibers are made with the DC technique with extremely good core/clad geometry control. Core/clad concentricity error is better than 2 μm. Also the fiber diameter is controlled with a precision of ±1 μm. Typical draw can produce several hundred meters of As-S fiber.

The numerical aperture of the fiber is determined by the difference in the chemical composition between the core and clad glasses. Typical compositions for the sulfide fiber are: $As_{39}S_{61}$ for the core and $As_{38}S_{62}$ for the clad. This core/clad combination gives a numerical aperture (NA) of 0.3. Lower and higher NAs are possible with different chemical compositions. NAs from 0.2 to 0.5 have been achieved.

Single-mode fiber with 9 μm core diameter is tested for high-power transmission with a fiber laser CW at 2 μm wavelength. The fiber under test is one meter long and liquid gallium was applied on the bare fiber at both ends to strip out any light in the clad. The coupling lens is 10 mm focal length. The focal spot size is estimated at 9.3 μm. An iris and optical isolator are used between the laser and the focusing lens. The available maximum laser power at the fiber input is 3.5W CW and the output laser power from the fiber is 2.1W. Figure 2 shows the high-power transmission results.

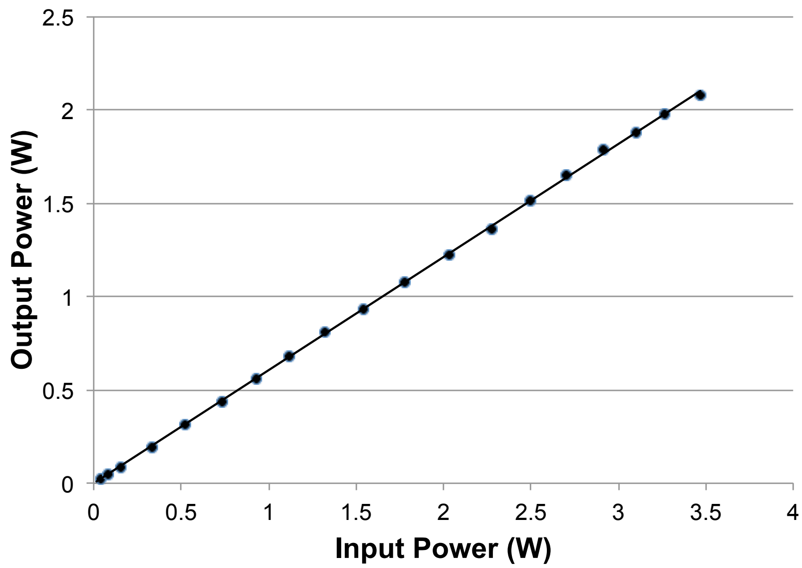

Figure 2. Output power transmission versus input power for As-S single-mode fiber with 2 μm fiber laser.

The transmitted power is a linear function of the input power. There is no saturation of the transmitted power and no laser-induced damage is visible up to the available laser power (3.5W). The estimated laser power density at the input of the As-S single-mode fiber is ~5 MW/cm^2. This power density is impressive when you consider that one could potentially couple over 400W of laser power in a 100 μm As-S multimode fiber core.

Based on the slope (m) of the transmitted power (0.61) in Figure 2, the Fresnel reflection loss (R) at both ends of the fiber (2 x 17%), and the fiber loss (α) at 2 micron (0.25 dB/m), we can estimate the coupling loss (L_c) in the single-mode fiber according to equation (1). The calculated coupling loss L_c is approximately 6.6% (0.3dB). We believe that L_c could be reduced with shorter focal length lens and higher precision translation stages.

$$L_c = \frac{(1-R)^2 10^{-\alpha L/10}}{m} - 1 \tag{1}$$

4.2 Mechanical property

As-S glass has Young's modulus of 16.7 GPa[3], which is 4.3 times smaller than that in silica (72.1 GPa). Commercial As-S fibers are usually screen proof tested at 20 kpsi to detect and remove fiber defects. Inclusions in the glass, defects at the fiber surface, or bubbles in the coating can cause breaks. Proof test at 20 kpsi is sufficient to handle chalcogenide fiber in actual applications.

A new coating material is evaluated to increase the overall mechanical properties of the fiber. Fluoropolymer coating is used to improve the mechanical properties of the fiber and also reduce aging effects (mechanical and optical). Low-purity As-S glasses are used for the evaluation tests. Two 100/170 μm core/clad As-S fibers are produced. The first As-S fiber has 5 μm thick thermally cured fluoropolymer coating and 350 μm diameter UV cured acrylate coating. The second As-S fiber is coated with 340 μm diameter acrylate coating only.

We use a tensile test system to estimate the actual strength of the fiber. The ends of the fiber samples are wrapped around two 50 mm diameter capstans coated with a double-sided adhesive tape. The gauge length is 500 mm. Constant extension rate (200 μm/s) is applied to the fiber and the breaking load is recorded for each fiber sample. Several fiber samples (~30) are tested in order to have a representative sample size. Weibull analysis is used to predict failure times of products, even based on small sample sizes. Weibull toolkit[4] is used to generate the probability of failure (%) versus the failure stress (kpsi). Figures 3 and 4 show the results for the As-S fibers with and without fluoropolymer coating respectively.

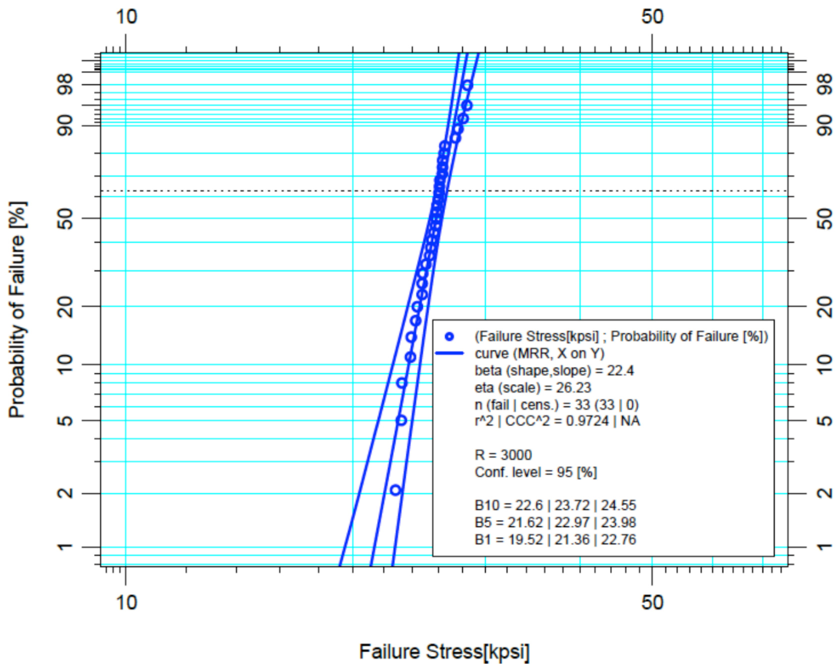

Figure 3. Weibull plot for the probability of failure versus failure stress for As-S fiber with fluoropolymer.

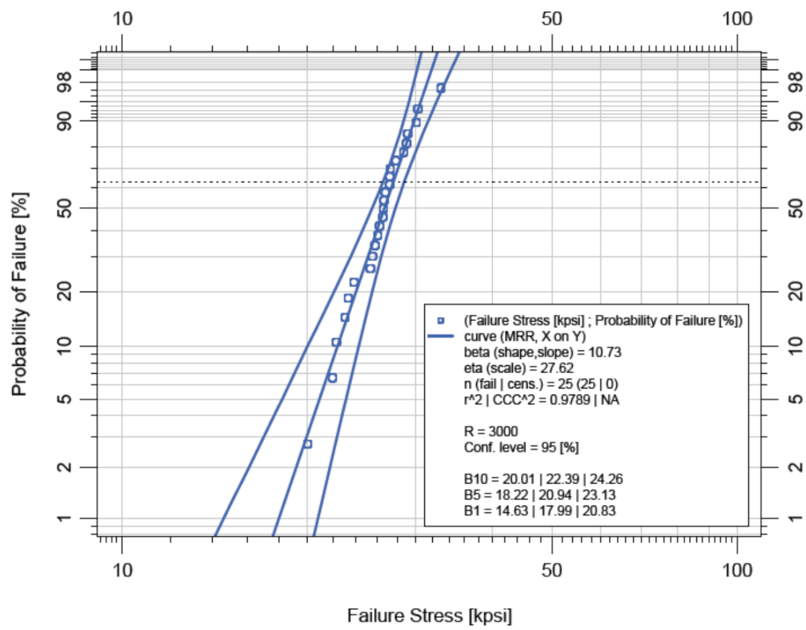

Figure 4. Weibull plot for the probability of failure versus failure stress for As-S fiber without fluoropolymer.

The analysis and conclusions of the probability failure results on optical fiber may vary significantly from one source to the other. Different failure stress studies and Weibull analysis software can lead to different conclusions. The current study uses tensile strength measurement and other study uses two-point bending test[3]. Both techniques will lead to different results. Also it is important to have extensive background knowledge and proper software training to draw the right conclusions from the Weibull plots. For small sample sizes (2-100) it is best practice to use Median Rank Regression (MRR) to determine the Weibull parameters. A straight line is fitted through the data points (the middle line in the plots of Figures 3 and 4). This line represents the 50% confidence level. Two other curves are shown on the plots. The curve on the right is the confidence level of 5% and the curve on the left is the confidence level of 95%. As a rule of thumb, we use the left curve to specify the fiber strength with 95% confidence level and for 1 % probability of failure. So as we see from Figures 3 and 4, the As-S fiber with fluoropolymer has strength of 19.52 kpsi and the fiber without fluoropolymer has strength of 14.63 kpsi. This is 33% improvement in the mechanical strength. Also the slope of the Weibull plot for the fiber with the fluoropolymer (Figure 3) is much steeper than for the fiber without (Figure 4), indicating more uniform strength performance. The As-S glasses used for the strength tests were low-purity. Other tests will be made with high-purity glasses and different thicknesses of fluoropolymer coating.

4.3 Laser ultramicroscopy

Heterophase inclusions (SiO_2, C, etc.) are impurities that limit mechanical strength as well as the laser damage threshold of the As-S fiber[5]. These inclusions consist of substances that are hardly soluble in the chalcogenide melts. The sizes of these impurities range between 0.05 μm to several μm and enter the glass from the initial elements and the interaction of glass melt with quartz glassware. The size and concentration of inclusions present are evaluated by scattering based on the laser ultramicroscopy - LUM. Two As-S glass samples are prepared for LUM evaluation: one low-purity sample and one high-purity sample. The glass samples are polished in a parallelepiped shape. He-Ne laser @ 632 nm transmits through the glass sample and a CCD camera and piezo-electric stage positioner are used to record images at different positions of the laser beam inside the test sample. The LUM calibration was made using 4 sizes of standard polystyrene beads (40 nm to 500 nm), in unmixed and mixed populations. Figures 5 and 6 show the LUM results for the low-purity and high-purity As-S glass samples respectively.

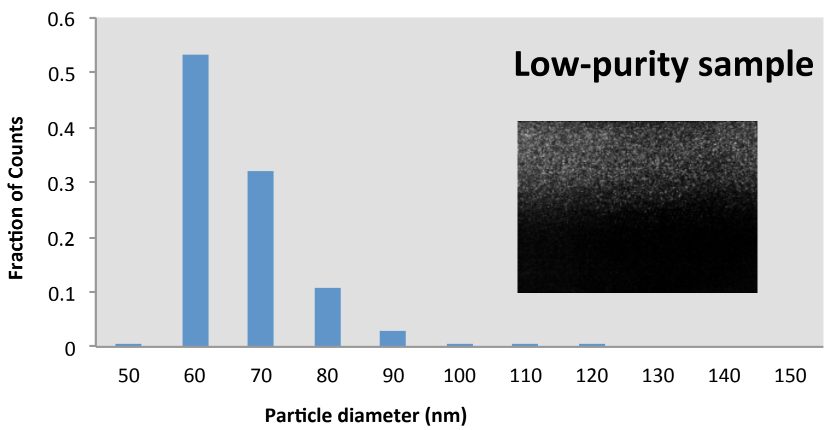

Figure 5. Histogram of the particle diameter fractional population for scatterers in low-purity As-S glass sample. The insert shows a characteristic LUM CCD image.

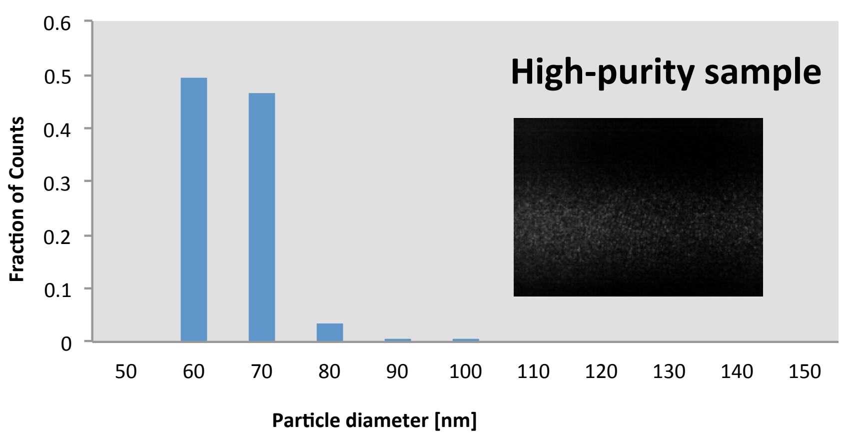

Figure 6. Histogram of the particle diameter fractional population for scatterers in high-purity As-S glass sample. The insert shows a characteristic LUM CCD image.

The low-purity sample has larger size scatterers (up to 100 nm) compared to the high-purity sample (70-80 nm). The distribution of scatterers in the low-purity sample is exponentially decreasing, as the size of the particles increases from 60 nm to 100 nm. The high-purity sample has a limited size particle population, almost equally divided between 60 nm and 70 nm sizes. LUM CCD captured photographs at 3.5x magnification are shown as inserts to the histograms, in order to have a qualitative picture of the measurements.

5. AS-SE FIBER

Selenide (As-Se) glass has tendency to crystallize and special time-temperature conditions must be used to draw As-Se fibers. Figure 7 shows the loss spectrum of the 200/250 μm core/clad As-Se fiber. The As-Se fiber transmits well in the 1.5-9.5 μm range. The Se-H absorption peak is 1.4 dB/m at 4.56 μm. Several hundred meters of As-Se fibers can be drawn without crystallization. Typical As-Se fibers have 0.3 NA and 15 kpsi proof-test.

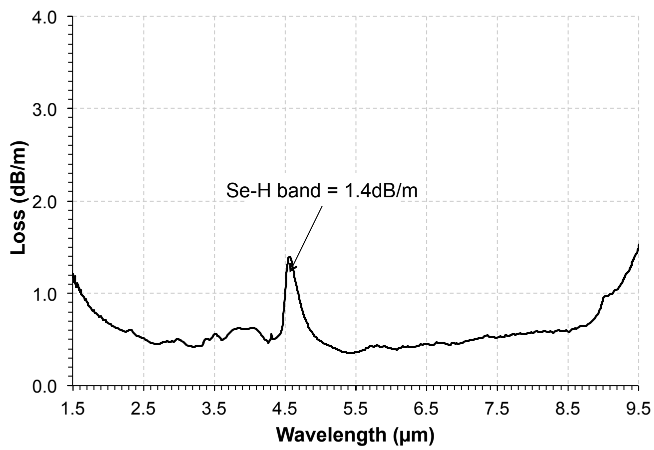

Figure 7. Loss spectrum for the 200/250 μm As-Se fiber.

The 200/250 μm As-Se fiber (1 m long) is tested with a CO_2 laser at 9.3 μm. The laser pulse width is fixed at 40 μs and the frequency is varied to increase the average power in the fiber. Figure 8 shows the output laser power versus the laser modulation frequency. The maximum output average laser power recorded from the As-Se fiber output is 6.8W before the input fiber end is damaged. The corresponding average laser power at the input fiber end is estimated at 14W. Dust particles falling on the input fiber end are most likely responsible for the laser damage. We believe that higher power could be transmitted under clean room conditions.

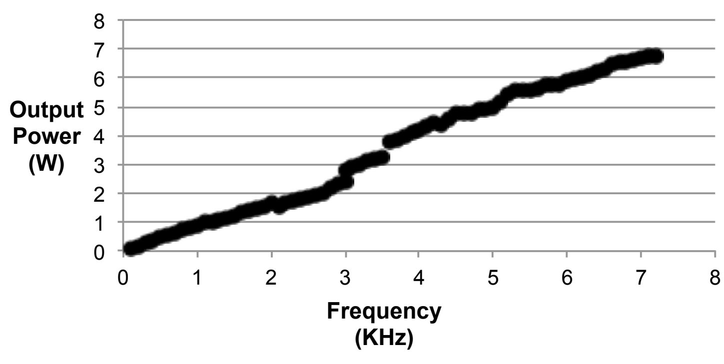

Figure 8. Output power transmission versus modulation frequency for As-Se fiber with CO_2 laser at 9.3 μm.

6. CONCLUSIONS

Multimode and single-mode As-S and As-Se fibers are developed for commercial applications with good optical and mechanical properties. As-S transmits well in the 1.5-6 μm wavelength range. Single-mode As-S fiber with 9 μm core diameter is tested for high-power laser transmission at 2 μm wavelength. No laser-induced damage is visible up to the available laser power (3.5W CW). The estimated laser power density at the input of the As-S single-mode fiber is >5 MW/cm^2. The use of fluoropolymer coating just 5 μm thick on As-S fiber improves the mechanical strength by 33%. The laser ultramicroscopy technique is used to evaluate the density and size of heterophase inclusions in As-S glasses. High-purity As-S glass has a limited size particle population, almost equally divided between 60 nm and 70 nm sizes. As the size particle population of the low-purity As-S glass decreases exponentially from 60 nm to 100 nm. As-Se fiber transmits in the 1.5-9.5 μm range. Multimode As-Se fiber 200/250 μm core/clad diameter transmits up to 6.8W of CO_2 laser at 9.3 μm. Higher transmitted power could be achieved under clean room conditions.

REFERENCES

[1] Sanghera, J.S., Florea, C.M., Shaw, L.B., Pureza, P., Nquyen, V.Q., Bashkansky, M., Dutton, Z., and Aggarwal, I.D., "Non-linear Properties of Chalcogenide Glasses and Fibers", J. Non-Cryst. Solids , vol. 354, 462–467 (2008)

[2] Comparison of IR Materials, Amorphous Materials, www.amorphousmaterials.com

[3] Snopatin G. E., Shiryaev V. S., Plotnichenko V. G., Dianov, and Churbanov M. F., "High-Purity Chalcogenide Glasses for Fiber Optics", Inorganic Materials, Vol. 45, No. 13, 1439–1460 (2009)

[4] Jurgen Symynck, Filip De Bal, "Weibull Analysis using R, in a nutshell", The XVI-th International Scientific Conference, University of Suceava - Romania, 2011

[5] Devyatykh, G. G., Churbanov, M. F., Scripachev, I. V., Shipunov, V. A., Dianov, E. M. And Ptotnichenko, V. G., "Heterophase impurity inclusions in chalcogenide glass optical fibers", SPIE 1228, 119 (1990).