Impact of optical and structural aging in As$_2$S$_3$ microstructured optical fibers on mid-infrared supercontinuum generation


Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR 6303 CNRS - Université de Bourgogne, 9 Av. Alain Savary, BP 47870, 21078 Dijon, France

* frederic.smektala@u-bourgogne.fr

Abstract: We analyze optical and structural aging in As$_2$S$_3$ microstructured optical fibers (MOFs) that may have an impact on mid-infrared supercontinuum generation. A strong alteration of optical transparency at the fundamental OH absorption peak is measured for high-purity As$_2$S$_3$ MOF stored in atmospheric conditions. The surface evolution and inherent deviation of corresponding chemical composition confirm that the optical and chemical properties of MOFs degrade upon exposure to ambient conditions because of counteractive surface process. This phenomenon substantially reduces the optical quality of the MOFs and therefore restrains the spectral expansion of generated supercontinuum. This aging process is well confirmed by the good matching between previous experimental results and the reported numerical simulations based on the generalized nonlinear Schrödinger equation.

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References and links


1. Introduction

Among the wide range of functionalities currently realized by photonic devices, providing reliable and stable light source that covers a broad spectral bandwidth is of major importance. Such supercontinuum (SC) sources can be obtained through nonlinear propagation of a pump beam into an optical waveguide by exploiting various nonlinear wavelength conversion processes [1]. For efficient SC generation, one has to use a low loss and highly nonlinear medium pumped with high power density close to its zero dispersion regime. Many applications exist for broadband mid-infrared (MIR) sources operating in the chemical and biological fingerprint regions within the atmospheric transmission windows [2-5]. To this end, MIR SC sources based on chalcogenide fibers and waveguides appear as an attractive solution thanks to their wide transparency, high nonlinearity [6-8], and thanks to the latest achievements of synthesis of low loss As2S3 fibers [6, 9–13]. However, this glass composition suffers from weakness represented by an uncontrolled drift in performance over time. This is mainly due to physical and chemical aging processes [14]. Thus extending efficient MIR SC generation requires a detailed understanding and control of the evolution of optical and chemical properties for such a material [9, 15, 16].

We previously reported on experimental observation of MIR SC generation in low-loss As2S3 suspended-core MOFs [9]. The spectral broadening was beyond 2000-nm bandwidth from 1 µm to 3.2 µm. Numerical simulations were performed in order to check the underlying nonlinear processes. When considering the fiber losses which were experimentally measured in a single-index fiber, numerical results predicted a theoretical broadening with the MIR edge until 5.5 µm, whereas that experimentally recorded was located around 3.2 µm. In order to better fit the experimental SC, in particular close to the SH and OH absorption bands, extra losses were taken into account around 2.9 µm and 4 µm. This confirmed the under-evaluation of extrinsic absorption bands experimentally measured, or an aging process of our fibers under room atmosphere. Optical degradation is a natural consequence of the aging process [9, 15, 16]. However, the origin, mechanism and kinetics of chemical as well as optical aging of As2S3 MOFs remain unclear. The objective of this study is to show unequivocally the aging process of an As2S3 based suspended-core MOF in atmospheric conditions and its impact on
SC generation. We perform numerical simulations that confirm the dynamic evolution of spectral broadening and its relation to extrinsic losses related to aging process evolving over storage at ambient atmospheric conditions. We identify the chemical and the inherent optical aging behaviors of the sulfide MOF by using a Fourier Transform InfraRed (FTIR) spectrometer. We present a first attempt to follow and prove the evolution occurring on the As$_2$S$_3$ glass surface upon naturally induced aging process in atmospheric conditions by means of Atomic Force Microscopy (AFM). The inherent chemical composition deviation on the surface is also studied thanks to X-ray Photoelectron Spectroscopy (XPS). Such an analysis confirms that the aging process substantially reduces the optical quality of the MOF, thus limiting SC generation further in the MIR.

2. Preparation of glass and fiber samples

Glass used in this work was fabricated by the traditional melt quenching method. The detailed fabrication process of glass and fibers was described earlier [9]. The obtained glass rod is 80 mm long with a diameter of 16 mm. It was cut evenly to two samples using a diamond saw. The first one was designated to draw MOFs with well defined parameters responding to experimental need. The corresponding MOF cross-section is shown in Fig. 1. The second one was dedicated to preparation of specimens for AFM and XPS experiments.

Figure 1 gives the attenuation spectrum of our low-loss As$_2$S$_3$ single-index fiber shortly after being drawn [9]. Losses of optical fiber was estimated in free space by means of a FTIR spectrometer and using cut-back technique. Measurements were carried out on 5-m-long fiber segment with 20% of accuracy primarily caused by the quality of fiber cleaves. Similar spectral loss measurements could not be successfully performed on suspended core fiber because of the small core diameter. However, cut-back measurements for the small-core MOF were performed using a continuous laser source emitting at 1.55µm, again readily after drawing, confirming thus the previous results registered on single-index fiber. Note that fundamental OH and SH absorption peaks emerge around 2.9 and 4.0µm respectively. According to the extinction coefficient $\varepsilon = 5$ dB/m/ppm (wt.) [17, 18], the OH absolute content is about 0.5ppm (wt.). SH concentration (≈3.2 ppm) can be estimated from the spectrum referring to [19] for which extinction coefficient associated to the SH vibration at 4
μm is 2.5 dB/m/ppm. The peak arising at 4.26 μm is due to CO₂ absorption. This absorption does not evolve over time unlike those of OH and SH groups. Consequently, the CO₂ absorption was neglected in this study. Absorption peaks around 3.4 μm are unequivocally assigned to C-H bonds present in the modeling clay systematically used to fix the fiber during cut-back measurements. They are not always eliminated through cut-back data treatment because of the possible irreproducibility in the way we fix the fibers. Note that clay is not used during SC generation experiments. The MOF design is such that it allows to tailor its zero-dispersion wavelength (ZDW) as close as possible to the range of maximum emission capability of the pump source near 2.3 μm while keeping a very high nonlinear coefficient as well as an efficient coupling of light into the core. We computed the fundamental mode properties of suspended core MOF based on the cross-section profile (see Fig. 1 and [9] for more details). The combined material and waveguide modal dispersions result in a ZDW wavelength located close to 2.3 μm for the 3.2 μm core size. The corresponding effective mode area is about 6.5 μm² at the ZDW. Combined with high nonlinear refractive index ~2.8×10⁻¹⁸ m²/W at 1.55 μm, the resulting nonlinear Kerr coefficient γ is 1175 W⁻¹.km⁻¹ [9].

3. SC generation and impact of absorption bands

Figure 2(a) shows the experimental SC spectrum obtained with a 12-days aged 45-mm-long MOF segment pumped by 200-fs pulses at 2.3 μm with 4.6 kW injected power (see [9] for more details about the setup). The spectral broadening extends from 1.2 to 3.2 μm in the -20dB range with a dip around 2.9 μm, where the different combinations of strongly and weakly bonded OH groups manifest themselves (Fig. 1). Eventual influence of atmospheric absorptions in this wavelength range have been checked by registering the atmospheric spectrum in the conditions of our measurements. The absorptions of atmospheric water remains in the noise of the experimental measurements and are not detectable in the configuration of our set up. Here we provide a detailed analysis based on numerical simulations and chemical analysis to elucidate the strong limitations imposed in the nonlinear dynamics of this SC generation. Numerical results are obtained through the split-step Fourier-based solving of the generalized nonlinear Schrödinger equation [1] taking into account the full dispersion curve from [9], measured fiber losses as well as self-steepening and analytical model of the Raman gain spectrum [9]. We recall that our pumping condition induces a strong and rapid self-phase modulation process followed by random soliton fission in the earlier centimeters of fiber [1, 9]. The generated SC is then associated to significant fluctuations from pulse to pulse and high degradation of the coherence degree. As a result, averaging over 50 simulations with different input noise imposed on the pulse pump was carried out to obtain spectral smoothing, similarly to our optical spectrum analyzer. Taking only into account the loss level experimentally measured for the single-index fiber (see Fig. 1 and Fig. 2(b2)), the simulated SC spectrum does not match with the experimental one, as shown in Fig. 2(b1). Indeed considering measured losses on fibers freshly drawn implies a theoretical spectral broadening up to 5.5 μm, Fig. 2(b1). In order to reach a good agreement, extra losses at 2.9 and 4.0 μm have to be taken into account as previously suggested in [9]. This underlines that a time evolution of deleterious extrinsic absorption bands occurs over time upon exposure to atmosphere. This aging is mainly related to the chalcogenide glass sensitivity to ambient moisture [14–16].

To reveal the impact of OH and SH absorption bands on SC generation, we simulated extra losses at 2.9 and 4 μm by considering a simple Gaussian envelope for each absorption band while keeping background losses at the same level. We increased step by step absorption peaks of the two bands as shown in Figs. 2(c2)–2(e2) until retrieving a good agreement between the simulated SC and the experimental one. The amount of losses added for each step corresponds to approximately 10 times increase of OH and SH contents in ppm. We used the same factor for the two bands. Corresponding simulated SC spectra are shown in Figs. 2(c1)–2(e1). The impact of absorption peaks on SC generation in few centimeters of
fiber becomes noticeable when considering extra losses at the level of several dB/cm (see Figs. 2(d1)–2(d2)). In particular, one can note the small dip around 2.9 µm in the MIR SC as well as a clear limitation of the SC expansion near 4 µm (in the ~20dB bandwidth range). Finally, we have to extend losses up to 25 dB/cm for OH-peak and 75 dB/cm for the SH-peak so as to better match with our experimental SC spectrum. Such optical losses correspond to OH and SH concentrations near to 500 and 3200 ppm, respectively. We can then notice in Fig. 2(e1) an erosion of the MIR SC upper edge, which is now limited close to 3.35 µm as well as the clear presence of the OH absorption band centered at 2.9 µm. The output energy is about 60% of the input energy in Fig. 2(e1) (without taking into account Fresnel reflections), while being ~80% in Fig. 2(d1), thus corresponding to the range of the experimental measurement from [9]. From these considerations, we highly suppose that an aging process occurs on the surface of the suspended MOF core, leading to an increase of OH and SH absorptions.

![Fig. 2.](image)

**Fig. 2.** (a) Experimental SC generated in a 45-mm-long sample of MOF, (b1-e1) Corresponding numerical simulations taking into account different levels of OH and SH absorption bands depicted in (b2-e2), respectively.

4. Optical and structural aging

In order to confirm the preceding dynamics, we investigated the effect of atmospheric conditions on our sulfide MOF as a function of exposure time, in particular for hydroxyl species. We used a 3-m-long segment of 10-µm-large-core As$_2$S$_3$ MOF for FTIR analysis. Unlike the previous small core MOF, with such a large core MOF, spectral recording of transmission is possible with our FTIR setup and transmission spectra were systematically recorded over a 46-h period until a significant evolution of the transmission around 2.9 µm was obtained (Fig. 3).
This study was performed at a temperature varying from 15 to 20°C and relative humidity between 50 and 60%. The fibre sample was mounted onto 3 axis holder in order to optimize coupling and detection of the light signal exclusively transmitted through the core of the MOF. An infrared camera was used to ensure that light was effectively coupled within the core of the MOF only. One can note that the suspended core is embedded in a robust clad which acts as a filter absorbing the unsuitable surrounding radiations potentially inducing photo-oxidation phenomena [20]. Despite that, the probed fiber was preserved in dark throughout the study period. A NICOLET 6700 Fourier Transformed InfraRed (FTIR) spectrometer was used to characterize the transmission spectra. The FTIR is seeded by an external halogen lamp providing higher power within the range of study (1.6-3.3µm) comparing to the standard light sources integrated within the spectrometer. In addition, signal outgoing the probed fibre was detected by means of external In-Sb detector, exhibiting high sensitivity within the range of interest. Our measurements are depicted in Fig. 3 and show a naturally induced decrease in transmission and a substantial extinction of the signal around 2.9 µm upon exposure to atmospheric conditions. The deleterious impact of atmospheric moisture on As₂S₃ MOF occurs in the short time frame over the first hours (Fig. 3). Few hours are sufficient to completely attenuate the light signal in this wavelength region. These results prove the critical need for a moisture-free storage immediately after the drawing process and prior to nonlinear experiments. Additionally, a degradation of the transmission occurs (Fig. 3), in the short wavelength range. After 46 hours of exposure, this degradation reaches almost 20% below 2.0 µm. Such a phenomenon could be due to surface defects that emerge on the surface of the waveguide [15, 16], thus leading to light scattering.

To confirm this point, we therefore investigated the impact of the atmospheric moisture on surface roughness of As₂S₃ bulk glass. For that purpose, a glass sample was polished using SiC paper and diamond suspensions. One can precise that there is a difference in initial surface quality between AFM bulk samples and fiber samples, due to the polishing of bulks that might enhance aging through preliminary OH contamination or As₂O₃ formation. However, the impact of polishing does not interfere substantially in the aging process studied here. Indeed, rectangular fiber samples carefully prepared under dry atmosphere and exposed to similar conditions show, as on bulk samples, a substantial increase of their surface roughness. The specimen was stored under atmospheric conditions similar to those reported for fiber transmission study. Since all the surface of the sample is exposed to the environment, it is thus most prone to any contaminations. The evolution of glass surface at the nanometric scale was observed through AFM analysis (Bruker, Nanoscope 8) under controlled atmosphere in Peak Force mode. Throughout the exposure period, the bulk
specimen was kept in a cleanroom dedicated for AFM measurements, in dark away from any surrounding light. As shown in Fig. 4, the exposure to the previously defined conditions during 12 days, induces the appearance of random bumps which develop into faceted pyramids with square cross-section. However, the dimensions of these evolving defects substantially increase from ~15 nm on fresh sample to reach ~60 nm after 12 days of exposure to ambient conditions. The similarity of morphology in the present work and previous studies [21, 22] strongly suggests that surface defect are As$_2$O$_3$ crystals.

![Fig. 4. Top view of AFM 3D-pictures of the As$_2$S$_3$ bulk glass surface: (a) fresh sample; (b) 12 days of exposure.](image)

We have also checked the evolution of the chemical bonds at the bulk sample surface through XPS analysis, by comparison of a fresh glass sample and a sample exposed to atmospheric conditions inside a dark compartment during 7 days. Note that fresh sample is probed immediately after polishing. XPS measurements were carried out by means of PHI Versaprobe 5000 apparatus (AlKa monochromated X-Ray source and 58 eV of pass energy for best resolved core level acquisitions). Peaks arising on XPS survey spectra are assigned to As and As-O core levels using a PHI Handbook for XPS spectra. Such measurements demonstrate a deviation from ideal As$_2$S$_3$ composition as illustrated in Fig. 5, with the apparition of As-O bonds when the sample is exposed to ambient atmosphere. This observation is consistent with the AFM ones, and strengthens the hypothesis of As$_2$O$_3$ crystals growing at the glass surface. It demonstrates that the sulfide glass is susceptible to room temperature chemical reaction naturally induced in ambient atmosphere. This reaction process may diffuse in depth leading to local shift of the chemical composition inside the bulk glass [23].

![Fig. 5. XPS spectra of As 3d core level of As$_2$S$_3$ glass: (a) fresh glass; (b) exposed to air during 7 days.](image)

Finally, all of these results suggest an initial reaction of the glass with the atmospheric moisture surrounding the MOF core, which leads to the rapid apparition of absorbing -OH and -SH groups in the glass, with a subsequently evolution towards As$_2$O$_3$ species formation.
associated with an increase of glass surface roughness. These different phenomena contribute to increase the optical losses of As$_2$S$_3$ MOFs and degrade all their optical properties, including SC generation. However, it might be mitigated by the storage of freshly drawn MOF samples in dry atmosphere. In order to confirm the aforementioned hypothesis, the previous nonlinear experiment was recently reproduced using a sample stored in dry atmosphere [10]. Thus, an improvement of SC generation in the protected sample was indeed achieved by reaching a longer MIR edge around 4 µm without significant OH-induced dip at 2.9 µm as shown in Fig. 6.

5. Conclusion

Through FTIR, AFM and XPS measurements, we demonstrate the deleterious time evolution of As$_2$S$_3$ MOFs upon exposure of the MOFs core to atmospheric moisture. FTIR experiments confirm that extra losses related with OH bands at 2.9 µm occur in the MOFs. Moreover a deleterious evolution of SH absorption band is likely to occur simultaneously. The exposure of As$_2$S$_3$ glass to atmospheric conditions leads to the development and the growth of pyramidal shapes surface defects, which increase glass surface roughness observed by AFM. These surface structures arise from reaction with the atmosphere and strong suggestion for As$_2$O$_3$ crystals formation is emphasized by XPS results. Substantial amplification of OH absorption bands occurring over the first hours imposes the necessity of specific storage of As$_2$S$_3$ MOFs in dry conditions, immediately after the drawing process. The efficiency of specific storage allowed to overcome the OH limitation and to extend the supercontinuum up to 4 µm.

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