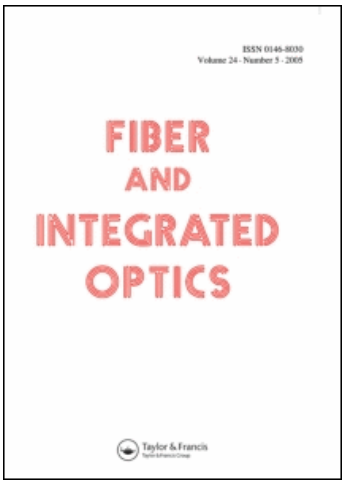

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Chalcogenide Microstructured Fibers for Infrared Systems, Elaboration Modelization, and Characterization

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Chalcogenide Microstructured Fibers for Infrared Systems, Elaboration Modelization, and Characterization

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Abstract *Chalcogenide fibers present numerous possible applications in the IR field. For many applications, single mode fibers must be obtained. An original way is the realization of microstructured optical fibers (MOFs) with solid core. These fibers present a broad range of optical properties thanks to the high number of freedom degrees of their geometrical structure. In this context, we have developed MOFs for near and mid IR transmission with different geometries and properties such as multimode or endless single-mode operation, small or large mode area fibers. We have also investigated numerically the main linear properties of such MOFs.*

Keywords chalcogenide glass, fiber drawing, infrared glasses, microstructured fibers, nonlinear materials, single-mode fiber

1. Introduction

Since the pioneering works on nonlinear optics, great interest has been devoted to the fabrication of new materials exhibiting high nonlinear properties. Chalcogenide glasses are very promising in the near and mid infrared spectral range for third or second order nonlinear processes. Moreover, one great interest is to associate their high nonlinear properties with their large infrared transmission windows from 0.5–1 μm to 12–18 μm.

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Indeed, they present high third order optical properties [1–4] (100–1,000 times as high as the nonlinearity of silica glass at 1.55 μm).

The applications field of chalcogenide glasses is wide. In telecommunications, nonlinear materials present a great interest for optical regeneration [4], all optical switching, or Raman amplifiers [5, 6]. Due to the infrared transmission in the 3–5 μm and 8–12 μm windows the chalcogenide glasses present also applications such as power transmission and generation of super-continuum sources. For these different applications, single mode guides must be obtained. A first way consists of the preparation of classical step index fibers with a core-clad structure [7–10]. To achieve this goal, two compositions (core and clad) exhibiting compatible thermal and optical properties have to be considered. The second way is the realization of original solid-core microstructured optical fibers (MOFs) [11–13]. MOFs present interesting optical properties depending on their geometrical structure, such as broadband single mode guidance, adjustable dispersion, and large mode or small mode area [14]. The association of small mode area MOF with the intrinsic properties of the chalcogenide glasses allows nonlinear effect to be exploited as reported in other highly nonlinear materials such as lead silica [15, 16], telluride [17], and bismuth oxide glasses [18]. In another field of applications, the elaboration of endless single mode fiber in infrared is studied in the spatial DARWIN project as a broadband wave front filter [19, 20]. The realization of MOFs composed from chalcogenide glasses is rarely reported. A first holey fiber based on Ga-La-S glass system was realized with one ring of non-regularly arranged holes, but it was not optically characterized [21]. In [22], a MOF based on As2Se3 has been used to generate a super continuum from 2.1 to 3.2 μm. This preform was fabricated only with one ring of tubes and 7 rings of rod around a central rod with no outer glass jacket.

This article presents the actual state of the art in the realization of solid core MOFs is the Ge-Sb-S-(Ga) glassy system since our first steps in the field [23, 24]. The improvements we have reached in the glass synthesis (glass composition, purifications) are described. This article also presents some modelling results concerning the linear properties of MOFs from high refractive index glasses like chalcogenide ones. The improvements in the control of the MOF geometry are then described. The measured mode profile and the losses of a single mode Ge-Sb-S MOF are given together with the computed value.

2. Glass Synthesis, Purifications and Material Losses

Chalcogenide glasses are based on sulfur, selenium, tellurium, and the addition of other elements such as arsenic, germanium, antimony, gallium, etc. The chalcogenide glasses chosen for this study are from the Ge-Sb-S-(Ga) system. The first fibers have been prepared with classical quality glasses using the $Ge_{20}Sb_{10}S_{65}Ga_5$ (2S2G) glass composition elaborated by a simple synthesis [10]. In a second stage, the fibers were made of purified glasses with high optical quality and we have proved that better fiber transmission could be obtained when the glass was entirely distilled. However, gallium cannot be distilled at appropriate distillation temperatures. This element has then been removed from the glass composition and the purified glass is now the $Ge_{15}Sb_{20}S_{65}$ (2SG) glass. The main optical and thermal properties of the 2S2G and 2SG glasses are given in Table 1.

In the simple synthesis, glasses are prepared from elemental high purity 5N starting products. Sulphur, which is polluted by water, is previously dried by heating at 120°C under vacuum and distilled. The different elements are then placed into a silica ampoule and pumped under vaccum (10^{-5} mBar) for a few hours (Figure 1a). After sealing, the

Table 1
Characteristics of the Ge-Sb-S-Ga glasses used for the elaboration of the chalcogenide MOFs

Glass composition (mol %)	Glass transition temperature, Tg (°C)	Crystallisation temperature	Refractive index at 1.55 μm	Nonlinear refractive index at 1.06 μm [25]
$Ge_{20}Sb_{10}S_{65}Ga_5$ (2S2G)	310	None	2,250	3.2 10^{-18} m^2/W
$Ge_{15}Sb_{20}S_{65}$ (2SG)	250	None	2,370	—

ampoule is introduced in a rocking furnace and heated to 900°C at 1°C/min heating rate. The ampoule is maintained at that temperature for 12 hours. Then, the melt is quenched to room temperature by immersion in water and the glass is annealed at the glass transition temperature (Tg).

The process used to elaborate purified glasses and to obtain low losses fibers consists of the distillation of the glass after a first treatment of the melt by a chlorine reactive atmosphere [26]. First, a glass is prepared with 1,000 ppm of $TeCl_4$. In a second time, as illustrated in the Figure 1b, the treated glass is distilled at 650°C under dynamic vacuum to remove the volatile compounds such as CCl_4 or HCl produced by the addition of $TeCl_4$. Finally, the reactional tube containing the distillated glass is placed once again in a rocking furnace, quenched in water, and annealed like in the case of the simple synthesis.

To qualify the materials losses, single index fibers have been drawn from the realized glass rods. Attenuation curves presented in the Figure 2 have been obtained by the cut back technique on 400 μm cross section fibers of 3 m length. The transmission losses of the fibers are given for a glass without purification (gray line) and for a high quality glass (black line). Several absorption bands are observed at 4.0 μm and 3.1 μm due to S−H chemical bonds, at 2.1 μm due to O−H bonds and finally at 4.95 μm due to the presence of C−S bonds. The losses above 6 μm are induced by multiphonon absorption and M−O bonds, where M is a semi-metallic species of the glass. The extrinsic absorption bands are due to the pollution of the raw materials, especially sulfur, by water and carbon. The water reacts with the chalcogenides during the synthesis and leads to the formation

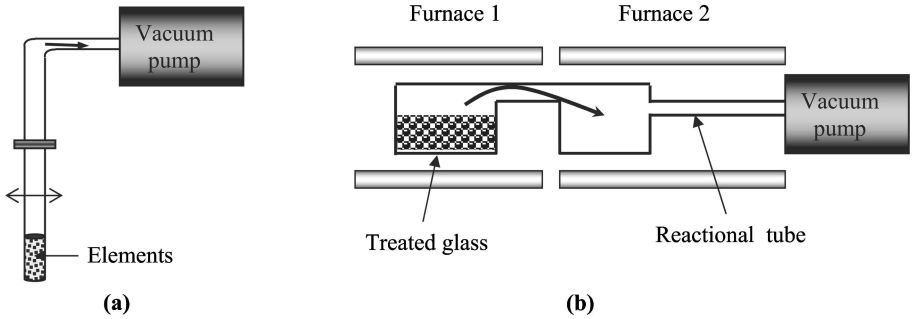

Figure 1. Chalcogenide glasses synthesis set-up: (a) simple synthesis and (b) purified synthesis.

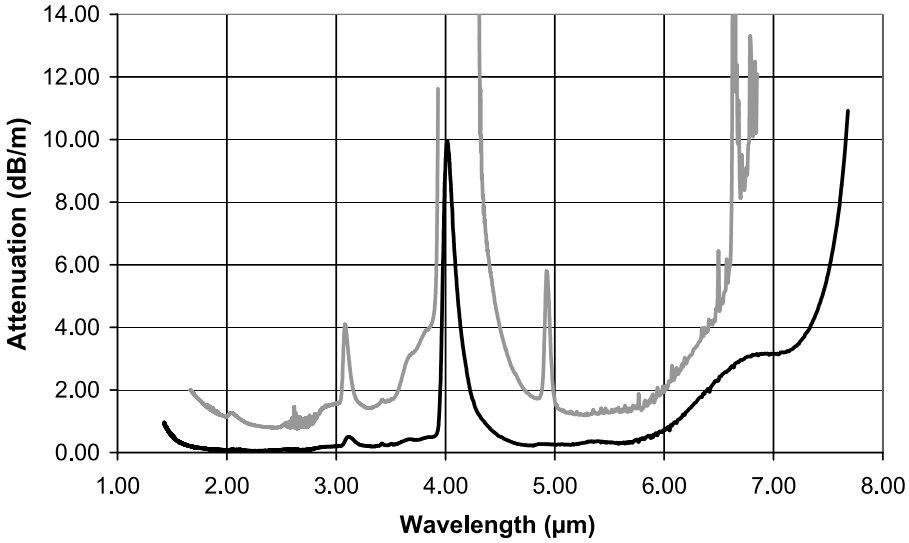

Figure 2. Attenuation curve of single index Ge-Sb-S-(Ga) fibers: without purification (gray line) and with purification (black line).

of S−H and M−O bonds. Carbon reacts also with sulfur and gives C−S bonds. The purification process enables to remove almost entirely the O−H and C−S absorption bands. In the same time the S−H band can be strongly reduced towards 10–12 dB/m instead of 50–60 dB/m in the unpurified glass. Finally, the background level of losses can be reduced near 0.2 dB/m at 5 μm (Figure 2).

3. Modeling Results

In this section, the main linear properties of chalcogenide MOFs obtained from numerical simulations are described. The losses of the fundamental mode, the endlessly single-mode regime, and the chromatic dispersion properties of the fundamental mode are described underlining the specificities of high index matrices.

These results and conclusions have been obtained using several methods that allow to accurately compute the effective indices and the fields maps of the modes [14, 27, 28]. The modes of solid core MOFs made of a finite number of low index inclusions embedded in a infinite high index matrix are leaky modes [14]. This means that the effective indices have a non-null imaginary part. The mode guiding losses L are linked to this last quantity using the formula:

$$L = \frac{40\pi \,\mathrm{Im}(n_{eff})10^6}{\lambda \ln 10}$$

in which λ is given in μm.

The modal properties of these solid core MOFs have already been studied in details especially for silica matrices with air hole inclusions [14, 29] (see also the quoted references). The linear properties of the same geometrical structures, but made with a high index glass matrix, are globally the same; no new phenomenon occurs. Nevertheless, some differences are observed that must be known in order to facilitate the achievement of feasible and useful devices. Since only a few realizations of chalcogenide MOFs are

reported, only a few numerical studies are currently available [24]. The first property that must be studied is the behavior of the guiding losses versus the geometrical parameters describing the considered structures and versus the wavelength. The considered MOFs are made of identical circular inclusions, with a diameter d, regularly spaced by a pitch denoted by Λ. Consequently, the key geometrical parameters are the ratio d/Λ and the number of air hole rings Nr surrounding the core. When the fundamental is confined in the MOF core (that is to say when the wavelength is not too large compared to the pitch) its guiding losses decrease exponentially with the number of hole rings [27, 14].

In Figure 3, the losses of the fundamental mode of solid core MOFs are plotted as a function of the ratio d/Λ for several values of Nr. This figure demonstrates that four rings of holes are sufficient to ensure guiding losses below 1 dB/m (the order of magnitude of the lower limit of material losses in current chalcogenide MOFs) from the moment that the d/Λ ratio is above 0.3. This figure can be compared to the similar one, already obtained for MOFs with a silica matrix, as described in chapter 7 of [14].

In [24], in order to study quantitatively the influence of the matrix refractive index on the fundamental guiding losses, we introduced the ratio of the fundamental mode guiding losses $L(m+1)$ for a microstructured fiber made of $Nr = m+1$ hole rings over the fundamental mode losses $L(m)$ for a $Nr = m$ fiber. To make this ratio unique and useful for MOF design, we computed its average value for m between 1 and 4. This ratio is noted by R. To illustrate the stronger confining capacity of chalcogenide matrix compared to silica one, the ratio R is plotted in Figure 4 as a function of d/Λ for two matrix refractive indices: the first being similar to the one of silica and the second being representative of the chalcogenide glass studied in this article. As an example, if one considers the losses between a MOF made of three rings of holes and a MOF with only one ring but with the same ration $d/\Lambda = 0.45$, then the guiding losses of the fundamental mode are approximatively decreased 1,000 times more for a chalcogenide matrix than for a silica one. Since the order of magnitude of the material losses is 1 dB/m, the high refractive index of chalcogenide matrix allows one to consider MOFs with only 3 or 4

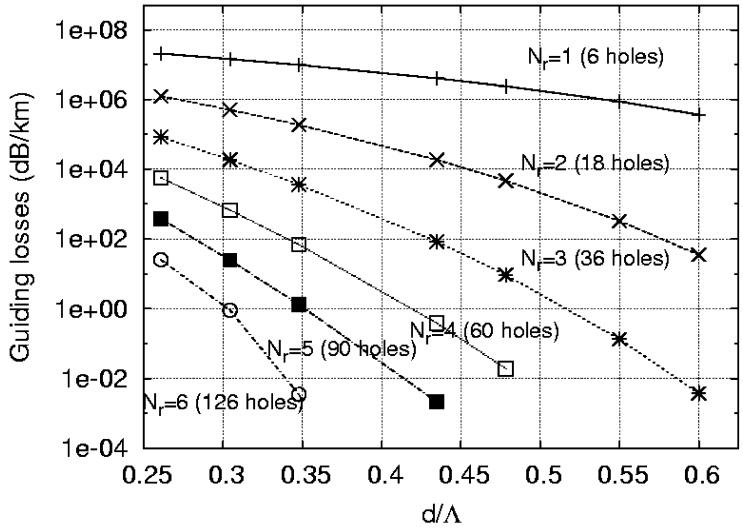

Figure 3. Fundamental mode losses in dB/km as a function of the number of air hole ring Nr and of the ratio d/Λ for MOFs with $n_{matrix} = 2.5$, $\Lambda = 2.3$ μm at $\lambda = 1.55$ μm.

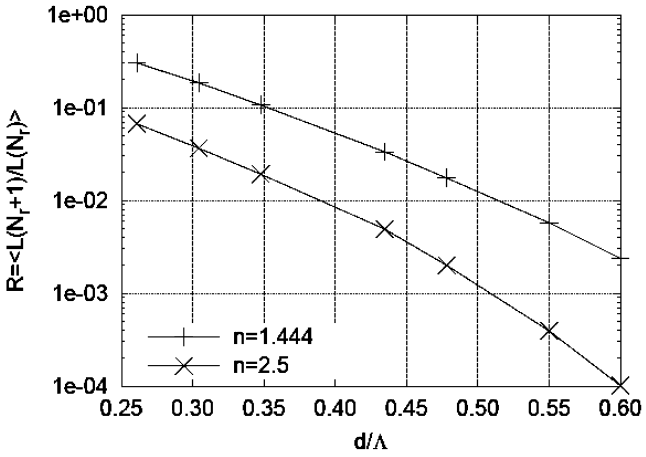

Figure 4. Average ratio R of the losses of a $Nr = m + 1$ MOF over the losses of a $Nr = m$ fiber for the fundamental mode as a function of d/Λ for $n_{matrix} = 1.444$ and $n_{matrix} = 2.5$. The picth Λ is set to 2.3 μm and $\lambda = 1.55$ μm (see the text for more details).

rings of holes to ensure that the guiding losses are below the material ones for most of the conventional d/Λ values. This is not the case for silica MOFs in which material losses are much lower requiring much higher value for Nr in order to make the guiding losses smaller than the material ones.

The second key issue for most MOF-based devices is the endlessly single-mode behavior. For solid core MOFs made of silica matrix, the numerical results have been obtained a few years ago [30, 31, 14]. They have been checked in several experimental works [32, 33]. More accurate modelling results are also valid for high refractive index materials and take into account finite size effects that have been published more recently [34]. For structures with a large number of air hole rings, the critical ratio d/Λ is in the interval [0.42, 0.425] both for silica and chalcogenide matrices [34]. Nevertheless, for the already fabricated chalcogenide MOFs, the number of hole rings is limited to three or four. This technological constraint implies that the finite size effects modifying the ratio d/Λ limiting the endlessly single-mode behavior must not be forgotten. As an example, for a MOF such that the matrix refractive index is set to 2.25 with a d/Λ ratio that is equal to 0.35, and a pitch Λ fixed to 8 μm, it requires at least 6 rings of holes to ensure a single-mode behavior at 1.55 μm both in terms of second mode field delocalization and of differential losses between the fundamental mode and the second one. Consequently, in order to determine theoretically the single-modeness of a MOF, one must compute numerically the modal properties for the exact opto-geometrical structure considered especially for d/Λ slightly below the critical ratio obtained for large structures.

The last issue considered in the present works is the chromatic dispersion. In Figure 5, the fundamental mode chromatic dispersion of several MOFs is shown for two values of the matrix refractive index. For these curves, no material dispersion is considered, as a consequence only the chromatic dispersion Dw is due to the waveguide itself. As can be seen, both the amplitude and the wavelength gap between extremal values of Dw increase with the value of the matrix refractive index. Consequently, these properties permit us to find MOF geometrical profiles with strong enough Dw to compensate the highly

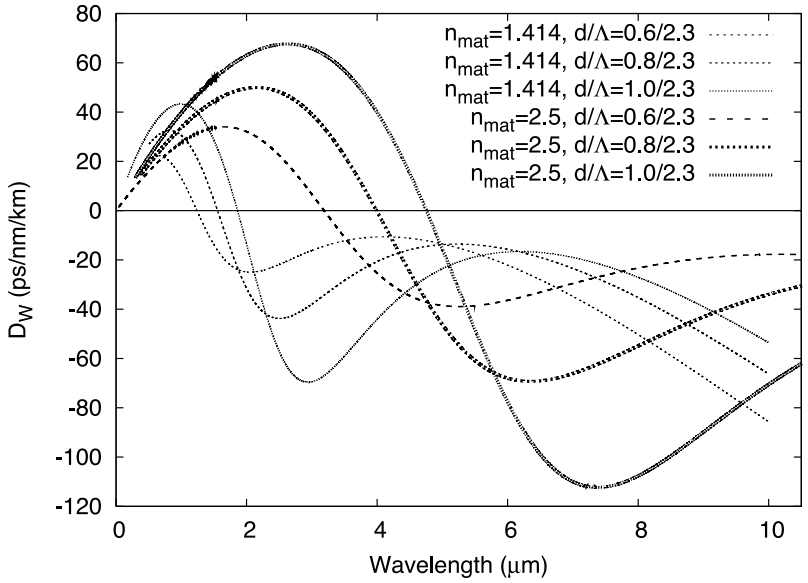

Figure 5. Waveguide chromatic dispersion Dw as a function of the wavelength for MOFs with three different d/Λ ratios for $n_{matrix} = 1.444$ and $n_{matrix} = 2.5$ (the number of air hole rings is set to three).

negative material dispersion estimated for As_2Se_3 chalcogenide glass [35] or for other chalcogenide glasses. To compute accurately the total chromatic dispersion of MOFs, one must include the material dispersion in the input parameters of the numerical simulations for the full range of studied wavelengths. Such data are not yet available for the 2S2G or 2SG glasses we are using to draw chalcogenide MOFs but this issue is currently under investigation.

4. Chalcogenide MOFs Fabrication

Chalcogenide MOFs are elaborated by the stack and draw process. For that purpose it is necessary to shape chalcogenide tubes. They are obtained by centrifugation of the melt during the cooling of the silica ampoule. The tube sizes are typically 12 cm in length, 12 mm outer diameter, and 5 mm inner diameter. The tube is then stretched on the drawing tower to obtain capillaries of around 650 μm outer diameter. These are then stacked in a hexagonal lattice around a glass rod of identical diameter placed in the central region (Figure 6). A jacket tube is then collapsed around the microstructure via an initial rapid descent through the furnace of the drawing tower, with a little deformation of the capillary tubes. After this step, the fiber is drawn at the rate of 1 m/min at a temperature around 400°C. A variable gas pressure system enables precise control of hole size during the draw. Figure 6 summarizes the different steps of the stack and draw process. The preliminary modelling results permit to determine the number of rings necessary to obtain sufficiently low guiding losses, compared to the materials ones. In most cases, modelling results show that 4 rings of holes and even 3 rings are sufficient to ensure guiding with losses below 1 dB/m.

Numerous drawings have been necessary to optimize the different parameters of the drawing, such as temperature, pressure in the capillaries, and pressure in the interstices,

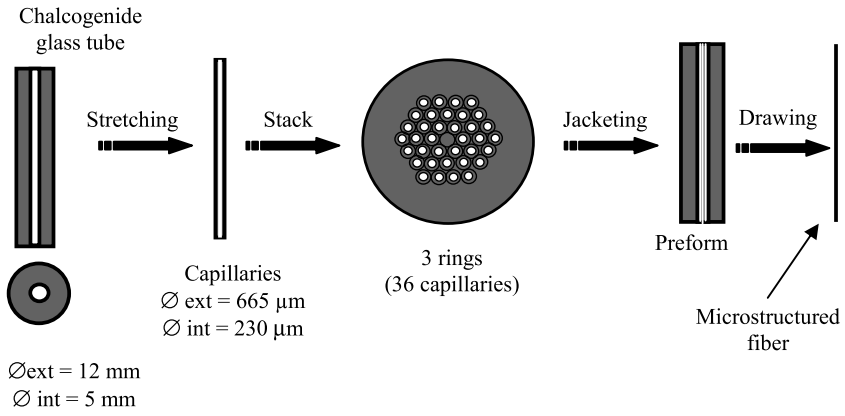

Figure 6. Stack and draw process for chalcogenide MOFs.

for example. Indeed, the elaboration of a MOF needs to consider the different types of holes present in the preform. Obviously, the first type corresponds to the capillaries' holes (type 1), the second one is related to the interstices between the capillaries (type 2), and finally the last family is for the interstices between the hexagonal stack and the outer jacketing tube (type 3). The aim of the drawing process under controlled pressure is to remove the holes of type 2 and 3 and to control in the same time the size of the inner holes of the capillaries (type 1). Figure 7 presents several cross sections of the first fibers obtained in the Ge-Sb-S-(Ga) system considering 2, 3, or 4 rings of capillaries. Their external diameter is in the 150–200 μm range. Each fiber is a typical example of the role of the different process parameters. In the case of fiber 7a, no pressure has been

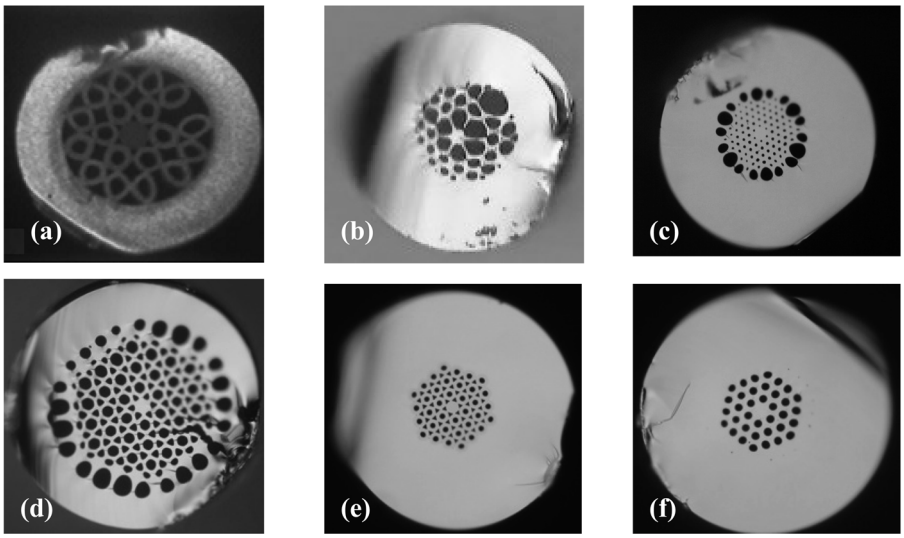

Figure 7. Evolution of chalcogenide MOFs obtained with variable process parameters: (a), (b), and (c) are 2S2G glasses and (d), (e), and (f) are 2SG glasses (outer diameter of the fibers are in the range 150–200 μm).

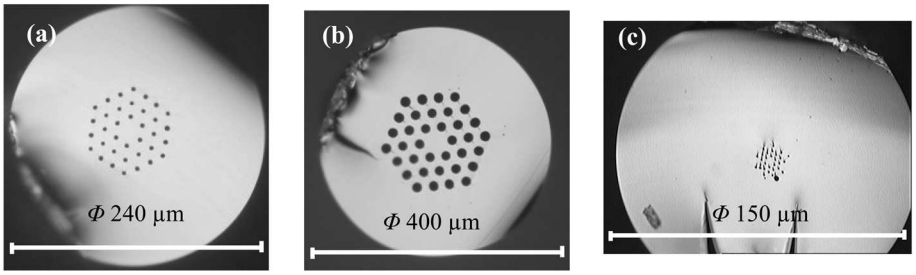

Figure 8. Different geometries obtained on chalcogenide holey fibers: (a) Endlessy single mode fiber ($\Phi_{fiber} = 240\ \mu$m, $A_{eff} = 150\ \mu$m^2, $\Lambda = 14\ \mu$m, $d/\Lambda = 0.31$), (b) large mode effective area fiber ($\Phi_{fiber} = 400\ \mu$m, $A_{eff} = 1{,}000\ \mu$m^2, $\Lambda = 28\ \mu$m, $d/\Lambda = 0.5$), and (c) small effective area fiber ($\Phi_{fiber} = 150\ \mu$m, $A_{eff} \sim 13\ \mu$m^2, $\Lambda \approx 2.5$, $d/\Lambda = 0.36$).

used during the drawing. For fiber 7b, the pressure in the capillaries and/or the drawing temperature was too high. After several tries, considering several steps and different pressures in the 3 types of holes, we have obtained suitable geometries (fiber 7c, 7d, 7e, 7f). In fiber 7e, all of the holes between the microstructure region and the jacketing tube have been removed, while interstitial holes and capillaries' holes have been voluntarily controlled. In the case of fiber 7f, only the holes of the capillaries have been maintained, all other interstitial holes have been filled.

This work demonstrates the possibility to develop MOFs from the sulphide 2S(2)G glasses. Now, the geometry of chalcogenide MOFs can be precisely controlled and numerous fibers with various effective mode areas can be obtained [36]. Figure 8 illustrates several achievements with different effective mode areas from 13 μm^2 to 1,000 μm^2. The effective mode area is calculated in the case of a Gaussian approximation following the formula $A_{eff} = \pi(MFD/2)^2$. The mode field diameter (MFD) is measured in the near field and corresponds to the $1/e^2$ of the maximum of the Gaussian fit.

5. Near Field Capture, Loss Characterizations, and Comparison with Numerical Results

The guiding properties of the fibers are deduced from the output profiles captured in the near field at 1.55 μm as it is illustrated on Figures 9 and 10. Light from a broadband source at 1.55 μm was injected into the chalcogenide MOF via a standard single mode

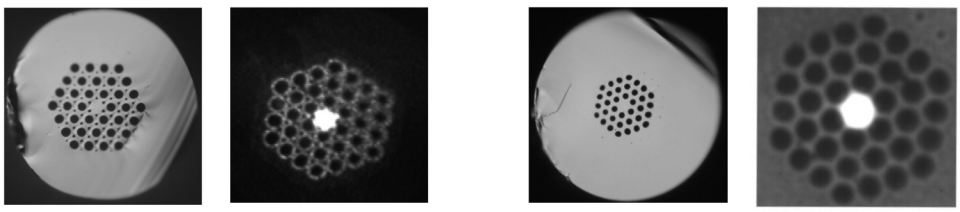

Figure 9. Cross section and near field capture at 1.55 μm of chalcogenide MOFs obtained with a fine control of the process parameters: (a) $\Phi_{fiber} = 415\ \mu$m, $\Lambda = 32\ \mu$m, $d/\Lambda = 0.58$ and (b) $\Phi_{fiber} = 140\ \mu$m, $\Lambda = 7.7\ \mu$m, $d/\Lambda = 0.63$.

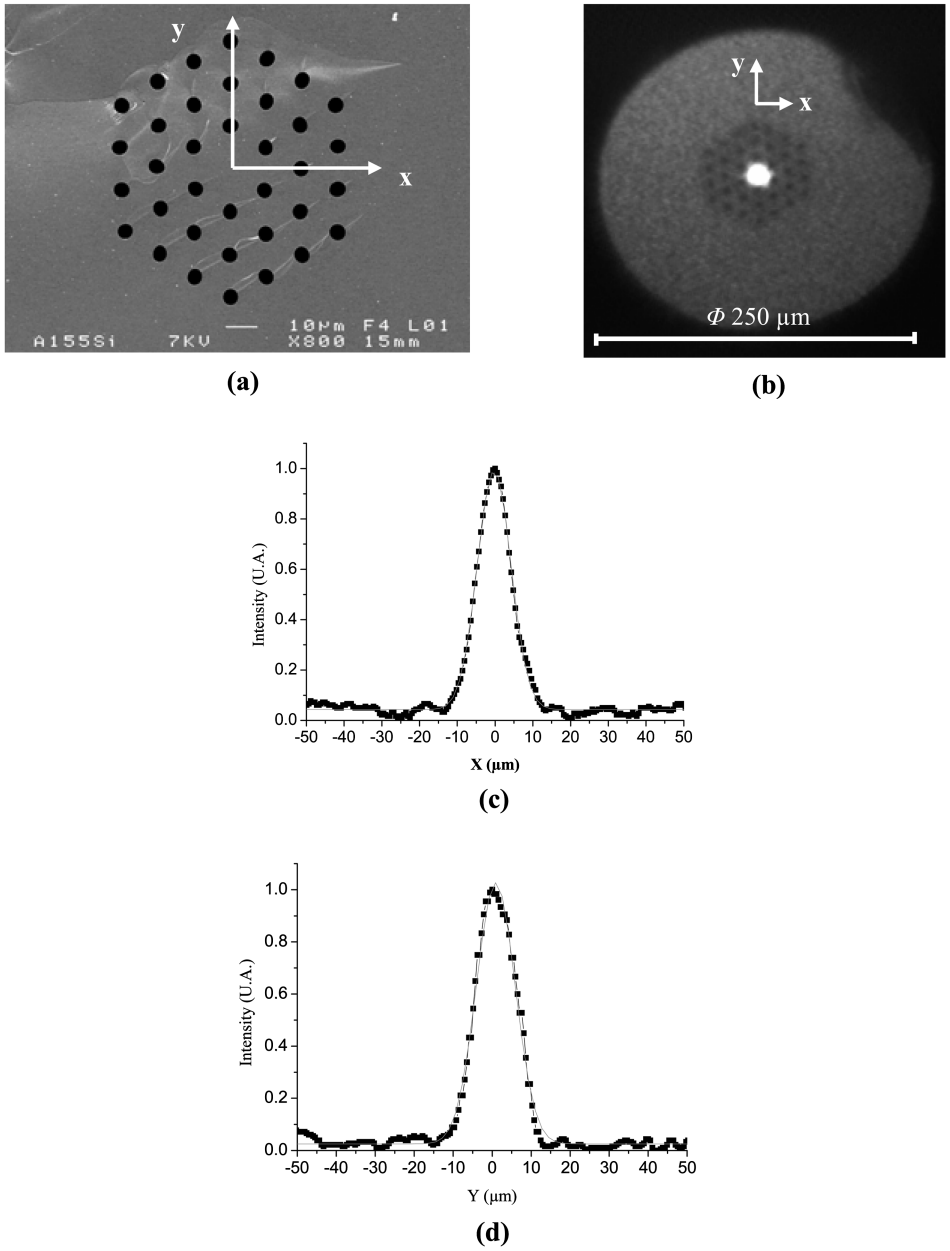

Figure 10. Single-mode behavior of a chalcogenide MOF at 1.55 μm with $d = 4.62$ μm, $\Lambda = 13.2$ μm, and $d/\Lambda = 0.35$: (a) MEB image, (b) near field capture, (c) mode profile X axis, and (d) mode profile Y axis.

fiber (SMF) and the output from the fiber end was imaged onto an infrared camera. An indium coating was applied to inhibit cladding modes guidance. In Figure 9, the parameter d/Λ of the fibers is around 0.6 and corresponds to a multimode guiding at 1.55 μm. In Figure 10, the design of the preform and the process parameters permit to obtain a d/Λ around 0.35 ($d = 4.7$ μm and $\Lambda = 13.2$ μm). After propagating in 30 cm, the output profile can be accurately fitted with a Gaussian function (Figures 10c and 10d). Any other propagating mode has been observed that indicates a single mode behavior. The mode field diameter (MFD) at $1/e^2$ of maximum intensity is measured to be 19.7 μm for the y axis and 18.5 μm for the x axis. The computed MFDs are 19.55 μm for the y axis and 18.30 for the x axis. These theoretical values are in good agreement with those obtained by near field measurement.

The losses at 1.55 μm of this single mode fiber are around 25 dB/m. However, the improvement realized in the purification of the glasses and the drawing process permits to decrease the losses of a single mode chalcogenide MOF under 6 dB/m at 1.55 μm. Indeed, the purifications permit to obtain materials losses close to 1–2 dB/m (see section 2). Excess losses in the MOFs are due to defect centers, such as bubbles or crystals, for example, located in the interfaces between the capillaries. Concerning the guiding losses, computed with any materials losses for the glass, the fundamental ones are around 10 dB/km, whereas the second mode are above 200 dB/m. Therefore, the measured fundamental mode losses are fixed by the materials losses. The huge guiding losses of the second mode and also its partial delocalization in the hole region ensure an effective single mode behavior for this MOF.

6. Discussion

The interest of chalcogenide MOFs is that it is possible to combine the infrared transmission and high intrinsic nonlinear properties of chalcogenide glasses with the properties of the MOFs such as broadband single mode guidance, adjustable dispersion, large mode area, or nonlinear properties. In one hand, the combination of the intrinsic nonlinear properties of chalcogenide glasses with a small effective area obtained in MOFs will allow to design short length, highly nonlinear devices. Indeed, the effective nonlinear coefficient γ at the wavelength λ is given by:

$$\gamma = \frac{2\pi n_2}{\lambda A_{eff}}$$

where n_2 is the nonlinear refractive index and A_{eff} is the modal effective area.

Thus, for an effective area (A_{eff}) of 10 μm^2 and $n_2 = 3.2\ 10^{-18}$ m^2/W, γ will be around 1,400 $W^{-1}.km^{-1}$ as estimated at 1.55 μm. These MOFs have a great interest in particular for the realization of super continuum sources at the telecom wavelengths and in the mid infrared range. On the contrary, for example, for military applications in the 3–5 μm windows, large effective mode area (1,000 μm^2) can be designed to permit the propagation of high power Gaussian laser beams.

All the elaborated chalcogenide MOFs have been optically characterized at 1.55 μm by near field observation and by the measurement of their losses thanks to the cut back method. The total losses at the beginning of our work were around 30 dB/m, even sometimes higher. The choice of a glass composition, which can be entirely distilled, and the improvements of the drawing process have allowed reducing them to 6 dB/m for our best result today. This is comparable to the loss level of MOFs made from lead

silicate or from arsenic selenide glasses, and corresponds to the lowest attenuation level obtained in this kind of fibers [17, 22]. However, we are still working to decrease these total losses in order to reach those observed on the purified glasses. Indeed, the losses of single mode chalcogenide MOFs are actually at least six times higher than the ones of classical multimode fibers.

This work demonstrates the possibility to design chalcogenide MOFs with controlled and various geometries. Indeed, we control the hole pattern, the size of the fibers, and thus their effective area. We produce both large mode field diameter (1,000 μm^2) and small mode field diameter (13 μm^2) fibers. The near field captures at 1.55 μm have shown evidence for light guidance in the core of these fibers when all the steps of the elaboration process are correctly controlled. Besides, the MOF in Figure 10, behaves like a single mode fiber even if the endless single mode property cannot be guaranteed due to the small number of hole rings [34].

7. Conclusion

This article presents the evolution and the improvements that have been achieved in the elaboration of chalcogenide MOFs by the stack and draw technique, as well as results from modelization and characterizations. From the point of view of the elaboration, a gallium-free glass offers the advantage of a complete glass distillation and allows it to reach a better level of losses. We demonstrate the control of the process and the possibility to design fibers with various geometries and effective areas. The working range of these fibers is in the near and mid infrared, between 1 to 6.5 μm. The losses at 1.55 μm can reach 6 dB/m, but their reproducibility still needs to be controlled and their level must be further lowered. The aim of our future works will be to decrease the losses of the chalcogenide MOFs to those of the purified glasses that are currently around 1 dB/m at 1.55 μm and 0.2 dB/m at 5.0 μm.

The chalcogenide MOFs present a great interest for the realization of various infrared optical devices. Telecom signals regeneration, supercontinuum sources, high power infrared laser guides, and infrared optical sensors are several examples of the optical functions that can be achieved with these non conventional fibers.

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