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Fluoride glass microstructured optical fiber with large mode area and mid-infrared transmission

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We demonstrate the first fluorozirconate microstructured fiber for use in the mid-infrared. The fiber preform was manufactured via extrusion of a 200 g billet through a complex graphite die. The fiber exhibits large mode area of 6600 μm^2, loss of 3 dB/m at 4 μm and only marginal excess loss relative to a corresponding unstructured fiber. © 2008 Optical Society of America

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Fibers for high-power transmission in the mid-infrared (MIR) have attracted much attention for thermal decoy, medicine, and sensing applications [1]. To date, step-index fibers have been demonstrated for a range of MIR transmitting materials such as fluoride, chalcogenide glasses, and polycrystalline silver halides [1,2]. However, with these fibers, only limited mode area can be achieved in combination with good beam quality. Microstructured optical fiber (MOF) technology allows this restriction to be overcome [3]. Recently, a single-mode silver halide MOF at 10 μm was demonstrated [2].

In the spectral region from 2 to 5 μm, fluoride glasses are particularly promising materials owing to their low intrinsic loss (<1 dB/km at 2.5 μm), linear index ($n_0=1.5$), and nonlinear index ($n_2 \sim 3 \times 10^{-20}$ m^2/W) [1,4,5]. The low linear index results in low Fresnel loss at the fiber ends. The low nonlinear index minimizes detrimental nonlinear effects for high-power transmission. Recently, a large mode area MOF made from fluorozircoaluminate glass has been demonstrated using the drilling technique for preform fabrication [6]. Although this glass exhibits low loss in the range of 2–4 μm [7], for longer wavelengths (>4.0 μm) the intrinsic loss of the glass increases considerably owing to the relatively high phonon energy of 650 cm^{-1} of the main glass component AlF_3 [4]. In contrast, fluorozirconate glasses exhibit low intrinsic loss <1 dB/m up to 4.5 μm [3] owing to the lower phonon energy of 500 cm^{-1} of the main glass component ZrF_4 [3,4]. Within this glass type, the so-called ZBLAN glass composition has been most widely used for step-index fiber fabrication owing to its relatively high crystallization stability [4].

In this Letter, we report the design, fabrication, and properties of the first large-mode-area MOF made from ZBLAN fluoride glass. The preforms were made using the extrusion technique, which was successfully employed to produce low-loss oxide glass MOFs with a variety of structures [8]. We adapted the extrusion technique to the fabrication of complex fluoride glass preforms for the first time.

To explore the potential of extruding structured fluoride preforms, we commenced with a relatively simple fiber structure with a single ring of holes (Fig. 1). Single-mode guidance can be achieved in this class of structure by making use of the significantly higher confinement loss of the higher-order modes [9]. For structures with five to eight holes, we numerically modeled the mode area and the confinement loss of the fundamental mode (FM) and the first higher-order mode (FHM) at 4.0 μm using the commercial FEMLAB software package from Comsol. The distance, Λ, between the center of a hole and the center of the structures was 50–70 μm (Fig. 2). The hole diameter, d, relative to Λ was $d/\Lambda=0.50-0.85$. For the five-hole case, the confinement loss of both the fundamental and the first higher-order modes is too large (>1 dB/m) for the range of structures considered here to be practical. For structures with six to eight holes, d/Λ regions exist where the confinement loss of the FM is smaller than 1 dB/m, and the loss of the FHM is more than ten times larger than that of the FM and at least 1 dB/m (Fig. 2), providing effective single-mode guidance. The d/Λ values that correspond to this region of effective single-mode guidance decrease with the number of holes. Since the mode area increases with decreasing d/Λ, the mode area values in the region of effective single-mode guidance increase with the number of holes. Thus eight-hole structures in the desired d/Λ region exhibit the largest mode areas of ~ 4500 μm^2. However, the features in the corresponding extrusion dies cannot be machined readily, since the gap between the pins forming the holes in the preform is <0.5 mm.

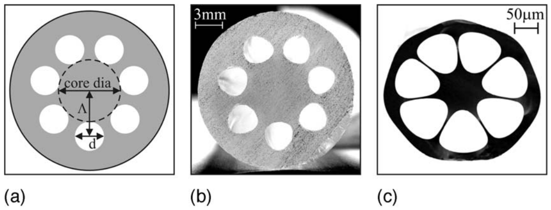

Fig. 1. (a) Target preform structure, (b) extruded preform, (c) scanning electron microscope image of the microstructured fiber.

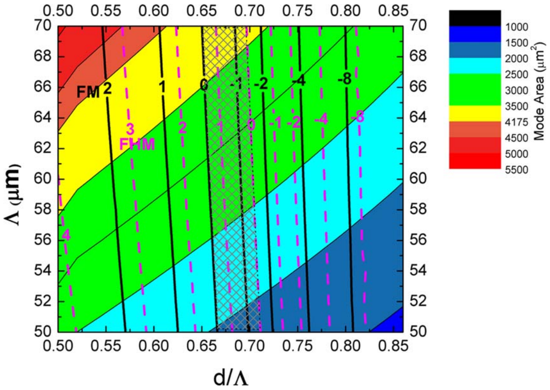

Fig. 2. (Color online) Modeling results of seven-hole structures: solid black and dashed magenta lines show the confinement loss of the FM and of the FHM [log(dB/m)], respectively, background colors show the contour of mode area, hatched area designates the region of effective single-mode guidance as defined in the text.

Hence, we selected a structure with seven holes, $d/\Lambda = 0.65$, $\Lambda \geqslant 70\ \mu\text{m}$ (core diameter $\geqslant 95\ \mu\text{m}$), confinement loss of 1 dB/m for the FM and 24 dB/m for the FHM, and mode area of 4000 μm^2 (Fig. 2).

The first step of the fiber fabrication was the preparation of bulk glass billets. ZrF_4, BaF_2, LaF_3, AlF_3, and NaF were used as raw materials, which were acquired in different purities. We started using raw materials of 99.99% metals purity (4n) except ZrF_4, which was available only in 99.9% metals purity. The corresponding glass billets contained scattering centers, which were attributed to the low raw material purity of the main component ZrF_4. Next, we used ZrF_4 raw material designated as fiber grade (fg), which led to billets without scattering centers. Thus for the subsequent upscaling of the batch size, we also used fg raw materials for the other glass components BaF_2, LaF_3, and AlF_3 (NaF was not available as fg material). A small quantity (8% of the batch weight) of NH_4HF_2 was added to the fluoride batch to fluorinate oxide impurities in the raw materials [4]. The raw material mixtures were melted in platinum crucibles. The molten glass was cast into preheated brass molds and slowly cooled down to room temperature in controlled dry atmosphere. We commenced with a small batch size of 30 g and gradually increased the batch size to 200 g. This upscaling of the batch size was required to obtain billets of sufficient volume for preform extrusion without reducing the extrusion die features to unmanageably small dimensions. For example, the billets obtained from the maximum batch size of 200 g yielded preforms of 17 mm outer diameter that were also of sufficient length (~200 mm) for fiber drawing. Via careful optimization of melting and casting times and the mold temperature, we prevented crystal formation for even the largest glass billets made.

The glass billets were used for preform extrusion. For oxide glasses, stainless steel extrusion dies have been successfully used to extrude complex preforms without glass crystallization [8]. Preliminary extrusion trials using fluorozircoaluminate glass from HOYA Co. showed that the glass temperature required for extrusion through complex stainless steel dies is above the onset of the glass crystallization. The high friction for glass flow through a stainless steel die [10] requires low glass viscosities of $\sim 10^7$ Pa s for complex dies (i.e., relatively high glass temperatures) to overcome the friction between the glass and the steel. However, for fluoride glass, these temperatures are within the surface crystallization region (Fig. 3), making stainless steel dies unsuitable for complex fluoride preform extrusion.

Graphite is an alternative die material, which to date has been used for extrusion of oxide and chalcogenide glass rods [10,12]. In contrast to steel, graphite is not wetted by glass, which considerably reduces the friction within a die [10], enabling the use of higher glass viscosity of $\sim 10^8$ Pa s (i.e., lower glass temperatures) for complex preform extrusion. Using graphite dies and the ZBLAN glass billets made, we extruded both crystal-free rods for bare (unstructured) fiber drawing and preforms with seven holes. This demonstrates that the relatively low glass temperatures possible for extrusion through graphite dies allowed us to extrude complex fluoride preforms below the onset of glass crystallization (Fig. 3). The die exit (i.e., target) structure of the complex graphite die is well preserved in the seven-hole preform over 110 mm preform length (Fig. 1).

The preform was drawn into an ~20 m long seven-hole MOF with ~100 μm core diameter (Fig. 1). As frequently done for oxide glass preforms, we sealed the holes at the top of the preform to prevent hole closure. However, in contrast to oxide glasses, the resulting self-pressurization of the holes led to hole inflation within the fiber, which is attributed to the small surface tension of ZBLAN glass compared with silica [13].

Using the cutback method, the fiber loss of two bare fibers (drawn directly from extruded unstructured rods) and the MOF was measured in the range of 500–1750 nm using a white light source and at 4.0 and 4.7 μm using a tunable broadband laser spectrally narrowed with bandpass line filters (linewidths of ~150 nm FWHM). During the cutback measurements the minimum bend radius used was 300 mm.

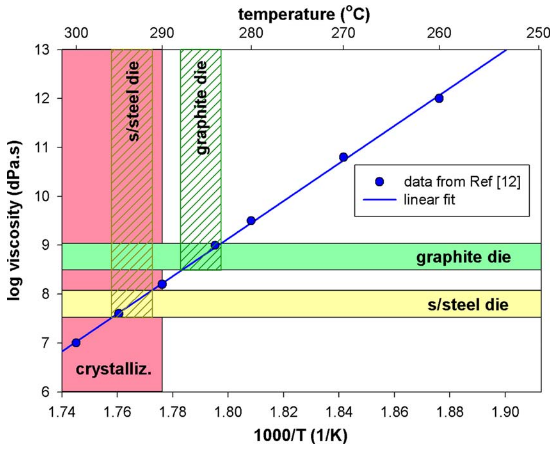

Fig. 3. (Color online) Viscosity of ZBLAN glass as a function of temperature. The line represents a linear fit of the data from [11].

No sensitivity to bend loss was apparent at this radius. The loss of the bare fibers was not sensitive to surface cleanliness, which is consistent with loss results for oxide glass bare fibers with losses >0.1 dB/m [14]. Since fluoride glass degrades in ambient atmosphere via reaction with moisture [4], we stored the fibers under dry conditions and measured the loss within a few days after fiber fabrication. For a bare fiber that was stored six months in ambient atmosphere after fiber fabrication, fiber degradation led to a loss increase by ~ 2 dB/m at 1550 nm. The bare fiber/4n, which was made using 4n BaF_2, LaF_3, AlF_3, NaF, and fg ZrF_4 raw materials, exhibits low loss (1.1 ± 0.5 dB/m at 4.0 μm), which is comparable with the loss of commercially available multimode ZBLAN fibers [15] and 1 to 2 dB/m larger than the intrinsic glass loss owing to multiphonon absorption, which is the ultimate limit for IR transmission [3]. The bare fiber/fg has higher loss (2.1 ± 0.5 dB/m at 4.0 μm) due to use of different raw materials (namely fg ZrF_4. BaF_2, AlF_3, LaF_3, and 4n NaF). The loss of the MOF (3.2 ± 0.5 dB/m at 4.0 μm) is only marginally more than the loss of the bare fiber/fg, which was made using the same raw materials. This demonstrates that the microstructure did not result in significant excess loss, and thus that MOFs are indeed an attractive route to fluoride fibers for the MIR. This is consistent with recent results, showing that the use of extrusion allows the production of MOFs with negligible excess loss for oxide glasses [14].

The mode profile of the MOF at 4.0 μm is shown in Fig. 4. It was measured at 4000 ± 75 nm to be $M^2 = 6.1 \pm 0.2$ and 6.5 ± 0.2 for the two axes, using ~ 2 m fiber length and the total output of the laser operating at 3–5 μm. The relatively high M^2 values are due to the unexpected increase in hole size relative to the target structure as noted above. Using a scanning electron microscope image of the fiber cross-section and the commercial FEMLAB software package from Comsol, the mode area of the fundamental mode was numerically calculated to be ~ 6600 μm^2 at 4.0 μm, which is even larger than the target owing to larger core size in the fiber fabricated relative to the modeled structure.

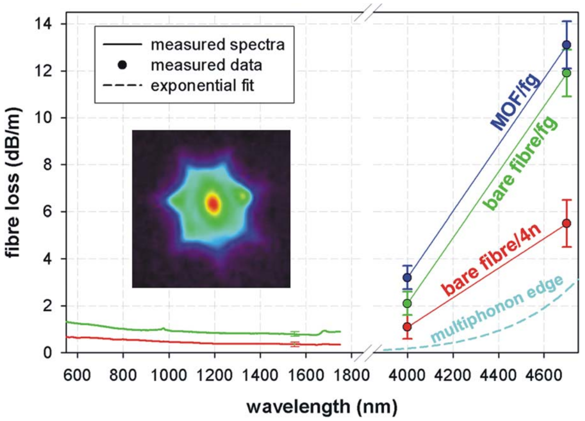

Fig. 4. (Color online) Fiber loss of two bare (unstructured) fibers and the MOF. The lines connecting the measured loss values at 4.0 and 4.7 μm are shown as a guide for the eyes. Inset, measured mode profile of the MOF at 4.0 μm.

In conclusion, we demonstrate the production of crystal-free fluorozirconate ZBLAN glass billets large enough to be suitable for preform extrusion. Building on this, we extruded the first complex fluoride glass preforms using extrusion dies made of graphite and used this approach to realize the first large-mode-area ZBLAN MOF. The unstructured extruded ZBLAN fiber with the lowest loss exhibits 1.1 dB/m at 4 μm, which demonstrates the high quality of the large glass billets, the extruded rods, and the fibers produced. The MOF and corresponding bare fiber have similar loss of 3.2 and 2.1 dB/m at 4 μm, respectively. This indicates that the upsizing of the glass billets and the introduction of the microstructure did not result in significant excess loss. These results demonstrate the viability of extrusion for the fabrication of low-loss fluoride MOFs. Further improvement in the raw material purity and fiber fabrication conditions (including precise hole size control) will enable the demonstration of large-mode-area single-mode fibers with losses close to the intrinsic glass loss.

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References

1. J. A. Harrington, *Infrared Fibers and Their Applications* (SPIE, 2004).
2. L. N. Butvina, O. V. Sereda, E. M. Dianov, N. V. Lichkova, and V. N. Zagorodnev, Opt. Lett. **32**, 334 (2007).
3. T. M. Monro and H. Ebendorff-Heidepriem, Annu. Rev. Mater. Res. **36**, 467 (2006).
4. P. W. France, *Fluoride Glass Optical Fibres* (CRC Press, 1990).
5. R. Adair, L. L. Chase, and S. A. Payne, J. Opt. Soc. Am. B **4**, 875 (1987).
6. P. McNamara, D. G. Lancaster, R. Bailey, A. Hemming, P. Henry, and R. H. Mai, "A large core microstructured fluoride glass optical fiber for mid-infrared single-mode transmission," J. Non-Cryst. Solids, submitted for publication.
7. K. Itoh, K. Miura, I. Masuda, M. Iwakura, and T. Yamashita, J. Non-Cryst. Solids **167**, 112 (1994).
8. H. Ebendorff-Heidepriem and T. M. Monro, Opt. Express **15**, 15086 (2007).
9. W. S. Wong, X. Peng, J. M. McLaughlin, and L. Dong, Opt. Lett. **30**, 2855 (2005).
10. E. Roeder, J. Non-Cryst. Solids **5**, 377 (1972).
11. C. R. Day, P. W. France, S. F. Carter, M. W. Moore, and J. R. Williams, Opt. Quantum Electron. **22**, 259 (1990).
12. D. Furniss and A. B. Seddon, J. Mater. Sci. Lett. **17**, 1541 (1998).
13. N. P. Bansal and R. H. Doremus, J. Am. Ceram. Soc. **67**, C197 (1984).
14. H. Ebendorff-Heidepriem, Y. Li, and T. M. Monro, Electron. Lett. **43**, 1343 (2007).
15. www.infraredfibersystems.com/SGfiber-specs.htm.