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PERFORMANCE OF THE SOL-GEL METHOD FOR THE PREPARATION OF OPTICAL FIBERS

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This paper deals with two principal sol-gel approaches for the preparation of silica optical fibers. The first approach consists in the fabrication of preforms for fiber drawing, such as silica tubes, silica rods or rods with air holes, through sol-gel casting and preparation of monoliths. The second one is based on the application of thin layers into substrate tubes, their thermal treatment and viscous transformation into preforms of optical fibers under the effect of surface tension. The paper discusses principles and main results of these approaches. In addition to information from a literature review, it shows results achieved by the authors in the area of preparation of preforms doped in the core with aluminium oxide, phosphorous or boron oxide, bismuth oxide and rare-earth elements. Properties of the prepared preforms and fibers are discussed along with chemical compositions of the prepared materials, their refractive-index profiles, and optical losses.

INTRODUCTION

Modern communications can hardly be imagined without optical fibers. Now, optical fibers are involved in technical support of nearly all services available on telecommunication market (Internet, mobile phones, etc.). Moreover, optical fibers have also been investigated as means for improving the performance of electronic devices by interconnecting electronic integrated circuits.[1]

Optical fibers are cylindrical dielectric waveguides that transmit light along their axis. The fiber consists of a core surrounded by a cladding. For confining light in the core, the refractive index of the core has to be greater than that of the cladding. In novel types of optical fibers, microstructure fibers (MSFs), air holes are introduced in the fiber cladding along the entire length of the fiber. In photonic crystal fibers (PCFs) these holes are arranged into a regular grid.[2]

Optical fibers are usually drawn from preforms fabricated by methods based on gas-phase deposition. These methods include modified chemical vapor deposition (MCVD), outside vapor deposition (OVD) or vapor axial deposition (VAD).[3] In these methods raw materials are oxidized or hydrolyzed in gaseous phase -forming aerosol particles of multicomponent oxides. The particles are deposited onto silica substrates and the prepared porous deposit is consolidated into glassy materials. In the MCVD and OVD methods, this material is transformed into preforms for fiber drawing through a viscous flow controlled by surface tension.

Several stages of the preparation of fiber-optic preforms by gas-phase deposition techniques, particularly the deposition of porous layers and consolidation of porous materials to glass below melting temperatures, show close similarity with the fabrication of optical glass materials by the sol-gel method. This similarity and advantages of the sol-gel based techniques, such as low processing temperatures, high purity and homogeneity of products, possibility of precise composition control, may explain why the sol-gel method has also been investigated for the fabrication of fiber-optic perforns.[4-20] This paper shows performances of two sol-gel approaches to the preparation of optical fibers. It deals with the preparation of preforms through the formation of monoliths or through the application of thin layers inside silica tubes. Performances of approaches so far

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published elsewhere are discussed in the paper and their results are compared with those achieved by the authors, namely in the preparation of monoliths doped with rare-earth elements, Al_2O_3, and P_2O_5 or optical fibers doped with Bi_2O_3 .

EXPERIMENTAL

1. Fabrication of optical fibers through monoliths

Several approaches have been developed for the fabrication of monolithic silica tubes and rods of doped silica.[4-17] There are two principal approaches that have been used for the preparation of gels and glasses. The first approach uses colloidal sols, the second one uses alkoxide sols. Examples of compositions of the prepared preforms, raw materials used, and important processing parameters are shown in Tabs. 1 and 2.

In general, the preparation of glass monoliths for drawing optical fibers by the sol-gel method should satisfy two basic requirements. They are namely the preparation of crack-free xerogel bodies and their consolidation into glass without foaming at temperatures around 2000 °C. Colloidal-based sol-gel methods use sols prepared of fumed silica (usually commercially available materials with a surface area of 50 or 200 m^2/g) dispersed in water by using efficient blenders.[4-9] One principal method is based on a two-step process, which includes gelling, drying the gel, its heat treatment at 900°C, milling, and re-dispersing in water. This method gives broader pore-size distributions of gels from the twice dispersed raw material than from the once dispersed one.[4-6] However, milling of the heat-treated gel has to be optimized in order to avoid the formation of large pores which may remain open during the gel densification.[6] Thus, another principal method has been developed to avoid this disadvantage.[8,9] It uses sols of fumed silica dispersed in water with a base (tetramethylammonium hydroxide-TMAH), lubricant (glycerol) and polymer binder. A gelling agent, an ester (methyl formate). Is added into the sol. The ester hydrolyses and decreases the pH, which causes gelling.

Table 1

Characteristics of colloidal-based approaches to the preparation of monoliths

Sample	Components of sols	Key preparation conditions	Remarks	Ref.
Silica tubes	Fumed silica Water	Twice dispersed gel	Tubes used in the MCVD process; Fiber losses - 0.7 dB/km at 1.15 μm	1, 5
Silica tubes	Fumed silica (200 m^2/g) Water	Twice dispersed gel Attrition in mills		6
Silica tubes and rods	Fumed silica, water 1% of hematite	Effect of Cl_2	C(Fe)=40 mol. ppb in treated glass	7
Silica tubes	Fumed silica (50 m^2/g) water, TMAH base, lubricant, polymer	Controlled gel drying Dehydroxylation in $SOCl_2$	Tubes used in the MCVD process; Fiber losses - 0.35 dB/km at 1.15 μm	8, 9

In the preparation of monoliths, colloidal sols are cast into a mold containing mandrel elements, which determine the number and shapes of air holes in the gel rods. A long-term (around one week) drying at special conditions has been developed that is necessary for eliminating the effects of drying shrinkage.[9] The drying is followed by dehydroxylation in an atmosphere of chlorine compounds ($SOCl_2$) and by sintering in an atmosphere containing He. No trouble with foaming during fiber drawing has been reported in the papers dealing with the preparation of pure silica preforms by these methods.

Alkoxide-based sol-gel methods usually employ tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) together with alkoxides of doping elements (denoted further as M, see Tab. 2).[10-17] Base catalysis (NH_4OH) has been used mainly for the sol preparation. The sols are cast into molds, in which gelling, aging the gel, and its drying at elevated temperatures (50-120° C) take place.[10,11,13-15] The prepared xerogel monoliths are heat-treated (temperatures up to 800 °C), dehydroxylated in a flow of chlorine, and consolidated at temperatures up to 1100-1400 °C. Foaming during fiber drawing was observed in some doped silica glasses, which was related to the strength of M-Cl bonds.[12,15] Several attempts have been described for suppressing the foaming by precise controlling of the surface area of particles in silica sols and preparing large particles, or by an additional high-temperature heat treatment of sintered monoliths by using a hydrogen-oxygen torch.[15] However, a general approach has not been developed yet. Preforms with graded refractive-index profiles have been prepared by immersing xerogel monoliths doped with GeO_2 in water.[10]

In our experiments monoliths of multicomponent glass monoliths suitable for fiber drawing were prepared. Input sols were mixed of TEOS, $POCl_3$, $AlCl_3$, $ErCl_3 . 6H_2O$, $YbrCl_3 . 6H_2O$ (a minimum purity of 99.9% from Aldrich), isopropanol as a solvent and HCl as a catalyst. The composition of the mixed input sol is shown in Tab. 3. In the first stage, TEOS was prepolymerized to a sol (C(TEOS)= 2 mol/l, R_w=2,) by using an approach described elsewhere.[20] Solid $AlCl_3$ and/or rare-earth salts were dissolved in the sol, which was then mixed at 60 °C for 45 min. A solution of $POCl_3$ (C($POCl_3$)= 0.4 mol/l) in isopropanol was then added into the sol, which was intensively mixed at ambient temperature for 30 min. The final sol was kept in a closed plastic container and used for the application of layers (see Part 2.3.). It was stable for about one week.

For the preparation of monoliths, pH of the sol was increased by adding ammonia water (concentration of 0.01mol/l). The sol was poured into a loosely closed plastic container. The gelling occurred after about 30 min. The gel was aged for two days at 70 °C and then slowly dried at the same temperature for about one week. Xerogel rods with a diameter of 3-7 mm and lengths up to 5 cm were obtained.

Table 2

Characteristics of alkoxide-based approaches for the preparation of monoliths

Sample	Components of sols	Key preparation conditions	Remarks	Ref.
SiO_2/GeO_2 rods	TMOS, $Ge(OEt)_4$ Ethanol, HCl, water	Gel drying at 50 °C (days) Leach out GeO_2 from xerogel rods in water	Rods with graded refractive-index (GI) profiles prepared	10
SiO_2/GeO_2 rods	TMOS, $Ge(OEt)_4$ CH_3OH, NH_4OH	Gel drying at 70°C (1week); Foaming conditions	Rods with step-index (SI) profiles prepared; Losses 25 dB/km at 1 μm	11 12
SiO_2/Sb_2O_3 rods	TMOS, $Sb(OEt)_3$ n-propanol, NH_4OH	Drying gels at 70-120 °C (3 weeks); Rod-in-tube method for fiber drawing	SI and GI rods prepared; Losses 700 dB/km at 1 μm; Refractive index 1.5-1.6	13
SiO_2/Ta_2O_5 rods	TMOS, $Ta(OEt)_5$ CH_3OH (n-propanol), NH_4OH	Gel drying gels at 70°C (1 week); Rod-in-tube method for fiber drawing	SI and GI rods prepared; Losses 1000-5000 dB/km at 1 μm; Refractive index 1.5-1.6	14
SiO_2/M_xO_y	TEOS, $M(OEt)_z$, $Si(OEt)_3F$,	Particle-size control technique at 70 °C	SI rods prepared; Losses 0.4	15
SiO_2/F rods	EtOH (n-propanol), NH_4OH	Foaming conditions	dB/km at .1.55 μm for F-doping	17
SiO_2/Er	TEOS, $ErCl_3.6H_2O$, HCl, NH_4OH	Gelling by NH_4OH ; impregnation xerogel rods with an Er solution	Drawing fibers coated with polymer	16

Et = C_2H_5

Table 3

Composition of the input sol used for the preparation of monoliths

C_{Si}	C_{Al}	C_P	C_{Yb}	C_{Er}	R_W
1.40	0.,40	0.04	0.035	0.0036	2

Concentrations of elements in [mol/l]

The rods were heated up to 800 °C (a heating rate of 5°C/min) in a furnace. They were consolidated at temperatures of 1000-1700 °C in a flow of oxygen with a small amount of $POCl_3$ in order to suppress the evaporation of P_2O_5 at high temperatures and to remove OH groups in the presence of Cl_2 formed from $POCl_3$. The consolidation and drying were done on a rod placed inside a silica tube rotating in a glass working lathe. The tube with the rod was elongated at about 2000 °C by using a graphite furnace. The elongated rod (a diameter of 1-2 mm) was overcoated with a silica tube and a single-mode fiber with a diameter of 0.125 mm was drawn by using the same furnace.

The refractive-index profiles of the elongated rods were measured by using a profiler A2600 (Photon Kinetics, USA) with an accuracy of 10^{-4}. An example of the measured refractive-index profile is shown in Fig. 1. The attenuation of the drawn fibers was determined with an accuracy of 0.01 dB by the cut-back method (see Fig. 2).

2. Fabrication of preforms of microstructure fibers

Microstructure fibers are usually drawn from preforms of pure silica.[2,19] These fibers contain air holes in their cladding, which cause a decrease in the average refractive index of the cladding. The modified colloidal-based sol-gel methods described above have been employed for the preparation of preforms of MSFs.[18,19] In this modification, a colloidal silica sol is cast in a mold with an array of mandrels. After gelling and drying, the mandrels are removed and the xerogel is heat treated as described above. This approach makes possible to control the dimensions, shapes and numbers of air holes in the monoliths. Moreover, solid monoliths enable an easy application use of an increase of pressure (a pressure difference ΔP) inside the holes of MSFs during drawing.

In our work, the sol-gel method was employed for the modification of a current technique for MSF fabrication which is based on drawing stacks composed of a central silica rod surrounded by silica capillaries.[2,20] In this modification the interstices between the rod and capillaries were filled by pastes prepared from sols mixed of TEOS, and $POCl_3$ (BBr_3) into which fine particles containing the same oxides were added.[20] The particles were prepared from the same sols which had been gelled, heat-treated at 1000 °C, and milled. These pastes were applied onto one end of the stack and densified at temperatures up to 1000 °C for several hours. This technique has also enabled us to apply pressure during fiber drawing and to control the dimensions and shapes of air holes (see Fig. 3).

3. Preparation of fiber-optic preforms by the application of layers inside substrate tubes

This approach consists in the application of gel layers by a modified dip-coating method on the inner wall of a substrate silica tube.[21-25] The modification is based on lowering the sol level in the tube at a defined velocity. The applied gel layers are dried, dehydroxylated, and sintered at temperatures up to 1600 -1800 °C. Then the applied layers are transformed into bulk material by the effect of viscous flow driven by surface tension. This approach has been employed for the preparation of optical fibers doped in the core with Al_2O_3, P_2O_5, Nd, Yb, Er.[21-24]

In order to avoid the effect of substrate-deposit interactions at high temperatures (1300-2000°C) xerogel layers with a thickness above 3-10 μm have to be applied.[25] Otherwise, highly viscous silica of the substrate tube takes place at the consolidation and viscous transformation of applied porous layers. The required thickness can be achieved by employing

highly concentrated and viscous input sols[21] or by successive application of several layers.[22-24]

In this work novel results achieved in the preparation of silica optical fibers doped in the core with Bi_2O_3 are shown. Preforms for fiber drawing were prepared by the application of input sols mixed of TEOS, $BiCl_3$, $POCl_3$ (BBr_3), and/or chlorides of rare-earths (Er and Yb). In the preparation, TEOS dissolved in ethanol was prepolymerized by a mixture of water and HCl in ethanol. The sol was agitated at 60 °C for 30 min. Then $BiCl_3$, and in case when the rare-earth salts were used, were dissolved in this sol at 60 °C for 45 min. Finally, a solution of $POCl_3$ (C=0.4M) or BBr_3 (C=0.25 M) in ethanol was added and the sol was agitated at ambient temperature for 20 min. The sol was kept in a plastic container and was stable for approximately 1 week. The compositions of the sols used in experiments are shown in Tab. 4.

Table 4

Composition of the input sols used for the preparation of Bi_2O_3

	C_{Si}	C_{Bi}	C_P /C_B	C_{Yb}	C_{Er}	R_w
Sol A	2.5	0.6	0.6/0.0	0.04	0.003	1.5
Sol B	2.5	0.5	0.0/0.2	0.04	0.003	1.5

Concentrations of elements in [mol/l]

The sols were applied by lowering the sol level in a vertical substrate tube of pure silica. After the application of the sol, the gel layer on the inner wall was exposed to a stream of oxygen saturated with water at ambient temperature for 5 min. Then the layer was dried at 100 °C in an oxygen flow for 15 min and heat-treated at 600 °C for 15 min. A porous layer was obtained after this treatment. This application of the porous layer was repeated and four layers were applied as a maximum. Then the applied deposit was partially consolidated in a furnace at 900 °C for 1 hour in the oxygen atmosphere. The final consolidation was carried out at temperatures in a range 1000-1600 °C in a flow of $POCl_3$ (BBr_3) with oxygen under heating the rotating tube by a hydrogen-oxygen torch. The tube was converted into a preform by increasing the temperature of the tube to 1950 °C. The fibers were drawn from preforms at 2000 °C.

Refractive-index- profiles of the preforms were measured by the profiler mentioned above (see Fig. 4). Attenuation of the prepared fibers was measured by the cut-back method (see Fig. 5).The concentration profiles of dopants in the core were determined by the EDAX analysis (an accuracy of 0.1%).

DISCUSSION

Evaluating the performance of the sol-gel method for the preparation of optical fibers, one can conclude that the method can be suitable for the fabrication of silica monoliths. A fully controlled drying of large gel monoliths and their consolidation into glass tubes have been developed.[9] On the basis of this technique silica tubes with an outer diameter of 50 mm, inner diameter of 20 mm and a length of 1 mm are produced commercially in USA.[8,9] These materials have low losses of about 0.35 dB/km at 1330 nm, which can be explained that impurities are removed as volatile chlorides.[7]

A very promising directions seems to be the employment of colloidal-based approaches to the fabrication of different types of microstructure fibers for telecommunications and sensing.[19,26,27] Results of experiments presented in this work have shown that colloidal-based sol-gel techniques can be employed for improving the fabrication of MSFs from stacks of a silica rod and silica capillaries. They provide us with an approach to the treatment of the stack end, which makes it possible to apply and control the pressure inside the tubes. This pressure is one of variables controlling the dimensions and shapes of air holes in MSFs and consequently, also optical properties of MSFs. By using ΔP = 600 Pa “grapefruit” types fibers with large air holes have been prepared from stacks with the sol-gel treated end (see Fig. 3).

In the field of optical fibers drawn from doped silica glasses prepared by the sol-gel method, one can conclude that sol-gel approaches can be suitable mainly for the preparation of special fibers which can hardly be fabricated by methods based on gas-phase deposition. These special fibers include fibers for fiber lasers and amplifiers and for non-linear optical effects. They usually have cores of multicomponent glasses which contain volatile oxides (PbO, Sb_2O_3). Results of this work show that such fibers can be prepared through both the fabrication of monoliths and the application of thin layers.

No foaming was observed during the consolidation of the prepared multicomponent glass monoliths or multiple layers applied on the inner wall of the substrate tubes at temperatures above 1600°C. This finding can be explained by the composition of the prepared materials, which contain dopants with the both strong and weak M-Cl bonds.[15] Moreover, it may be related to the

employment of raw materials such as $POCl_3$ or BBr_3 in the consolidation atmosphere. This original method allows easily melting oxides P_2O_5 or B_2O_3 to be formed during the consolidation, which can decrease the viscosity of materials, and consequently, the final dimensions of pores at high temperatures.

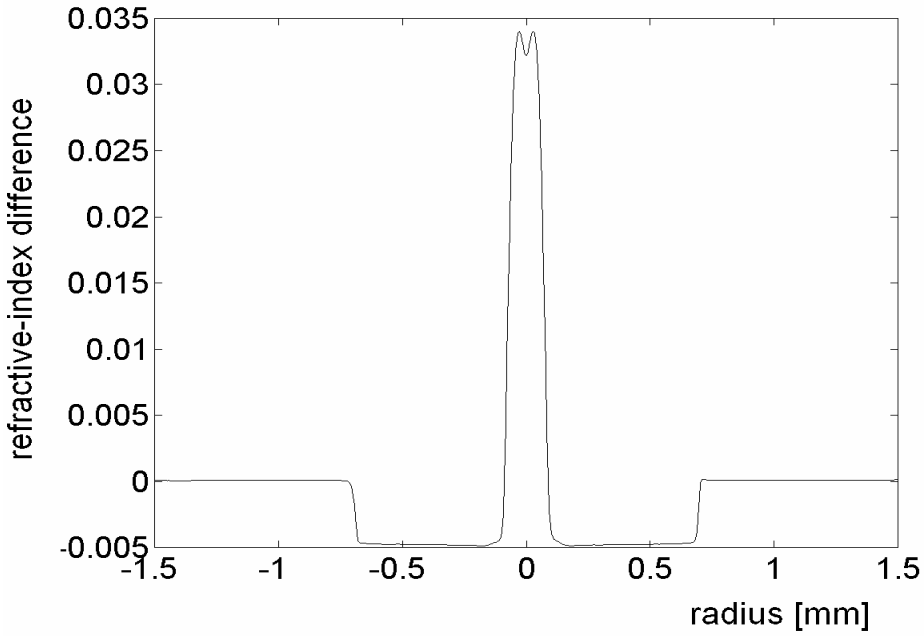

Fig. 1 – Refractive-index profile measured on an elongated rod prepared from a sol with the composition given in Tab. 3 through the monolith fabrication.

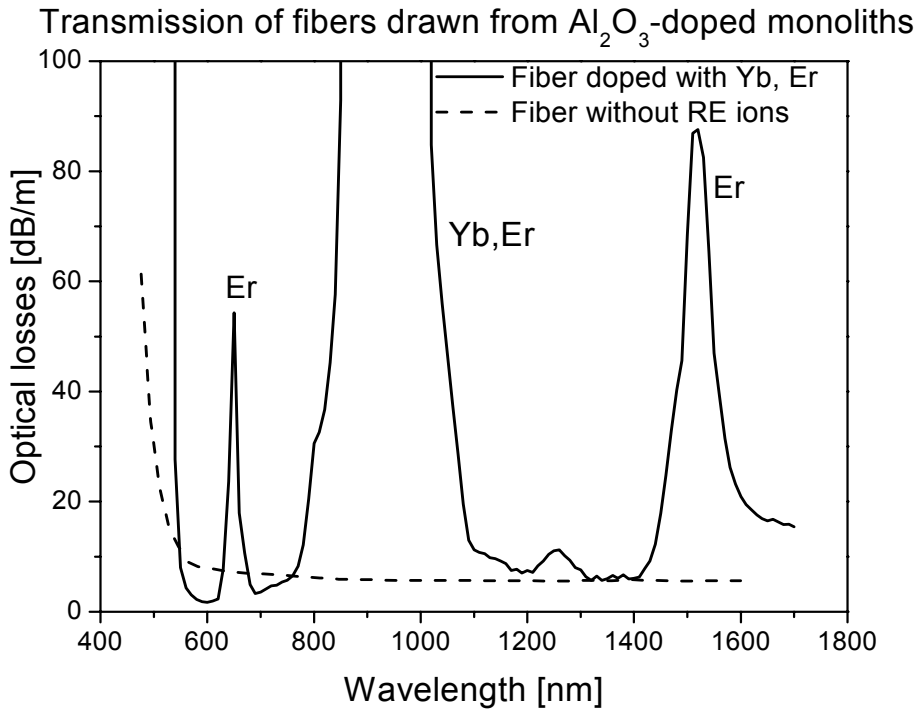

Fig. 2 – Transmission spectrum of a fiber drawn from the preform prepared on the basis of a sol with the composition given in Tab. 3; Contents of dopants $x(Al_2O_3)$=5 mol%, x(Yb) = 1.2%, Yb/Er = 10.

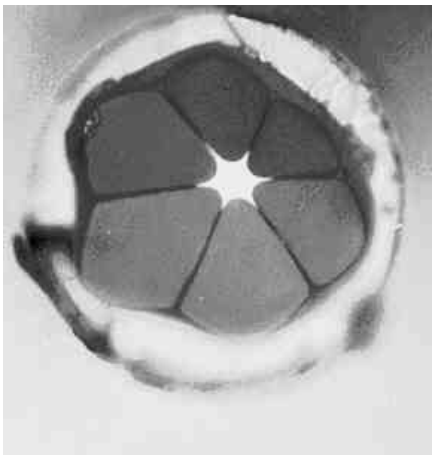

Fig. 3 – Photo of MSF prepared from the stack with the end filled with a SiO_2/B_2O_3 paste and drawn under pressure difference of 600 Pa.

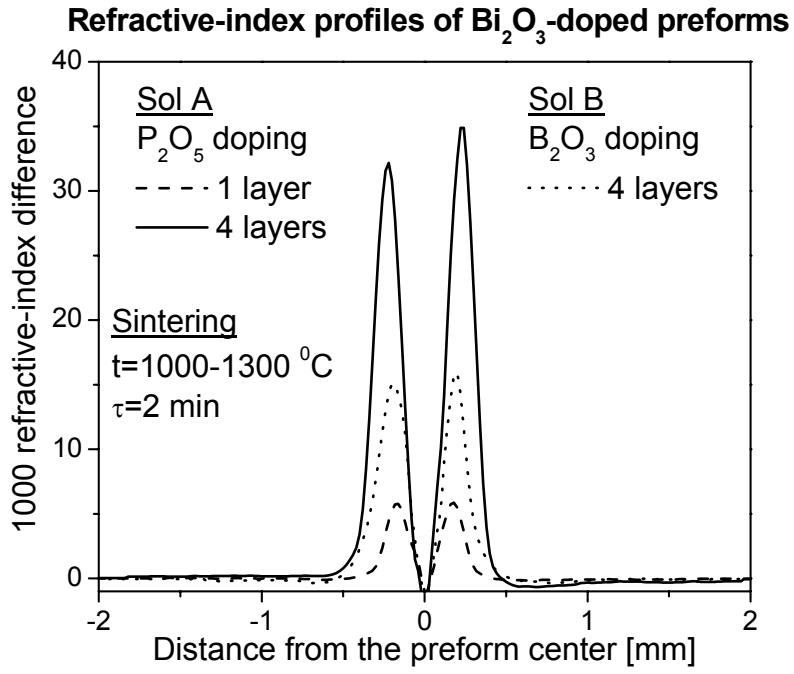

Fig. 4 – Refractive-index profiles measured on preforms prepared from sols with the compositions given in Tab. 4 through the application of layers.

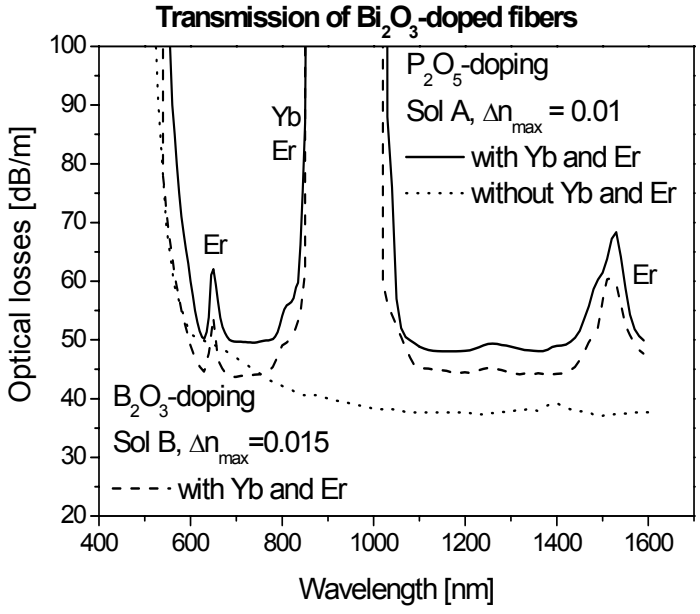

Fig. 5 – Transmission spectra of fibers drawn from the preforms prepared on the basis of sols with the compositions given in Tab. 4; Contents of dopants $x(Bi_2O_3)$=5 mol%, x(Yb) = 0.9%, Yb/Er = 10.

The approaches described in this paper enable to prepare optical cores with high refractive indexes (see Figs. 1 and 4). Optical fibers with maximum concentrations of P_2O_5 of about 10 mol.%, Bi_2O_3 of about 8 mol.%, Al_2O_3 of 6 mol.% in the cores were prepared in this work. The measured refractive-index profiles reflects the effect of substrate/deposit interactions which causes an decrease of the maximum refractive index for thin deposits (see Fig. 4, 1 layer and 4 layers).[25] Moreover, one can see an decrease of the refractive index due to B_20_3- doping (see Fig. 4, sol B). Optical losses of the fibers doped in the core with Al_2O_3 (see Fig. 2) are comparable with previously reported data measured on fibers prepared through the deposition of thin layers. [23-25] The measured losses of the prepared fibers were still high (see Figs. 2 and 5), which can be explained by longitudinal irregularities of the core dimensions due to imperfections of the layer or monolith surface. The measured losses are comparable with those published elsewhere.[13,14] Fibers with relatively low contents of OH groups were prepared (see Figs. 2 and 5, a peak around 1400 nm).

Comparing the preparation of preforms through the monoliths and inside deposition of thin layers one can expect that the monolithic approach can be more suitable for glasses containing easily evaporated components, because in this case their high contents can be preserved at least at the central region of the preform. In any case, one should expect the occurrence of the effect of diffusion and consequently, a decrease of the maximum refractive indices and an increase of the core diameters.[25] However, the preparation of preforms through monoliths is a technique taking a long time that can suffer from fractures of monoliths and their foaming. The diffusion effects have stronger influence during the inside deposition technique, because in this case the deposited layers are relatively thin. Thus, some combination of these two techniques would be useful for the preparation of preforms of doped silica.

CONCLUSIONS

It has been shown that the sol-gel method can be employed for the fabrication of preforms for drawing optical fibers, especially for special fibers which can hardly be prepared by the currently used chemical vapor deposition techniques. Colloidal-based approaches have been successfully employed for commercial fabrication of silica tubes. Different types of silica microstructure fibers have been fabricated by using colloidal sols.

It is expected that in the future the most promising directions will include the sol-gel fabrication of microstructure fibers, however not only from pure silica, but also from multicomponent glasses. Such fibers could be used in photonic devices based on non-linear optical effects. In addition, one can expect that silica optical fibers with the cores of multicomponet glasses prepared by the sol-gel method will be employed for this purpose as well. However, it means that approaches to suppressing foaming, fractures and concentrational changes during the heat treatment of xerogel materials will be further improved.

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REFERENCES

1. D. Fey, W. Erhard, M. Gruber, J. Jahns, H. Bartelt, G. Grimm, L. Hope and S. Sinziger, *Proc. IEEE,* **2000,** *88, 838-848.*
2. R.J. Eggleton, C. Kerbage, P.S. Westerbrook, R.S. Windler and A. Hale, *Opt. Express,* **2001**, *9*, 698-727.
3. L. Cognolato, *J. Physique IV,* **1995**, *5,* 975-987.
4. E.M. Rabinovich, J.B. MacChesney, D.W. Johnson Jr., J.R. Simpson, B.W. Meagher, F.V. Dimarcello, D.L. Wood and E.A. Sigety, *J. Non-Crystalline Soids,* **1984**, *63*, 155-161.
5. J.B. MacChesney, D.W. Johnson Jr., D.A. Fleming and F.W. Walz, *Electron Lett.,* **1987** , *23*, 1005-1007.
6. D.W. Johnson Jr., E.M. Rabinovich, D.A. Fleming and J.B. MacChesney, *J. Mater. Sci.,* **1989**, *24*, 2214-226.
7. J.B. MacChesney, D.W. Johnson Jr., D.A. Fleming, F.W. Waly and T.Y. Kometani, *Material Res. Bull.,* **1987,** 22, *24*, 1209-1216.
8. J.B. MacChesney, D.W. Johnson Jr., S. Bhandarkar, M.P. Bohrere, J.W. Fleming, E.M. Monberg and D.J. Trevor, *Electron Lett.,* **1997** , *33*, 1573-1574.
9. J.B. MacChesney, D.W. Johnson Jr., S. Bhandarkar, M.P. Bohrere, J.W. Fleming, E.M. Monberg and D.J. Trevor, *J. Non-Crystalline Solids.,* **1998**, *226*, 232-238.
10. K. Shingyouchi and S. Konishi, *Electron Lett.,* **1986**, *22*, 99-100.
11. K. Susa, S. I. Matsuyama, S. Satoh and T. Suganuma, *J. Non-Crystalline Solids,* **1990**, *119*, 21-28.
12 K. Susa, S. I. Matsuyama and S. Satoh, *J. Non-Crystalline Solids,* **1991** , *128*, 118-125.
13. K. Susa, S. Satoh and I.Matsuyama, *J. Non-Crystalline Solids,* **1997** , *221*, 125-134.
14. K. Susa, S. Satoh and I.Matsuyama, *J. Non-Crystalline Solids,* **2002** , *306*, 300-308.
15. S. Shibata, *J. Non-Crystalline Solids,* **1994**, *178*, 272-283.
16. E.M. Pawlik, W. Strek, P.J. Deren, J. Wojcik, G.E. Malaskevich and V.E. Gaishun, *Spectrochim. Acta.,* **1999**, *55*, 369-373.

17. S. Satoh, K. Susa, I. Matsuyama, T. Suganuma and H. Matsumura, *J. Non-Crystalline Solids,* **1997**, *217*, 22-29.
18. Y. De Hazan, J.B. MacChesney, T.E. Stockert, D.J. Trevor and R.S. Windeler, *U.S. pat.*, 6,467,312 B1, Oct. 22, 2002.
19. R.T. Bise and D.J.Trevor, Sol-gel derived microstructure fibers: Fabrication and Characterisation, http://www.specialtyphotonics.com/pdf/knowledge_base/white_papers/microstructure/bise_ofc_2005.pdf .
20. J. Mrazek, V. Matejec, I. Kasik, M. Hayer and D. Berkova, *J. Sol-Gel Sci. Technology*, **2004**, *31*, 175-178.
21. D.J. DiGiovanni and J. B. MacChesney, *Optical Fiber Communication, Osa Technical Digest Series,* **1991,** *4,* Paper WP4.
22. F.Q. WU, D. Machewirth, E. Snitzer and G.H. Siegel, *J. Material Res.,* **1994,** *9*, 2703-2705.
23. V. Matejec, M. Hayer, M. Pospisilova and I. Kasik, *J. Sol-Gel Sci. Technology*, **1997**, *8*, 889-893.
24. V. Matejec, I. Kasik, D. Berkova, M. Hayer and J. Kanka, *J. Sol-Gel Sci. Technol*., **1998**, *13*, 617-621.
25 V. Matejec, I. Kasik, D. Berkova, M. Hayer, M. Chomat, Z. Berka and A. Langrova, *Ceramics-Silikaty*., **1997**, *45*, 62-69.
26. Y. Zhu and H. Du, *Opt. Express,* **2006,** *14*,-3541-3546.
27. V. Matejec, J. Mrazek, M. Hayer, I. Kasik, P. Peterka, J. Kanka, P. Honzatko and D. Berkova, *Mater. Sci. Eng. - Biomimetic Supramolec. Systems*, **2006**, *26,* 317-321.