Germania-Based Core Optical Fibers

Evgeny M. Dianov, *Member, IEEE*, and Valery M. Mashinsky

Invited Paper

***Abstract*—Germania-glass-based core silica glass cladding single-mode fibers (Δn up to 0.143) with a minimum loss of 20 dB/km at 1.9 μm were fabricated by the modified chemical vapor deposition (MCVD) method. The fibers exhibit strong photorefractivity with the type-IIa-induced refractive-index modulation of 2×10^{-3}. The Raman gain of 300 to 59 dB/(km $\cdot$ W) was determined at 1.07 to 1.6 μm, respectively, in a 75 mol.% GeO_2 core fiber. Only 3 m of such fibers are enough for the creation of a 10-W Raman laser at 1.12 μm with a 13-W pump at 1.07 μm. Raman generation in optical fiber at a wavelength of 2.2 μm was obtained for the first time.**

***Index Terms*—Optical-fiber losses, optical-fiber materials, Raman lasers.**

I. INTRODUCTION

GERMANIA-DOPED silica or germanosilicate glass (with GeO_2 concentration up to $\sim$ 10 mol.%) has been the most frequently used core material of telecommunication optical fibers for more than 30 years. This is due to the many excellent physical properties of germanosilicate glass, which is close to silica glass. First, both germanosilicate and silicate glasses have long-term structural stability, high mechanical strength, low chemical activity, low sensitivity to ionizing radiation, close thermal expansion, and viscosities. These features make it possible to fabricate optical fibers of good geometrical quality and long operation life in different environments. Second, these glasses possess both low intrinsic absorption and Rayleigh scattering in the near-infrared (IR) spectral range. A typical minimum optical-loss level of less than 0.20 dB/km at a wavelength of 1.55 μm allows an increase of the distance between the amplifiers of up to 100 km. Third, germanosilicate glass has low-enough nonlinear optical characteristics so that optical signals with a total power of about 1 W can propagate in single-mode fibers without considerable nonlinear distortion.

At the same time, there are some scientific and application problems that can hardly be solved with silica-based fibers but could be solved easier if one relies on optical fibers with higher nonlinearities and photosensitivities and, simultaneously, with low optical losses. From this point of view, pure germania (or doped germania) proposed as a base glass for fiber optics could be very promising, especially in the spectral range of 1.7–3 μm. However, many technological difficulties in fabricating GeO_2-based fibers did not allow the attainment of the estimated loss level of $\sim$ 0.2 dB/km up to now. Nevertheless, a few years ago, we renewed the fabrication and study of germania-based core fibers and showed, in practice, that such fibers, even with higher losses, could be useful for some application.

II. PROPERTIES OF GERMANIA GLASS FOR FIBER OPTICS

Maurer and Schultz from Corning Glass Works were seemingly the first who, in 1975, proposed to use the germania and germania-based glasses as base materials for the fabrication of low-loss optical fibers [1].

In 1979, Olshansky and Scherer [2] analyzed the literature data and estimated the values of the zero material dispersion in the bulk GeO_2 glass ($\lambda_0 \sim 1.7-1.8$ μm) and of the Rayleigh scattering to be about two times higher than that in silica glass. Besides, they noted that both the intrinsic IR absorption of GeO_2 glass and the impurity of the Ge–OH absorption bands are shifted to longer wavelength, as compared with those in silica glass. So, they made a conclusion that these features of GeO_2 glass makes it an attractive candidate for low-loss optical fibers.

High-purity GeO_2 glass was fabricated and its properties were experimentally studied in 1980 [3], [4]. Soot glass was obtained by $GeCl_4$ oxidation in the silica tube with a concentration of the transition metals of less than $10^{-6}\%$. Then, the soot was sintered in a vacuum furnace at 1100 °C into bulk glass samples of about 20 mm in size. The density of the glass was measured to be 3.65 g/cm^3.

Plates of different thickness (from 0.2 to $\sim$ 10 mm) and prisms were cut and polished for optical and other measurements. Because of the high-enough water solubility of germania glass, the final polishing to obtain the surface of optical quality was made in nonwater conditions. Note that after about a few months of storage in laboratory conditions (room temperature and usual humidity of 50–80%), a thin polycrystalline film appeared on the polished surfaces of the samples. A time period of a few years was enough to fully crystallize a glass plate of $\sim$ 1-mm thick.

Refractive index dispersion was measured in an autocollimation scheme in the spectral range 0.5–2.5 μm on a 30° prism with 6 × 6 mm refractive faces. Sellmeier model approximation gave the zero material dispersion in the bulk GeO_2 glass as $\lambda_0 = 1.73-1.74$ μm, depending on the thermal history of the samples (compared to 1.27 μm in silica glass). A very close result for λ_0 was received by Fleming [5].

Manuscript received November 1, 2004. This work was supported in part by the Moscow Government under Grant 1.1.16 (2004).

The authors are with the Fiber Optics Research Center (FORC), A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow 119991, Russia (e-mail: dianov@fo.gpi.ru; vmm@fo.gpi.ru).

Digital Object Identifier 10.1109/JLT.2005.855867

TABLE I
PROPERTIES OF GERMANIA AND SILICA GLASSES

Property	GeO_2	SiO_2	Ref
Single bond strength, kcal/mol	108	106	9
Melting point (of crystals), °C	1116	1723	9
Heat of fusion, kcal/mol	10	2.1	9
Glass-transition temperature, °C	650-513	1127	10,11
Viscosity at 2000°C, Pa·s	~25	$\sim10^4$	9
Viscosity at 1250°C, Pa·s	$\sim10^6$	$\sim10^{11}$	9
Longitudinal sound speed v_L, m/s	3752	5960	3, 6
Transverse sound speed v_T, m/s	2269	3730	3, 6
Photoelastic constant p_{11}	0.130	0.121	3, 12
Photoelastic constant p_{12}	0.288	0.270	3, 12
Optical stress coefficient B, $10^{-12}Pa^{-1}$	7.5	3.45	6
Young's modulus E, GPa	45.5	74	3, 6
Shear module G, GPa	18.8	32	3, 6
Poisson's ratio	0.212	0.17	3, 6
Rayleigh coefficient a_{RS}, $\mu m^4 \times$ dB/km	2.6	0.7	3
Refractive index at 589 nm, n_d	1.605	1.4585	13
Wavelength of zero material dispersion λ_0, µm	1.74	1.27	3, 5
Density ρ, g/cm^3	3.65	2.202	3, 6
Thermal expansion coefficient, $10^{-7}K^{-1}$	77	5	13
Speed of solution in water at 80°C, µm/hour	60		6

Rayleigh scattering loss, elastic, and photoelastic properties of GeO_2 glass were determined from the Mandelstam–Brillouin scattering spectrum with an excitation wavelength of 514.5 nm. This spectrum was calibrated on the spectrum of fused silica. Results obtained are summarized in Table I. Note that almost the same elastic parameters were obtained in [6]. Scattering loss in germania-glass samples was additionally compared with the scattering in fused silica at two wavelengths (1064 and 532 nm). In both glasses, λ^{-4} dependence was observed that confirms the Rayleigh character of the scattering in bulk germania glass, with an intensity of about 3.8 times higher than that in silica glass.

The amount of optical absorption in the ultraviolet (UV) and IR spectral ranges measured and its extrapolation to the low absorption range are shown in Fig. 1. The fundamental Ge–OH absorption band was measured at 2.85 μm. Adding of absorption and scattering predicts a minimum loss value of about 0.22 dB/km at $\lambda \sim 2$ μm and of 0.4 dB/km at $\lambda_0 \approx 1.74$ μm (Fig. 1).

Among the main glass-forming oxides (SiO_2, GeO_2, B_2O_3, and P_2O_5), GeO_2 glass has the highest peak value of the Raman-scattering cross section (9.2 times higher than in silica glass at a frequency shift of 420 cm^{-1}) that allows the development of highly efficient Raman fiber lasers (RFLs) and amplifiers tunable in a wide spectral range [7].

Potentially high nonlinearity of germania-glass fibers (n_2 should be about three times higher than that in SiO_2 as it follows from its dependence on germania concentration in germanosilicate glass [8]) makes them a promising medium for light frequency conversion by the four-photon process.

Besides, the high photorefractive effect (refractive index change under UV irradiation) can be predicted in germania-based optical fibers because photosensitivity of germanosilicate fibers increases with an increase in GeO_2 concentration. This can be connected with, potentially, a larger concentration of photoactive germanium oxygen-deficient centers (GODCs) and with a more transforming network in germania glass, as compared with the germanosilicate one. The higher is the photorefractivity, the easier the refractive index gratings can be written in fibers, i.e., with a low UV dose and without hydrogen loading.

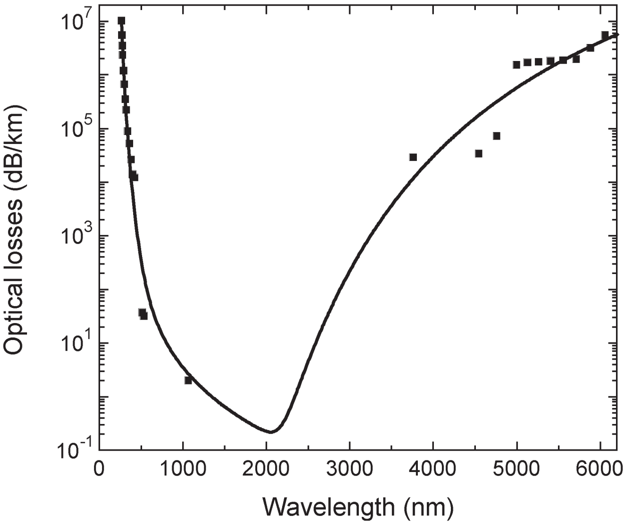


Fig. 1. Estimation of intrinsic optical losses from the data measured (shown by symbols) on bulk GeO_2 glass. Extrapolation of UV and IR absorption tails was made by exponential functions of λ^{-1} and of scattering by λ^{-4} function.

III. GeO_2-BASED FIBER DEVELOPMENT

A. OVD

Maurer and Schultz [1] described in detail the multistage outside vapor deposition (OVD) technique combined with the drilling of auxiliary rods and the polishing of the preform's surfaces. Optical losses approaching the level of about 6 dB/km at an 800-nm wavelength were obtained in the fiber with pure germania core and $63GeO_2-37SiO_2$ cladding (core diameter was 68 μm and outer diameter was 142 μm). The losses in such fibers are determined by the Rayleigh scattering corresponding to a level of bulk germania and by OH absorption corresponding to a concentration of $\sim$ 100 ppm. This result was claimed only in [1] and was not repeated by other researches.

B. Rod-in-Tube

One of the possibilities to escape high mismatching in thermal expansion between the germania-glass core and the cladding is to use cladding material with a large thermal expansion. In [14], pure germania-glass core was inserted into a drilled $P_2O_5-SiO_2$ tube (both made by the vapor-phase axial deposition (VAD) method), and after that, this composed rod was inserted once more into a $P_2O_5-SiO_2$ or Pyrex tube. As a result, the fiber with a high index difference and a small core diameter suitable for low-threshold Raman generation was made. However, losses reported were about 400 dB/km at

1.06 μm, seemingly because of many mechanical operations that can hardly be made adequately clean.

C. VAD

Systematic work in germania-based fiber fabrication was carried out in Japan (Furukawa Electric Company [15] and Nippon Telegraph and Telephone Corporation (NTT) [16]) using the VAD method. They developed multimode fibers with a large core diameter and a low index difference (both core and cladding are GeO_2-based with a low level of dopants, such as Sb_2O_3, SiO_2, or F). Even though a level of Rayleigh scattering was achieved in the short-wavelength spectral range ($\sim$ 12 dB/km at 0.85 μm) [16], absolute-minimum loss value obtained was 4 dB/km at 2 μm [15]. A serious problem for the fibers fabricated by this technology consists of OH-groups contamination (OH concentration of the order of 1 ppm gives an absorption band of $\sim$ 500 dB/km at 2.3 μm) and, possibly, in strong structural and mechanical degradation of the fibers exposed to atmospheric humidity.

D. Polymer Cladding [17]

The authors of [17] performed one of the simplest techniques in order to study the role of the core–cladding interface in scattering losses. As a result, 13 dB/km at 1.1 μm was obtained in the $GeO_2-Sb_2O_3$ core and the silicone-resin cladding fiber instead of 50 (or 20) dB/km in the fiber with the same core and GeO_2 cladding. Such a decrease of loss can be explained by the smoother interface between the core and the polymer cladding. However, this technique is not promising for fabricating fibers for a longer wavelength-spectrum range because of strong absorption peaks in the polymer cladding.

E. MCVD

MCVD fibers with a germania-based core deposited inside a silica glass-substrate tube seem to be more suitable for usage in telecommunication applications, because of the excellent physical properties of silica glass as cladding material and better compatibility with common silica-based fibers. Besides, a large refractive-index difference between the germania-based core and the silica-based cladding and, consequently, a small core diameter allow a decrease in the pump power and an increase in the efficiency of nonlinear effects. However, in the MCVD method, technological problems are also considerable. The fabrication of optical fibers with the germania-based glass core by the MCVD method using silica-glass substrate tubes is very much complicated by a large difference in thermal-expansion coefficients and by the temperature dependencies of viscosity of these glasses. For example, the viscosity of GeO_2 glass at the temperature of fiber drawing of $\sim 2000\ ^\circ$C is ~ 25 Pa $\cdot$ s, whereas the viscosity of SiO_2 glass is $\sim 10^4$ Pa $\cdot$ s.

The authors of the only paper on MCVD fibers (germania-based core and silica-based cladding) described the vaporization of the core material and its mixing with cladding glass during the drawing stage and reported on high optical losses (about 100 and 500 dB/km at 1.6 and 2.35 μm, respectively) [18].

IV. MCVD GeO_2-BASED CORE FIBER DEVELOPMENT AT THE FIBER OPTICS RESEARCH CENTER (FORC)

Great scientific and technological experience has been accumulated at the FORC and at the Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, in the development of MCVD single-mode optical fibers with highly mismatched parameters of a core (germanosilicate with up to 30 mol.% GeO_2 and phosphosilicate with up to 10 mol.% P_2O_5) and silica cladding. So, we concluded that the difficulties listed above can be overcome, in order to improve the MCVD technique for the fabrication of germania-glass-based fibers (50–100 mol.% GeO_2 in the core).

The following specific problems needed to be solved in order to obtain fibers of acceptable quality: 1) the mechanical instability of the fiber preform in the preparation process or at the storage stage due to the thermal-expansion-coefficient mismatch between germania-based and silica glasses; 2) the very small temperature range between the nonsintering and the evaporation of deposited core glass; 3) the tendency of the geometry of a central part of the preform to be noncircular because of the viscosity mismatch between germania-based and silica glasses. As a result, optical losses turn out quite high, especially scattering loss.

In order to solve these and other problems, we tried

1) to control the temperature during core glass deposition, collapsing a tube, stretching, and jacketing a preform, the pressure inside a tube, the speed of a torch, the use of an additional torch, and the variation of an oxidizing gas at the glass deposition;
2) to create a gradual change of the thermophysical properties of glass in the preform cross section, namely, to deposit an intermediate germanosilicate layer (GeO_2 concentration from 4 to 30 mol.%) between the cladding and the core;
3) to develop gradient core-refraction-index deposition without a central dip for GeO_2 concentration in the range 50–100 mol.% [19];
4) to vary the buffer cladding composition.

A. Structure of Preforms and Fibers

A series of preforms with variations of the core, intermediate layer, and buffer cladding glass composition was made. The main parameters of the best single-mode fibers made up until now are shown in Table II.

Ge, Si, and P concentrations were measured by X-ray microanalysis method, mainly in multimode fibers drawn from the initial preforms.

Double jacketing of the initial preforms was made to get a preform for single-mode fibers. We drew single-mode fibers with a graphite-heater drawing machine at a temperature of 1905 °C and a speed of 50 m/min. Besides, to estimate the loss and to determine the cutoff wavelengths, fibers from the initial and single-jacketed preforms were drawn with the aid of a drawing machine with an H_2-O_2 torch as a heater.

Fig. 2 shows the refractive-index profile of preform 343 measured by preform analyzer P102 (York Technology) and X-ray microanalyzer INCAEnergy+ (Oxford Instruments) as a typical

TABLE II
GERMANIA-BASED GLASS CORE FIBERS

Preform number	Core composition, mol.%	Cutoff wavelength, µm	Minimum loss (at 1.9-2 µm), dB/km
140	97GeO_2/3SiO_2	1.25	98
311	75GeO_2/25SiO_2	1.4	20
311	75GeO_2/25SiO_2	1.0	20
331	70GeO_2/30SiO_2	1.3	44
337	67GeO_2/33SiO_2	1.38	37
342	70GeO_2/30SiO_2	2.22	20
343	67GeO_2/33SiO_2	1.76	34
401	68GeO_2/32SiO_2	1.63	34
415	51GeO_2/49SiO_2	~ 3	7
421	61GeO_2/39SiO_2	~3	26
444	98GeO_2/2SiO_2	multimode	120
448	54GeO_2/46SiO_2	multimode	5
450	63GeO_2/37SiO_2	multimode	9
452	63GeO_2/37SiO_2	multimode	5

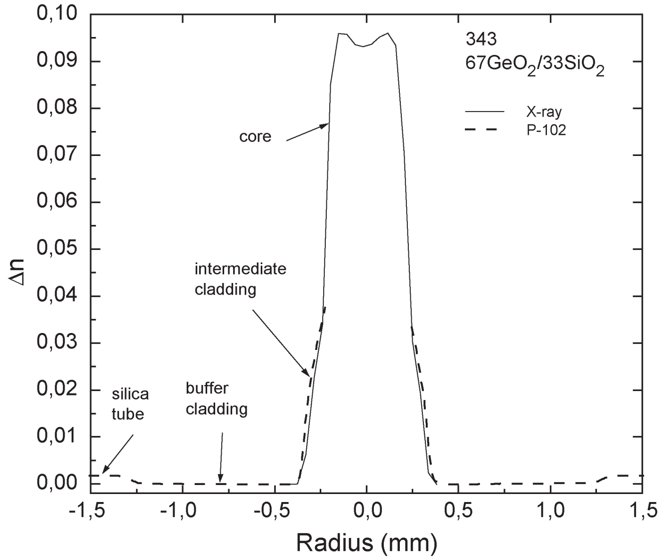


Fig. 2. Typical structure of germania-based glass core preform (343). Solid line—X-ray microanalysis; dashed line—preform analyzer.

example of the structure of a germania-based glass core fiber. The ratio $\Delta n = 0.00146 \times \mathrm{C}_{\mathrm{GeO2}}$ (mol.%) was used to draw this figure. It should be noted that the preform analyzer P102 cannot measure large index differences. Its upper limit turned out to be about 0.06–0.07 for core diameters of $\sim$ 1 mm.

Fig. 3 shows the radial distribution of GeO_2 and SiO_2 in fiber 140, which has the highest concentration, and in fiber 311.

Fig. 4 shows the refractive-index profile of fiber 415. It shows the possibility of creating the gradient profile, even for high levels of germania concentration. In this case, the core-index profile was created by the deposition of ten layers of glass, with a fit by the α-profile giving $\alpha \approx 3$. A characteristic feature of profiles in Figs. 2–4 is the possibility of eliminating the central dip, which can cause excess optical losses [19].

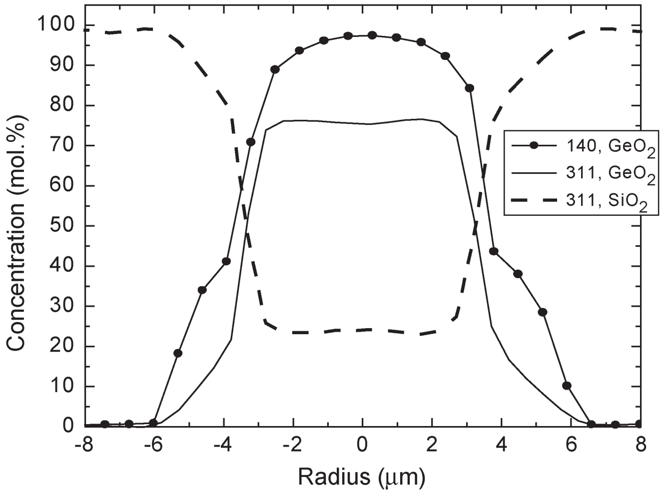


Fig. 3. GeO_2 and SiO_2 concentration profiles measured in multimode fibers 140 and 311.

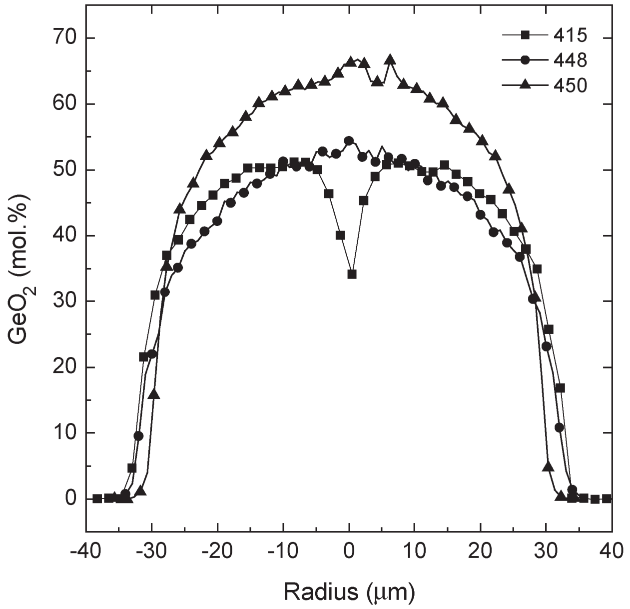


Fig. 4. GeO_2 concentration profile in fibers 415, 448, and 450 with gradient core-refractive index.

B. Optical Losses

A set of optical-loss spectra in these fibers is shown in Fig. 5. The divergence of the curves seems to be too large to be explained quantitatively by the varied technological parameters. However, the similarity of spectra shapes points out the stable regulation and the repeatability of the preform and fiber technology. Fig. 6 shows the best losses in single-mode fibers from three concentration categories (50, 70, and 90 mol.% GeO_2). Low losses for the gradient index samples 448, 450, and 452 shown in Table II were obtained only in multimode fibers (drawn from the initial preforms). There is also the possibility of reaching losses less than 20 dB/km in corresponding single-mode fibers (after jacketing the initial preforms).

In order to study the origin of the optical losses in germania-based fibers, scattering losses were measured at 0.647 and

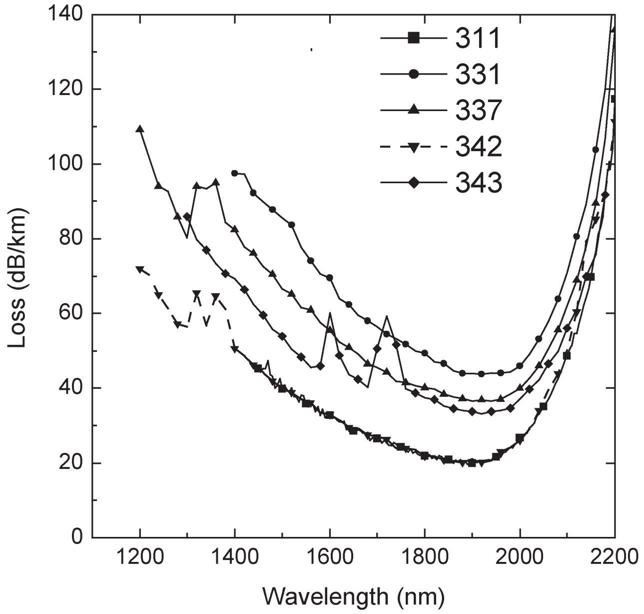


Fig. 5. Loss spectra in a series of germania-based glass single-mode fibers.

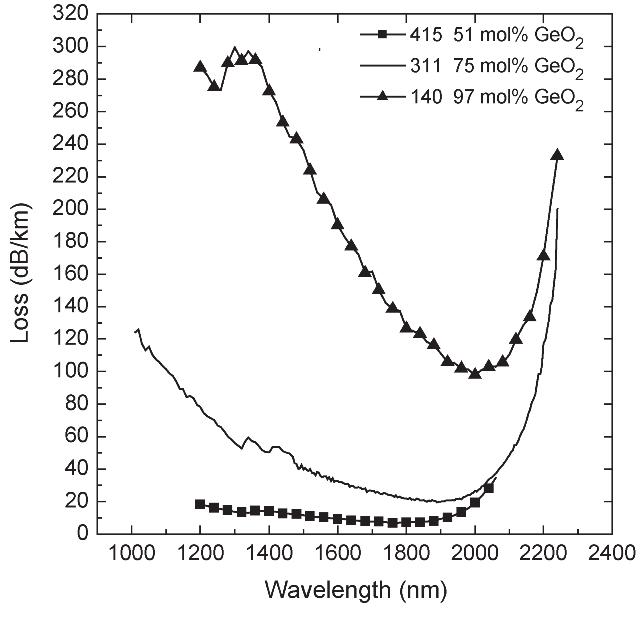


Fig. 6. Loss spectra in single-mode fibers 140 and 311 and in a few-mode fiber 415.

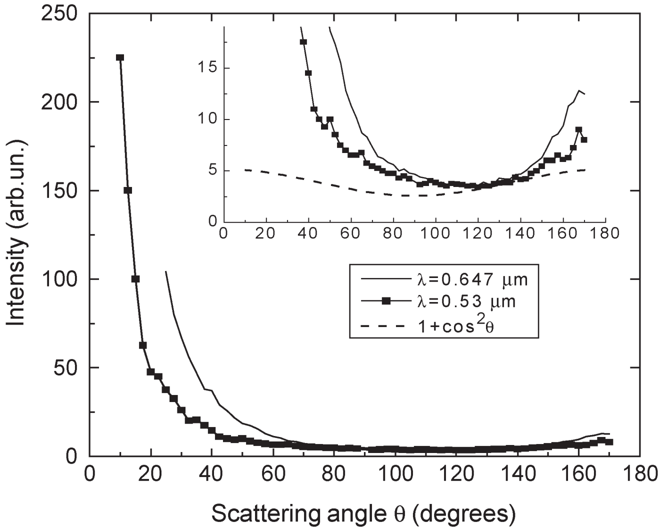


Fig. 7. Scattering indicatrix in multimode fiber A at wavelengths of 0.532 and 0.647 μm. Dashed curve in the inset is a Rayleigh scattering law $I_{\mathrm{sc}} \sim (1 + \cos^2\theta)$.

1.064 μm in multimode and single-mode fibers 140 using an integrating sphere technique. It turned out that the total attenuation was caused almost fully (within the experimental error) by scattering, with the measured scattering loss exceeding Rayleigh scattering in bulk GeO_2 by 10 to 100 times. It was revealed that the angular dependence of scattered light at 0.532 and 0.647 μm (see Fig. 7) has an intense forward-biased component, mainly in the angle range of $\theta < 60^\circ$ ($\theta = 0^\circ$ is a forward direction). This is indicative of the presence of relatively large-scale optical inhomogeneities in the core region. To understand the nature of these inhomogeneities, an additional study should be carried out. Earlier, a large anomalous scattering at small angles was observed in high Ge-doped fibers; see, e.g., [19] and [20].

C. Photorefractive Effect

It is generally considered that the photosensitivity of germanosilicate fibers increases with an increase of GeO_2 concentration. Therefore, a study of the photosensitive properties of GeO_2 glass fibers could provide novel information about photosensitivity mechanisms. We performed a comparative study of the dynamics of Bragg-grating (BG) formation in single-mode fibers 140, 311, and 921 (fiber 921 had a germanosilicate core doped with 24.5 mol.% GeO_2) [21]. The gratings were written in the interferometric scheme by continuous-wave (CW) 244-nm radiation ($I = 25$ W/cm^2, $\lambda_{\mathrm{Br}} \approx 1.55$ μm, $L = 4.5$ mm). The fibers were not hydrogen loaded. All the tested fibers exhibited type-IIa dynamics of the BG formation (Fig. 8). As is seen in Fig. 8(a), the larger the GeO_2 concentration, the higher the index-modulation amplitude Δn_{mod}, and the lower exposure required to saturate the grating. The value of $\Delta n_{\mathrm{mod}} = 2 \times 10^{-3}$ was achieved in fiber 140 at a UV dose of 3 kJ/cm^2 and in fiber 311 at 10 kJ/cm^2, whereas in fiber 921, nonsaturated type-IIa grating with $\Delta n_{\mathrm{mod}} \approx 3 \times 10^{-4}$ was written with a dose of about 200 kJ/cm^2.

Fig. 8 shows a strong GeO_2 concentration dependence of index-change dynamics in fibers 140, 311, and 921. In particular, the ratio of initial rates of type-IIa BG formation for fibers 140, 311, and 921 is approximately 110:50:1, whereas the GeO_2 concentration ratio is 4:3:1 for these fibers, respectively. Note that the electrostriction model of the BG formation also predicts a strong power-law dependence of the phenomenon on GeO_2 content [22].

Even a stronger concentration effect was observed in the dynamics of the mean-index change Δn_{mean} calculated from the Bragg wavelength shift [Fig. 8(b)]. In fiber 921, the value of Δn_{mean} is always positive and decreases only slightly at a high dose, whereas in fibers 140 and 311, Δn_{mean} quickly

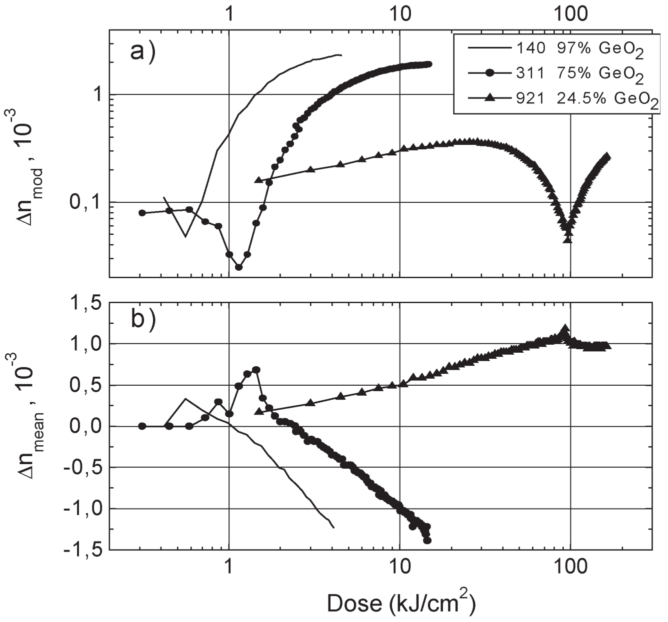


Fig. 8. Index modulation (a) Δn_{mod} and (b) mean index change Δn_{mean} in the BGs written in fibers 140, 311, and 921 versus a dose of 244-nm radiation.

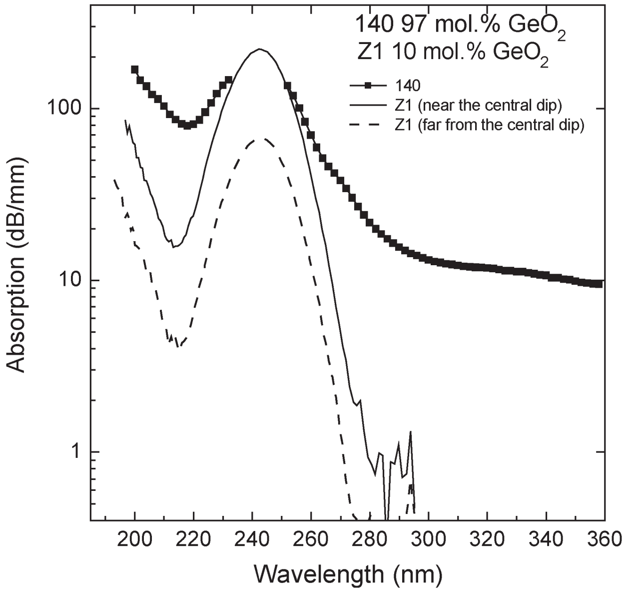


Fig. 9. Ultraviolet absorption spectra in germanate glass core preform 140 (97 mol.% GeO_2) and in multimode MCVD preform Z1 (10 mol.% GeO_2).

becomes negative and reaches a magnitude of -1.5×10^{-3}. To our best knowledge, this is the highest value of a negative mean-index change observed in BGs (see, e.g., [23]). Possibly, this effect is due to the rupture of valence bonds in the core glass, which are under very intense tension stress (of the order of 200 MPa in fiber 140). As a result, the lowering of the mean density of the core glass can decrease the mean refractive index.

There is a common opinion that this photosensitivity is tightly connected with the UV absorption band of GODC at 242 nm (singlet-to-singlet transition); the larger the absorption-band intensity, the higher the photosensitivity. To begin the study of the reason of this phenomenon, we measured the UV spectrum in the core of preform 140 with 97 mol.% GeO_2.

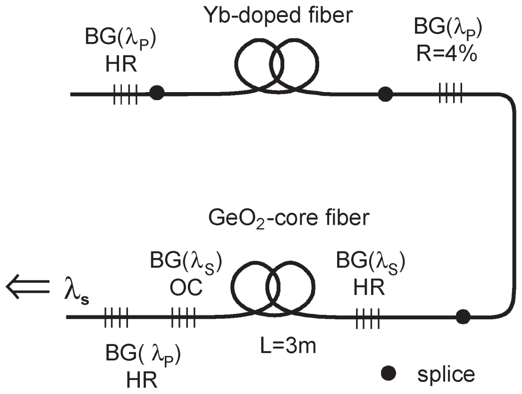


Fig. 10. Scheme of experiments with a 1.07-μm pump. HR—high reflection, OC-output coupler.

This is shown in Fig. 9, together with the spectra of typical multimode MCVD preform Z1 with 10 mol.% GeO_2. Although it was impossible to measure correctly the magnitude of the absorption coefficient at the maximum of the band around 242 nm in the germania-glass sample, it is seen that the intensity of this band is about the same as in the germanosilicate one. At the same time, as compared with the germanosilicate glass, it should be noted that this band in germania glass seems to be wider, and a short-wavelength absorption tail is higher. Besides, the absorption band at 270 nm (attributed to the GODC of another type [24]) and the weak absorption at 330 nm (singlet-to-triplet transition in GODC) are seen.

It is known that germanosilicate glass demonstrates photorefractivity under irradiation with a wavelength of $\sim$ 350 [25], and even $\sim$ 500 nm [26]. A preliminary study of the effect of near UV radiation at about 330 nm on the refractive index in fiber 140 showed that the effects take place, but the value Δn_{ind} of $\sim 10^{-3}$ can be achieved only with a hydrogen loading of fibers [27].

D. Raman Gain and Raman GeO_2-Based Fiber Laser Generation in the Spectral Range of 1.1–2.2 μm

Our fibers demonstrate a rather high loss level, but the high values of Δn and of nonlinearity should result in a high-fiber Raman-gain coefficient (g_0) that can compensate for a high loss level under a sufficiently low pump power. We have developed several schematics of RFL using a GeO_2-based fiber and various pumping sources. As an active Raman fiber, we have used fiber 311 (75 mol.% GeO_2, $\lambda_c = 1.4$ μm). All BGs were written directly in GeO_2-based fiber without hydrogen loading.

In the process of these measurements, a fusion splicing of fiber B (75 mol.% GeO_2 in the core) with the standard germanosilicate fiber (about 6 mol.% GeO_2 in the core) was made. Typical splicing losses were in the range of 0.3–0.8 dB. Thus, our fibers with a germania-based core are quite compatible with low-germania-core silica-based fibers.

1) Pump at 1.07 μm [28]: The scheme of the laser experiment is shown in Fig. 10. As a pump source, the single-mode Yb fiber CW laser with an output wavelength of 1.07 μm was used. Fig. 11 shows a spectrum of the Raman emission

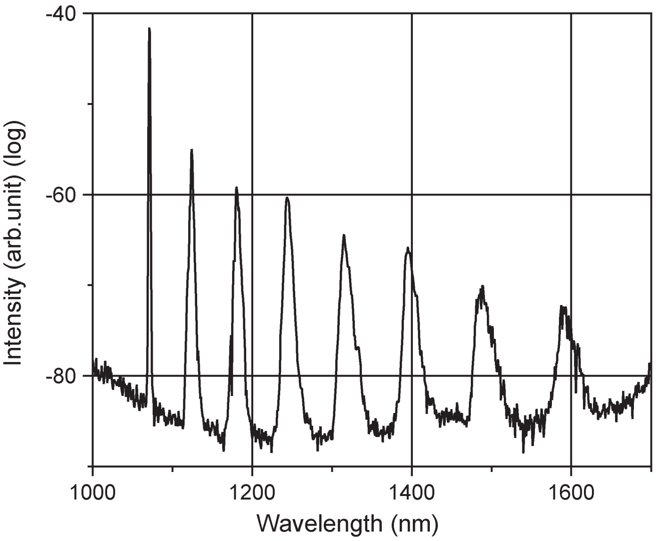


Fig. 11. Spectrum of Raman emission of germania-based fiber pumped by a pulsed Yb fiber laser at 1.07 μm.

in a GeO_2-based fiber (without BGs), when the pump laser at 1.07 μm operates in a pulsed mode (close to its threshold level). Seven Stokes components are clearly seen in the spectrum up to 1.6 μm. Note that the frequency shift of the first Stokes component corresponding to the maximum value of the Raman gain was measured for this fiber to be 427 cm^{-1}. This value is slightly lower than for silica fibers with moderate GeO_2 content (440 cm^{-1}).

The Raman gain of the fiber was measured at $\lambda_s = 1.12$ μm with the cleaved-end face of the fiber as the output coupler. The length of the fiber in this case was 20 m. Raman gain was determined to be $g_0 \approx 300$ dB/(km $\cdot$ W), using the condition of the equality of gain and losses in a cavity at the lasing threshold. This value is at least one order of magnitude higher than the Raman-gain coefficients for Ge-doped silica-core fibers published so far [29].

For a lasing experiment, an almost-optimum scheme of a single-stage RFL with a resonator formed by a pair of BGs (highly reflective (HR) and with $R \approx 50\%$ at $\lambda_s = 1.12$ μm) was developed. The length of the fiber turned out to be only 3 m. The highest output power of the RFL was about 10 W at 13 W of pump power (see Fig. 12) and was restricted only by the threshold of second Stokes lasing in the cavity, formed by end faces of the GeO_2-based fiber and of the Yb-doped fiber. The optical-to-optical efficiency of the RFL was as high as 70%.

2) Pump at 1.47 μm [30]: In a similar way, the Raman gain and the output power of germania-based glass fiber 311 were measured when a two-stage phosphorus-doped RFL at 1.47 μm [31] was used as a pump source (the single-mode Yb fiber laser was used again for pumping P-doped fiber). For the first Stokes at 1.57 μm, g_0 was determined to be 115 ± 5 dB/(km $\cdot$ W). The highest output power of the germania-based RFL (with HR BG at $\lambda_s = 1.57$ μm and the cleaved-end face as a resonator; fiber is 20 m long) was about 3.5 W at the output power of the pump from a P-doped RFL of about 5.6 W.

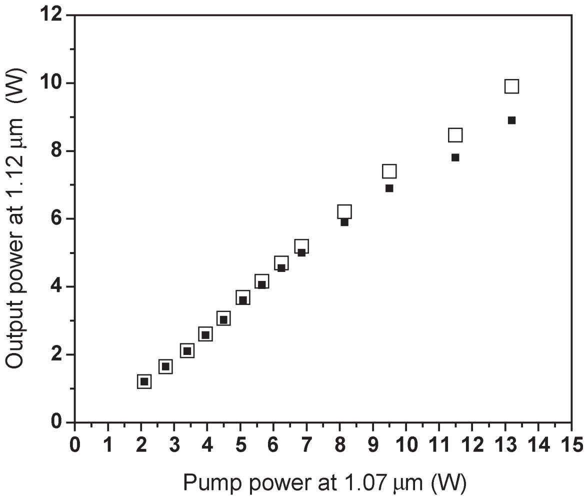


Fig. 12. Output power of the single-stage Raman laser versus output power of the Yb fiber laser. Solid symbols—power running out at the output-end face of the scheme. Open symbols—total power running out at both end faces.

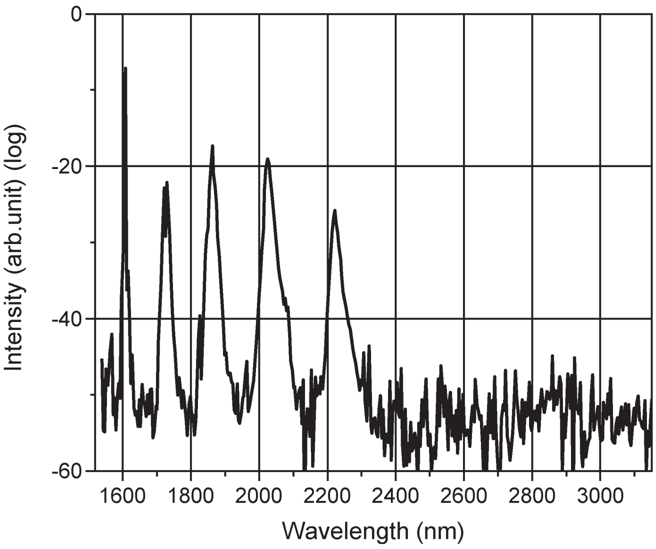


Fig. 13. Spectrum of Raman emission of germania-based fiber pumped by a pulsed Er/Yb fiber laser at 1.608 μm.

3) Pump at 1.6 μm [32]: The spectrum of the Raman emission of germania-based fiber 311 that was pumped by a pulsed Er/Yb fiber laser at 1.608 μm is shown in Fig. 13. In contrast to the 1.07-μm pump, only four Stokes components were obtained, mainly because of a rise of the optical losses with wavelength in this spectral range ($<$ 30 dB/km at 2 μm and 110 dB/km at 2.2 μm). However, a reasonably high Raman-gain coefficient of 59 dB/(km $\cdot$ W) at the pumping wavelength of 1.608 μm was measured (for the first Stokes at 1.725 μm).

Taking into account these values of Raman gain and optical losses, we have developed three- and four-cascaded germania-based RFLs using the CW Er/Yb fiber laser as a pump source. In the case of three-cascaded laser ($\lambda_s = 2.03$ μm), the length of the Raman fiber was 13 m. The output power of 900 mW at a wavelength of 2.03 μm has been obtained at a pump power of 4.2 W.

The output spectrum of the four-cascaded RFL is shown in Fig. 14. The wavelength of the fourth Stokes radiation equal

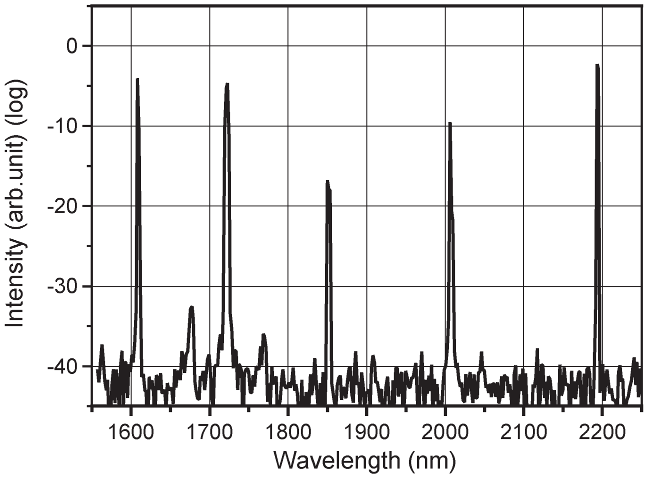


Fig. 14. Output spectrum of 2.2-μm four-cascaded RFL. The fiber length is 8 m.

to 2.2 μm is the longest one that has ever been obtained from an RFL. The output power at this wavelength amounted to 210 mW at a pump power of 4.2 W.

V. CONCLUSION

These results demonstrate the potential of the GeO_2-based fibers as low-loss, highly nonlinear, and photosensitive optical media, in particular, for the creation of efficient Raman lasers in the 2- to 3-μm spectral band. The short lengths, high Δn and low bending loss of such fibers enable one to develop miniature Raman fiber lasers (RFLs).

Further progress in this field will be connected with the study of the nature and a decrease of large scattering in MCVD fibers.

ACKNOWLEDGMENT

The authors would like to thank all of their coauthors for a fruitful cooperation for a long period of time (see the list of references).

REFERENCES

[1] R. D. Maurer and P. C. Schultz, "Germania containing optical waveguide," U.S. Patent 3 884 550, May 20, 1975.

[2] R. Olshansky and G. W. Sherer, "High GeO_2 optical waveguides," presented at the 5th Eur. Conf. Optical Communication (ECOC), Amsterdam, The Netherlands, 1979, Paper 12.5.1.

[3] G. G. Devyatykh, E. M. Dianov, N. S. Karpychev, S. M. Mazavin, V. M. Mashinsky, V. B. Neustruev, A. V. Nikolaichik, A. M. Prokhorov, A. I. Ritus, N. I. Sokolov, and A. S. Yushin, "Material dispersion and Rayleigh scattering in the glassy germanium dioxide—A substance with promising applications in low-loss optical fiber waveguides," *Quantum Electron.*, vol. 10, no. 7, pp. 900–902, 1980.

[4] E. M. Dianov, V. M. Mashinsky, and V. B. Neustruev, "Estimation of ultimate optical losses in glassy germanium dioxide," *Soviet Phys.—Lebedev Institute Reports*, no. 3, pp. 46–49, 1981.

[5] J. W. Fleming, "Dispersion in GeO_2-SiO_2 glasses," *Appl. Opt.*, vol. 23, no. 24, pp. 4486–4493, 1984.

[6] V. N. Polukhin, "Role of germanium dioxide in glass manufacturing and its properties in glassy state," (in Russian), *Fizika i Khimiya Stekla (Glass Phys. Chem.)*, vol. 8, no. 3, pp. 338–342, 1982.

[7] F. L. Galeener, J. C. Mikkelsen, Jr., R. H. Geils, and W. J. Mosby, "The relative Raman cross sections of vitreous SiO_2, GeO_2, B_2O_3 and P_2O_5," *Appl. Phys. Lett.*, vol. 32, no. 1, pp. 34–36, 1978.

[8] A. Boscovich, S. V. Chernikov, J. R. Taylor, L. Gruner-Nielsen, and O. A. Levring, "Direct continuous-wave measurement of n_2 in various types of telecommunication fiber at 1.55 μm," *Opt. Lett.*, vol. 21, no. 24, pp. 1966–1968, 1996.

[9] H. Rawson, *Inorganic Glass-Forming Systems*. New York: Academic, 1967.

[10] I. Avramov, "Viscosity of glassforming melts," *J. Non-Cryst. Solids*, vol. 238, no. 1–2, pp. 6–10, 1998.

[11] R. Bruning and T. Crowell, "A method to determine the kinetics of a supercooled liquid by temperature scanning measurements applied to (Li, Na)acetate and GeO_2," *J. Non-Cryst. Solids*, vol. 248, no. 2–3, pp. 183–193, 1999.

[12] R. W. Dixon, "Photoelestic properties of selected materials and their relevance for application to acoustic light modulators and scanners," *J. Appl. Phys.*, vol. 38, no. 13, pp. 5149–5153, 1967.

[13] O. V. Mazurin, M. V. Streltsina, and T. P. Shvaiko-Shvaikovskaya, *Handbook on Properties of Glasses and Glass-Forming Melts*. Leningrad, Russia: Nauka, 1973.

[14] T. Hosaka, S. Sudo, H. Itoh, and K. Okamoto, "Single-mode fibres with extremely high-Δ and small-dimension pure GeO_2 core for efficient nonlinear optical applications," *Electron. Lett.*, vol. 24, no. 13 pp. 770–771, Jun. 1988.

[15] H. Takahashi and I. Sugimoto, "A germanium-oxide glass optical fiber prepared by a VAD method," *J. Lightw. Technol.*, vol. LT-2, no. 5, pp. 613–616, Oct. 1984.

[16] S. Sakaguchi and S. Todoroki, "Optical properties of GeO_2 glass and optical fibers," *Appl. Opt.*, vol. 36, no. 27, pp. 6809–6814, 1997.

[17] H. Takahashi and I. Sugimoto, "Silicone-resine-clad germanium-oxide glass optical fiber," *Jpn. J. Appl. Phys.*, vol. 22, no. 5, pp. L313–L314, 1983.

[18] A. M. Peder-Gothoni and M. Leppihalme, "GeO_2-core/SiO_2-cladding optical fibers made by MCVD process for stimulated Raman applications," *Appl. Phys.*, vol. B42, no. 1, pp. 45–49, 1987.

[19] M. M. Bubnov, S. L. Semjonov, M. E. Likhachev, E. M. Dianov, V. F. Khopin, M. Y. Salganskii, A. N. Guryanov, J. C. Fajardo, D. V. Kuksenkov, J. Koh, and P. Mazumder, "On the origin of excess loss in highly GeO_2-doped single-mode MCVD fibers," *IEEE Photon. Technol. Lett.*, vol. 16, no. 8, pp. 1870–1872, Aug. 2004.

[20] M. E. Lines, W. A. Reed, D. J. Di Giovanni, and J. R. Hamblin, "Explanation of anomalous loss in high delta singlemode fibres," *Electron. Lett.*, vol. 35, no. 12, pp. 1009–1010, Jun. 1999.

[21] V. M. Mashinsky, O. I. Medvedkov, V. B. Neustruev, V. V. Dvoyrin, S. A. Vasiliev, E. M. Dianov, V. F. Khopin, and A. N. Guryanov, "Germania-glass-core silica-glass-cladding MCVD optical fibres," presented at the Eur. Conf. Optical Communication (ECOC)-ICOC, vol. 2, pp. 210–211, Rimini, Italy, 1999.

[22] E. M. Dianov and V. B. Neustruev, "Photoinduced refractive index subgratings in germanosilicate optical fibers," in *Proc. SPIE*, vol. 4083, *Advances in Fiber Optics*, E. M. Dianov, Ed., 2000, pp. 132–143.

[23] L. Dong, W. F. Liu, and L. Reekie, "Negative-index gratings formed by a 193-nm excimer laser," *Opt. Lett.*, vol. 21, no. 24, pp. 2032–2034, 1996.

[24] B. Poumellec, V. M. Mashinsky, A. N. Trukhin, and P. Guenot, "270 nm absorption and 432 nm luminescence bands in doped silica glasses," *J. Non-Cryst. Solids*, vol. 239, no. 1–3, pp. 84–90, 1998.

[25] E. M. Dianov, D. S. Starodubov, S. A. Vasiliev, A. A. Frolov, and O. I. Medvedkov, "Refractive-index gratings written by near-ultraviolet radiation," *Opt. Lett.*, vol. 22, no. 4, pp. 221–223, 1997.

[26] K. O. Hill, Y. Fujii, D. C. Johnson, and B. S. Kawasaki, "Photosensitivity in optical fiber waveguides: Application to reflection filter fabrication," *Appl. Phys. Lett.*, vol. 32, no. 10, pp. 647–649, 1978.

[27] A. A. Rybaltovsky, E. M. Dianov *et al.*, *Quantum Electronics*, to be published.

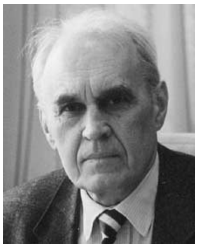
[28] I. A. Bufetov, V. M. Mashinsky, V. B. Neustruev, A. V. Shubin, O. I. Medvedkov, E. M. Dianov, A. N. Guryanov, V. F. Khopin, and M. Y. Salgansky, "Three meter long efficient germania-based core fiber Raman laser," presented at the Conf. Laser and Electo-Optics, San Francisco, CA, May 16–21, 2004, Paper CMD1.

[29] I. A. Bufetov, M. M. Bubnov, V. B. Neustruev, V. M. Mashinsky, A. V. Shubin, M. V. Grekov, A. N. Guryanov, V. F. Khopin, E. M. Dianov, and A. M. Prokhorov, "Raman gain properties of optical fibers with a high Ge-doped silica core and standard optical fibers," *Laser Phys.*, vol. 11, no. 2, pp. 130–133, 2001.

[30] V. M. Mashinsky, V. B. Neustruev, I. A. Bufetov, A. V. Shubin, O. I. Medvedkov, A. E. Rakitin, E. M. Dianov, A. N. Guryanov, V. F. Khopin, and M. Y. Salgansky, "Raman gain properties of germania-based core silica fiber," presented at the Optical Amplifiers and Their Applications, San Francisco, CA, Jun. 27–30, 2004, Paper OWC4.

[31] I. A. Bufetov, M. M. Bubnov, Y. V. Larionov, O. I. Medvedkov, S. A. Vasiliev, M. A. Melkoumov, A. A. Rybaltovsky, S. L. Semjonov, E. M. Dianov, A. N. Gur'yanov, V. F. Khopin, F. Durr, H. G. Limberger, R.-P. Salathe, and M. Zeller, "High efficiency one-and two-cascaded Raman lasers based on phosphosilicate fibers," *Laser Phys.*, vol. 13, no. 8, pp. 234–239, 2003.

[32] E. M. Dianov, I. A. Bufetov, V. M. Mashinsky, V. B. Neustruev, O. I. Medvedkov, A. V. Shubin, M. A. Melkumov, A. N. Gur'yanov, V. F. Khopin, and M. V. Yashkov, "Raman fiber lasers emitting at a wavelength above 2 μm," *Quantum Electron.*, vol. 34, no. 8, pp. 695–697, 2004.



Evgeny M. Dianov (M'97) was born in Tula Region, Russia, on January 31, 1936. He graduated from Moscow State University, Moscow, Russia, in 1960 and received the Ph.D. in 1966 and the Doctor of Science degrees in physics and mathematics in 1977 from the P.N. Lebedev Physical Institute, Russian Academy of Sciences, Moscow.

He has been the Academician of the Russian Academy of Sciences since 1994. He is now the Director of the Fiber Optics Research Center (FORC) at the A.M. Prokhorov General Physics Institute, Russian Academy of Sciences. His main fields of scientific interests are laser physics and fiber and integrated optics.

Prof. Dianov was awarded the State Prize of the Soviet Union in 1974 and the State Prize of Russia in 1998. He is a Fellow of the Optical Society of America.

Valery M. Mashinsky was born in Dushanbe, USSR, on February 14, 1951. He graduated from the Moscow Institute of Physics and Technology, Moscow, Russia, in 1975 and received the Ph.D. degree in physical and quantum electronics from the General Physics Institute, Russian Academy of Sciences, Moscow, in 1985.

He worked as an engineer at the Nuclear Physics Institute, Moscow State University, from 1975 until 1979. In 1979, he joined the Fiber Optics Research Center (FORC), A.M. Prokhorov General Physics Institute, Russian Academy of Sciences. Now, he is a leading research scientist. His research interests are in the study of point defects in germanosilicate glass for fiber optics. Recently, he has been engaged in the development of low-loss germania-based core fibers.