Quantum Electronics **32**(2) 124 – 128 (2002)

OPTICAL FIBRES

PACS numbers: 42.81.Cn; 42.70.Nq
DOI: 10.1070/QE2002v032n02ABEH002142

Peculiarities of the photosensitivity of low-loss phosphosilica fibres

Yu.V.Larionov, A.A.Rybaltovskii, S.L.Semenov, M.M.Bubnov, E.M.Dianov

Abstract. **The peculiarities of the refractive-index change in low-loss heavily P_2O_5-doped silica fibres fabricated by the MCVD method caused by irradiation with UV light are studied. The pre-exposure effect is found in these fibres. The mechanisms of the refractive-index change in phosphosilica and germanosilica fibres are considered and compared in the presence of this effect.**

***Keywords**: Raman converter, phosphosilica fibre, photosensitivity, pre-exposure.*

1. Introduction

Phosphosilica fibres (PSFs) have an advantage over germanosilica fibres (GSFs) for using in Raman converters [1]. However, low-loss PSFs required for efficient Raman converters were fabricated comparatively recently [2], and their properties are not adequately studied so far. One of these properties is the photosensitivity, which is manifested in the refractive-index change Δn_{ind} caused by exposure of fibres to UV radiation and is used for the formation of mirrors based on fibre Bragg gratings.

Recently the effect of an increase in the photosensitivity of fibre and planar waveguides was found, which was observed upon a two-stage exposure [3]. The essence of the effect is that before the main exposure (for example, upon writing refractive-index gratings in the fibre), the fibre is soaked with molecular hydrogen and is irradiated by a homogeneous beam (the exposure dose being relatively low). Then, the remains of molecular hydrogen are removed from the fibre. Upon writing the refractive-index grating, the refractive index increases in the pre-exposed region in the same manner as in the hydrogen-soaked fibre.

Upon exposing hydrogen-soaked fibres to light, the induced losses appear in them along with the induced refractive index [4]. These losses in low-loss PSFs fabricated for the use in Raman converters can be comparable with the main losses. This circumstance can noticeably reduce the efficiency of Raman converters. An important feature of the two-stage process of the refractive-index change is that the induced losses are noticeably lower when the fibre is irradiated by light in the absence of hydrogen [5]. For this reason, the use of two-stage exposure for writing fibre Bragg gratings seems to be most promising.

At present the pre-exposure effect was observed both in GSFs [3] and PSFs fabricated by the method of flash condensation [6]. This effect is especially important for PSFs because refractive-index gratings cannot be written in them if these fibres are not soaked with hydrogen. However, fibres fabricated in Ref. [6] cannot be used in Raman converters. They have high losses ($\sim 500 - 1000$ dB km^{-1}) [7] probably because of a great amount of impurities, and therefore the mechanism of the refraction-index change produced in them can differ from that for fibres with comparatively low losses.

The aim of this paper is to study the photosensitivity of low-loss PSFs fabricated by the MCVD method, to estimate the efficiency of pre-exposure of these fibres and to reveal the features of the pre-exposure compared to this effect in low-loss GSFs.

2. Experimental

The photosensitivity of PSFs is observed upon their irradiation at a wavelength of 193 nm, only when the fibre is soaked with hydrogen [8]. For this reason, we used in our experiments a Lumonics-500 193-nm ArF excimer laser to produce the refractive-index increase in PSFs, which were preliminary soaked with hydrogen at a pressure of 10 MPa at 100 °C for no less that 12 hours. The fibres were irradiated by 300-mJ cm^{-2} pulses with a pulse repetition rate of 10 Hz. The required radiation power was produced in the diverging beam behind a cylindrical lens with the focal distance $\sim$ 100 mm where the fibre was placed. The energy density was estimated from the radiation power in the laser pulse, which was measured behind the lens with an IMO-2H power meter, and from the laser-beam cross section at a certain distance from the lens. GSFs were prepared and irradiated similarly.

We produced the refractive-index increase in the initial and hydrogen-soaked GSFs using an EMG103 Lambda Physik 248-nm KrF excimer laser. The fibres were irradiated by 300-mJ cm^{-2} laser pulses with a pulse repetition rate of 10 Hz.

The refractive-index increase was estimated using a Mach – Zehnder interferometer (hereafter, the interferometer) that was formed by two long-period gratings in the fibre under study [9]. The first of the interferometer

---

Yu.V.Larionov, A.A.Rybaltovskii, S.L.Semenov, M.M.Bubnov, E.M.Dianov Fiber Optics Research Center, General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia

Received 30 November 2001
Kvantovaya Elektronika **32** (2) 124 – 128 (2002)
Translated by M.N.Sapozhnikov

gratings excited the cladding mode, which propagated together with the fundamental mode to the second long-period grating. The two modes interfered after propagation through the second grating. Upon producing the refractive-index increase in the fibre core, the path difference was created in the interferometer arms, resulting in the displacement of the interference pattern. For this reason, to determine the induced refractive index Δn_{ind}, we irradiated the part of the fibre between the interferometer gratings by a homogeneous laser beam and calculated the refractive index induced in the fibre core by the change in the interference pattern. The sensitivity of this method is higher than that of the method based on the reflection of light from a test Bragg grating, and the results are independent of the degree of coherence of the laser and the contrast of the interference pattern produced by a phase mask.

We studied the photosensitivity of experimental PSF samples fabricated by the MCVD method, which contained 12 % of P_2O_5 ($\Delta n \sim 0.01$) and had losses $\sim$ 1dB km^{-1}. As GSF samples, we used an analogue of the SMF28 standard fibre (hereafter, ASMF28) containing 3 % of GeO_2.

To test the pre-exposure effect and its reproducibility in PSFs, we created two identical interferometers. The distance between long-period gratings in each of the interferometers was divided into several intervals of length $\sim$ 6 mm, each of these intervals being pre-exposed using the radiation dose lying in the interval from 0.18 to 4.3 kJ cm^{-2}. To compare the results, a similar interferometer was created in GSFs.

3. Experimental results

Fig. 1a shows the dose dependences of the induced refractive index in several interferometer parts for a PSF. Curve (*1*) was obtained at the first stage of the exposure of the hydrogen-soaked fibre, while curves (*2*) and (*3*) were obtained at the second stage when hydrogen was removed from the sample. The fibre parts, for which curves (*2*) and (*3*) were obtained, were pre-exposed at the first stage using different radiation doses. One can see that the type of dose dependences at two exposure stages is qualitatively different: the dose dependence at the second exposure stage has no a threshold (an increase in the curve slope with increasing dose), which is typical for phosphorous-doped fibres [10]. For comparison, Fig. 1b shows the dose dependence obtained for the ASMF28 fibre exposed to light in the absence of hydrogen (curve *1*), for the hydrogen-soaked fibre (curve *3*), and after pre-exposure of the fibre with a dose of 1.06 kJ cm^{-2} (2). One can see that the dependence for the GSF is of the same type for these exposures and is similar to the dose dependence for the pre-exposed part of the PSF.

Fig. 1a also shows that the value Δn_{ind} of the induced refractive index noticeably depends on the PSF pre-exposure dose. We measured the dependences of Δn_{ind} on the pre-exposure dose D_{pe} and its reproducibility in two interferometers in the PSF. For comparison, similar measurements were performed for the interferometer in the ASMF28 fibre, which was irradiated at 248 nm. The results of these experiments are presented in Fig. 2. The exposure dose at the second stage for any fibres was 2 kJ cm^{-2}.

Curves (*1*) and (*2*) in Fig. 2 obtained for the PSF pre-exposed to light at 193 nm exhibit maxima at the dose 1.5–3.2 kJ cm^{-2}. No maximum of the dependence $\Delta n_{\text{ind}}(D_{\text{pe}})$ was observed for the GSF irradiated at 248 nm (curve *3*).

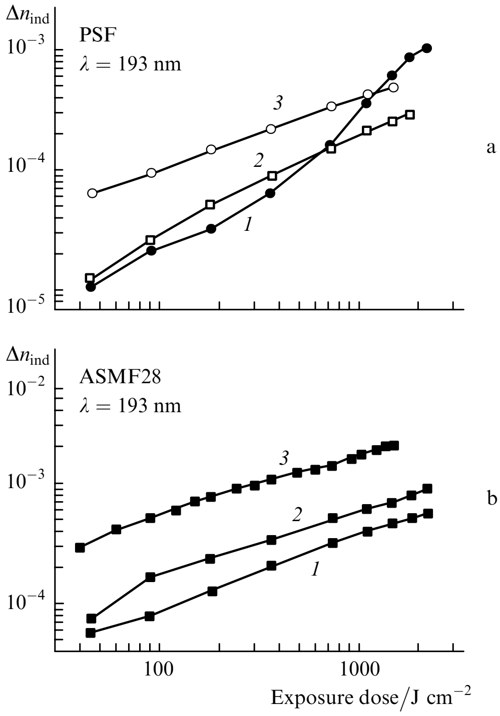

Figure 1. Dependences of the induced refractive index on the exposure dose in (a) the PSF for the first (*1*) and second (*2*, *3*) exposure stages for pre-exposure doses equal to 1.06 (*2*) and 4.32 kJ cm^{-2} (*3*) and (b) the ASMF28 fibre for the initial fibre (*1*), the second exposure stage (*2*, the pre-exposure dose is 1.06 KJ cm^{-2}) and the first exposure stage (*3*).

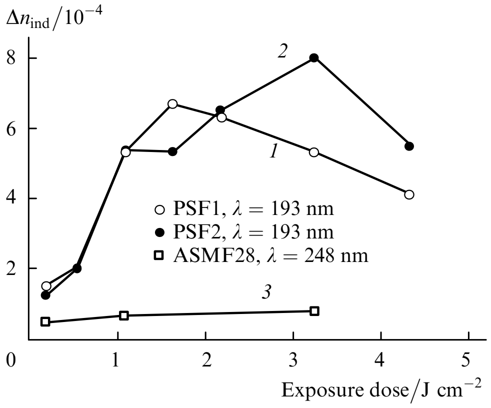

Figure 2. Dependences of the induced refractive index for two PSFs and the ASMF28 fibre.

The accuracy of the measurements presented in Figs 1 and 2 is determined by the errors in the choice of the exposure conditions and by the errors in the measurement of the phase shift in the interferometer. The error in the choice of the exposure conditions appears two times in the error of the estimate of the dose dependence of pre-exposed fibres. The total error of measurements can be estimated from the repeated exposure of the sample under the same conditions. The maximum total error in the estimate of the induced refractive index was observed at low exposure doses and did not exceed 20 %. The value of the total error in the measurement of the induced refractive index in pre-exposed fibres is demonstrated by the difference in curves (*1*) and (*2*) in Fig. 2. One can see that the error in the measurement of the curve maximum is $\sim 10^{-4}$, while the error in the measurement of the dose at which the maximum is achieved is ~ 1.5 kJ cm^{-2}.

4. Discussion of results

The experimental results presented above confirm the existence of the pre-exposure effect in low-loss PSFs.

The maximum of the function $\Delta n_{\rm ind}(D_{\rm pe})$ that we observed for the PSF (Fig. 2) was earlier detected for GSFs [6]. A similar behaviour of this function for fibres made of different materials suggests that photochemical reactions proceeding in them are also similar. Therefore, the analysis of photochemical reactions in the glass network of germanosilica fibres, which are studied now in more detail, can be used for the study of the pre-exposure mechanism in PSFs.

The presence of the maximum of the function $\Delta n_{\rm ind}(D_{\rm pe})$ can be explained in terms of chemical kinetics by the two-stage photochemical reaction between three chemical compounds (components): initial (A), intermediate (B), and final (C) [10].

The initial increase in the concentration of the component B occurs due to the destruction of the component A irradiated by light in the presence of molecular hydrogen. The maximum of the function $\Delta n_{\rm ind}(D_{\rm pe})$ can be explained by the exhaustion of the component A (resulting in the cessation of the growth of the component B) when the component B is transformed to C. The further transformation (consumption) of the component B to the resulting component C determines a decrease of the component B. This explanation was proposed in Ref. [6].

The dynamics of variation in the concentration of the component C can be determined in experiments from the values of the induced refractive index, while the dynamics of variation of the component B can be determined from the function $\Delta n_{\rm ind}(D_{\rm pe})$. Indeed, in the absence of hydrogen in the fibre, no transformation of the component A to the component B occurs, and the initial increase in the concentration of the component C is determined only by the accumulated concentration of the component B. This mechanism cannot explain the absence of a maximum of the function $\Delta n_{\rm ind}(D_{\rm pe})$ for the ASMF28 fibre irradiated at 248 nm.

It is reasonable to assume that at the first stage of exposure of PSFs and GSFs, hydrogen is incorporated into the glass network under the action of UV light, while at the second stage, the modification of a component formed during the first stage occurs, already without molecular hydrogen.

The photoinduced increase of the refraction index in fibres is caused by defects produced in the glass structure. The growth kinetics of the defect concentration ΔN in glasses is described by the expression $\Delta N \propto CD^f$, where D is the exposure dose; and C and f are empirical constants ($f < 1$) [12]. Therefore, the logarithmic dose dependences of the induced refractive index are, as a rule, linear. The increase in the refractive index of the PSF at the second stage and of the GSF at the first and second exposure stages (curve *2* in Fig. 1a and curves 1–3 in Fig. 2b) corresponds to this dependence. The threshold type of the increase in the refractive index of the PSF at the first exposure stage (curve *1* in Fig. 1a) clearly demonstrates that this process is more complicated and is determined at least by two successive stages with different values of f. The change in the refractive index correlates with an increase in the absorption band at 3.05 μm caused by the increase in the number of OH groups bound with phosphorous [11], but this change is not observed for pre-exposed samples. Therefore, we can assume that this change is determined by the dynamics of incorporation of hydrogen into the PSF network.

The pre-exposure effect has not been explained so far at the level of structural transformations even for GSFs; however, we can make some assumptions concerning the mechanism of this effect. It seems that the dependence of photochemical reactions on the exposure dose plays a key role in the mechanism of the pre-exposure effect in fibres of both types. Not only a superposition of mechanisms of the change in the refractive index takes place, whose relative contributions depend on the exposure [13], but also the conditions are produced at the given exposure stage which are required for a subsequent increase in the refractive index.

We can assume that colour centres in the glass network play a key role in a sequence of photochemical reactions. At the first stage of the exposure, the state of colour centres existing in the glass is change or new colour centres are formed during photochemical or thermal chemical reactions accompanied by the incorporation of hydrogen into the glass network. As a result, the absorption and luminescence spectra of colour centres and the concentration of paramagnetic defects are changed. The concentration of the intermediate component B becomes maximal at the end of this stage.

It was shown in many studies that the state of the colour centres existing in initial GSFs and hydrogen-soaked GSFs changed and new colours centres appeared at the exposure doses $\sim 10 - 100$ J cm^{-2}. Thus, the integrated intensity of the absorption bands of GOHC(1), GOHC(2), GeE′, Ge(1), and Ge(2) fibres cease to change noticeably already for the irradiation dose ~ 20 J cm^{-2}, resulting in the establishment of the dynamic equilibrium between these defects [13]. According to the data reported in Ref. [14], the intensity of the 3.3-eV and 4.4-eV luminescence bands excited with a Xe lamp at 5.2 eV was saturated at the radiation dose ~ 30 J cm^{-2}, and the total spin concentration of the GEC and GeE′ defects excited by pulses from a KrF laser was also saturated at the radiation dose ~ 30 J cm^{-2} [14].

According to the data of Ref. [15], the luminescence intensity of the GSF without hydrogen excited by the second harmonic of an argon laser at 244 nm saturates at the dose 100–200 J cm^{-2}. The maximum of blue luminescence (400 nm) of the hydrogen-soaked fibre was achieved at the dose ~ 30 J cm^{-2} [16]. The maximum of the function $\Delta n(D_{\rm pe})$ for the GSF was observed for the radiation dose 60 J cm^{-2} upon irradiation at 244 nm and for the dose 120 J cm^{-2} upon irradiation at 193 nm, which corresponds approximately to the dose at which the state of colour centres in the GSF is stabilised.

At these radiation doses, the refractive index of the GSF begins to increase. We assume that after the transformation of colour centres at the first stage of the exposure, the second stage begins, namely, the structural modification of the glass network involving modified colour centres. In this process, the involvement of molecular hydrogen is no longer required. During the second stage of the exposure, the modified colour centres are comparatively slowly destroyed (to the dose ~ 10 kJ cm^{-2}) and the concentration of GeE′ centres responsible for the structural transformation of the glass network monotonically increases [14]. After the destruction of a greater part of the colour centres, the dose dependence of the induced refractive index saturates. Therefore, the initial colour centres serve as a 'triggering mechanism' for a comparatively slowly process of the refractive-index increase.

Taking into account that the maximum of the function $\Delta n_{\rm ind}(D_{\rm pe})$ for the PSF is much greater than that for the GSF, we can assume that greater radiation doses are required to modify defects in the PSF (Fig. 2). This is confirmed by the dose dependences of the concentration of paramagnetic phosphorous oxygen–hole centres (POHCs) for the initial phosphorous sample without hydrogen (Fig. 3). One can see that the concentration saturates for the dose ~ 1 kJ cm^{-2}. For comparison, the concentration of paramagnetic defects in germanosilica glass (GeE′ + GEC) was stabilised at the dose ~ 30 J cm^{-2} [14].

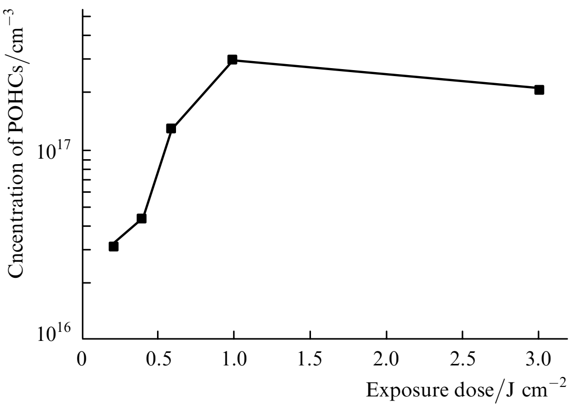

Figure 3. Dependence of the concentration of phosphorous oxygen-hole centres (POHCs) on the exposure dose.

Fig. 4 shows the dose dependences of the induced losses in a phosphosilicate hydrogen-soaked sample obtained upon irradiation at different wavelengths. One can see that the maximum (or stabilisation) of induced losses is achieved for the dose ~ 1 kJ cm^{-2} in a broad wavelength range. The absorption bands of GOHC(1) and GOHC(2) fibres are stabilised and the absorption bands of Ge(1) and Ge(2) fibres increase at the irradiation dose $\sim 10-20$ J cm^{-2} [13].

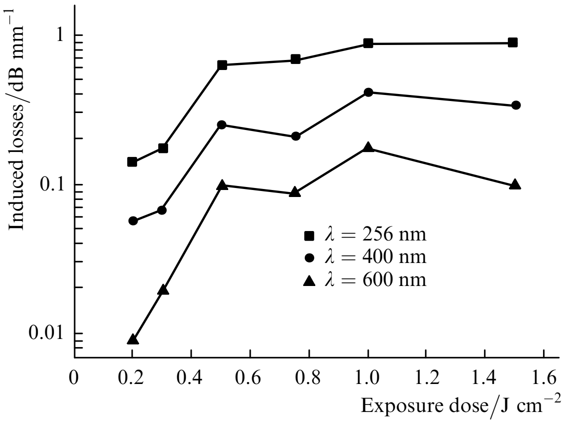

Figure 4. Dependences of induced losses in the PSF on the dose of irradiation at 600, 400, and 256 nm.

The threshold dose dependence of the refractive-index increase in the PSF (in contrast to this dependence in the GSF) observed in experiments clearly demonstrates the evolution of mechanisms of photochemical reactions and can be explained by the fact that a greater dose is required for the transformation of colour centres in this fibre than in the GSF. This is confirmed by approximately equal doses of the PSF exposure corresponding to the end of the first stage of the exposure (~ 1 kJ cm^{-2}, Figs 3 and 4) and to the break (the increase in the growth) in curve (*1*) in Fig. 1a (~ 0.8 kJ cm^{-2}). It seems that such process proceeds in the GSF at low exposure doses and cannot be detected experimentally. The absence of a threshold at the second stage of the refractive-index increase in the PSF after the removal of hydrogen indicates to the absence of reactions that would modify colour centres.

The above assumptions about the mechanism of the pre-exposure effect can explain the two-stage nature of the photoinduced refractive-index increase, as well as the refractive-index increase observed after the termination of the modification of colour centres during the exposure. However, they cannot explain the monotonic dependence on the pre-exposure dose, which was observed for the ASMF28 fibre irradiated at 248 nm. We can assume that this dependence is determined not by the destruction of colour centres produced at the first stage but by a continuous change in the glass structure during irradiation at the second stage. In this case, at the first stage, only the conditions for the proceeding of photochemical reaction at the second stage are created. The model describing such processes was proposed in Ref. [16].

The photoinduced refractive-index increase in the GSF was explained in Ref. 16] by two-photon processes resulting in the appearance of germanium electron centres (GECs) and self-trapped hole (STH) defects. The GEC centres are transformed to GeE′ centres due to thermal relaxation with the subsequent rearrangement of the local structure of glass and an increase in the refractive index. In this case, the STH defect, which is a hole localised at one of the sites of oxygen atoms, recombines with a nearest electron centre, so that this site becomes again a trap for holes. This cycle is repeated for the next two-photon process of creation of GEC and STH centres.

It was pointed out in Ref. [16] that the Ge^{2+} defects favouring the reconstruction of hole traps from STHs can play an important role in this cyclic process. Thus, if Ge^{2+} defects are created at the first stage in the presence of hydrogen, at the second stage after the hydrogen removal, these defects can favour the development of a cyclic process caused by the two-photon absorption of light. This is confirmed by the results of paper [17] in which the induced refractive index of a standard SMF28 telecommunication fibre irradiated by a KrF laser was studied as a function of the laser power density at fixed irradiation doses. An increase in the laser power density under these conditions resulted in the refractive-index increase, confirming the presence of a two-photon process. The existence of two-photon processes in low-doped SMF28 germanosilica fibres in the absence of hydrogen (in contrast to heavily doped fibres) was confirmed experimentally, although for fibres that have not been pre-exposed to light [18].

5. Conclusions

We have found the pre-exposure effect in low-loss PSFs fabricated by the MCVD method. The following features of the mechanism of a photoinduced increase in the refractive index in these fibres were revealed:

(i) The dependence of the induced refractive index on the pre-exposure dose has a maximum, which is similar to that observed for GSFs. This indicates to a two-stage process of the photoinduced refractive-index increase, in which three chemical components are involved, similarly to the situation that takes place in the hydrogen-soaked GSF. The maximum efficiency of the refractive-index increase in the two-stage process is achieved for the pre-exposure dose ~ 2 kJ cm^{-2}.

(ii) The irradiation dose of the PSF, at which a change in the state of point defects is terminated, corresponds to the dose at which the first exposure stage is completed and the concentration of the intermediate component B reaches a maximum. We found this correspondence in the literature for GSFs as well. It seems that the evolution of the states of various point defects during the exposure determines a change in the stages of the photoinduced refractive-index increase and is common for various materials.

(iii) The absence of a maximum for the dependence of the induced refractive index on the pre-exposure dose for the GSF (Fig. 2) can be explained by a cyclic photochemical reaction. The principle of this reaction is based on two-photon absorption in the presence of point defects produced at the initial stage of the exposure [16]

Acknowledgements. The authors thank V.M.Mashinskii and A.O.Rybaltovskii for useful discussions of the pre-exposure effect and its possible mechanisms and for valuable comments concerning the text of the paper.

References

1. Dianov E.M., et al. *Electron. Lett.*, **33**, 1542 (1997).
2. Dianov E.M., et al. *Techn. Digest OFC'99* (Stuart, Florida, 1999, PD25-1 – PD25-3).
3. Dyer P., Farley R., Giedl R., Byron K. *Electron. Lett.*, **30**, 1133 (1994).
4. Semenov S., Rybaltovsky A., Larionov Y., Bubnov M., Dianov E. *Techn. Digest Bragg Gratings, Photo-sensitivity, and Poling in Glass Waveguides Conf.* (Stuart, Florida, 1999, ThE8-1).
5. Canning J., Hu P-F. *Techn. Digest Bragg Gratings, Photosensitivity, and Poling in Glass Waveguides Conf.* (Stressa, Italy, 2001, BThA6-1).
6. Canning J. *Opt. Fiber Technol.*, **6**, 275 (2000).
7. Carter A.L.G., Sceats M.G., Poole S.B., Hanna J.V. *Techn. Digest OFC'94* (San Hose, California, 1994, TuB3).
8. Malo B., et al. *Appl. Phys. Lett.*, **65**, 394 (1994).
9. Dianov E.M., Vasil'ev S.A., Medvedkov O.I., Frolov A.A. *Kvantovaya Elektron.*, **24**, 805 (1997) [*Quantum Electron.*, **27**, 785 (1997)].
10. Denisov E.T., Sakisov O.M., Likhtenshtein G.I. *Khimicheskaya kinetika* (Chemical Kinetics) (Moscow: Khimiya, 2000).
11. Rybaltovsky A., Larionov Y., Semenov S., Plotnichenko V., Krukova E., Pyrkov Y., Bubnov M., Dianov E. *Techn. Digest Bragg Gratings, Photosensitivity, and Poling in Glass Waveguides Conf.* (Stresa, Italy, 2001, BthA3-1).
12. Griscom D.L., Gingerich M.E., Friebele E.J. *Phys. Rev. Lett.*, **71**, 1019 (1993).
13. Dianov E., Neustruev V. *Proc. SPIE Int. Soc. Opt. Eng.*, **4083**, 132 (2000).
14. Nishii J. In *Lecture Proc. of Euro-Summer School on Photosensitivity in Optical Waveguards and Glasses(POWAG)* (Universite de Paris Sude, France, 2000).
15. Kuswanto H., Goutaland F., Boukenter A., Ouerdane Y. *Techn. Digest Bragg Gratings, Photosensitivity, and Poling in Glass Waveguides Conf.* (Stressa, Italy, 2001, BThc26-1).
16. Essid M., Brebner J.L., Albert J.A., Awazu K. *J. Appl. Phys.*, **84**, 4193 (1998).
17. Poumellec B., et al. *J. Opt. Soc. Amer. B* (to be published).
18. Albert J., Malo B., Hill K.O., et al. *Appl. Phys. Lett.*, **67**, 3529 (1995).