

Borosilicate glass for photonics applications

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Abstract

In this paper, we present the use of three different processing techniques which can be used to manufacture low cost optical waveguides and fibers using commercially available borosilicate glass. The techniques used are rod and tube stacking for photonic crystal fiber fabrication, dual laser ablation processing for planar waveguides, and thermal poling, which could potentially be used for refractive index engineering of planar optical waveguides.

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1. Introduction

Research activities in vitreous materials for applications in photonics often deal with developing new or improved materials with enhanced properties, e.g. providing better stability at high temperatures, increased lifetime, enhanced optical properties compared to the traditional silica glasses, or simply provide a material with similar properties at a lower cost. More recent glass systems that have been studied for different photonics applications include calcogenides, bismuthates and oxyfluorides, to name a few. For optical devices used in photonics two main waveguide platforms are typically used, namely planar samples and optical fibers. Fabrication techniques for planar waveguides range from ion-exchange, ridge, and laser-written waveguides while optical fibers are typically drawn from a glass rod or preform, with dimensions of the order of cm diameter,

to provide optical fibers of typically 125 μm diameter. The drawing is performed under suitable conditions so the fiber maintains the structures and compositional variation of the original preform. A more recent type of optical fiber includes photonic crystal fibers (PCFs), which can be made using a single glass composition. Here the guiding structure is facilitated by the arrangement of arrays of longitudinal holes running along the length of the fiber [1].

In this work, we have chosen to study an old glass system, namely borosilicate glass, and we present three different techniques that provide means for fabricating low cost optical waveguides with this commercially available material. For the first technique, we used stacking and subsequent drawing of borosilicate capillaries and solid rods. This approach provides waveguides in the form of photonic crystal fibers. The second technique for planar waveguide fabrication, is based on direct laser ablation [2], while the third technique is based on the newly discovered ability to locally change the UV-absorption by means of thermal poling [3]. Here modification of the UV-absorption

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provides means to locally engineer the refractive index for fabricating planar waveguide structures.

2. Background

Borosilicate glass (BSG) is a low cost material which is commercially available in large quantities through several vendors (e.g. Schott and Corning) and can be easily tailored with a specific composition [4], including quantum dot composite [5] depending on the intended application [6,7]. Further, these glasses are also suitable materials for an ion-exchange processing. An additional advantage is that the refractive index of BSG is near to that of silica ($n_{\text{BSG}} = 1.473$ while $n_{\text{silica}} = 1.458$ at 587.6 nm), which allows potentially low loss connections between borosilicate and waveguides made of silica, which is the base material used for optical fibers in existing telecommunications networks. Further, borosilicate glasses also present an interesting platform for the development of integrated optical and microwave circuits [8].

2.1. Photonic crystal fibers

Using commercially available borosilicate rods and tubes we show the manufacture of photonic crystal fiber made with the powerful technique of stacking-and-draw [1]. This procedure relies on the fact that a macroscopic version of the fiber microstructure is prepared by manually stacking capillaries and rods. The whole set (the preform) which is typically ~cm-thick can then be drawn straight into fibers or into mm-thick canes. The latter allows one to add an extra glass jacket in order to tune the ratio between the outside diameter of the fiber and the microstructure size before drawing into the fiber. One should note that this procedure is only practical when the capillary tubes are commercially available as preparing homemade tubes is a laborious and time consuming process [9]. Others procedures for preparing PCF preforms include the drilling of holes directly into a solid preform, typically more suitable for polymers [10], or by extrusion [11]. We prepared solid core PCF made of BSG (Duran by Schott), which is the same BSG used in the following sections on waveguide fabrication techniques through laser ablation and thermal poling. Due to the impurities in the bulk material the optical loss of the fiber is high. Without taking any extra precaution during the preparation of the preform and fiber, the optical loss of the fiber was measured to be in the order of 10 dB/m at 1500 nm. While this value prevents their use for many telecommunications applications requiring long lengths, these fibers can provide a low cost alternative for different sensing applications or for devices that usually require less than a meter long structure. The bulk loss of the low quality borosilicate rods used in this work was measured to be around 3 dB/m at 633 nm. We believe this value is smaller at higher wavelengths as the glass looks green when observed in transmission. 3 dB/m is then the minimum theoretical value that could be obtained with a

fiber. Several other aspects, however, can influence the loss to be higher in microstructured optical fibers, e.g. confinement loss and scattering in the air glass interface. While the former can be improved by adding more periods of holes, the latter can be minimized by preparing the fiber in a clean room. In our case the fiber has just two rings of holes and the whole fabrication procedure (drawings, stacking etc.) was not done in a clean environment. We believe that improving both parameters we could decrease the loss toward 3 dB/m.

Fig. 1 shows an SEM image of a two period BSG PCF with an external diameter of 124 μm and a 3.6 μm diameter core. The cladding air filling fraction is high making the mode well confined to the core.

It should be noted that besides being a low cost material, the setup required to draw the fiber, mainly the fiber drawing tower, is simpler when compared to the process required for silica fibers. This is due to the low melting point of BSG: the softening point of Duran is 825 $^{\circ}\text{C}$; for silica it is around 1600 $^{\circ}\text{C}$. In practical terms this means that a fiber drawing tower equipped with a 1000 $^{\circ}\text{C}$ furnace is necessary rather than 2000 $^{\circ}\text{C}$ for silica fibers. In addition to the simplicity and low cost, one can also benefit from the material properties discussed in detail in Section 2.3.

2.2. Waveguides by laser ablation

Laser processing of materials is now well established and recent activities have led to the production of laser processed waveguides using a variety of methods, including direct writing of waveguides into photosensitive planar layers with a UV laser [12], or by the use of femtosecond lasers [13]. Recently we reported a new technique based on direct laser writing on almost any material [14]. Devices, such as

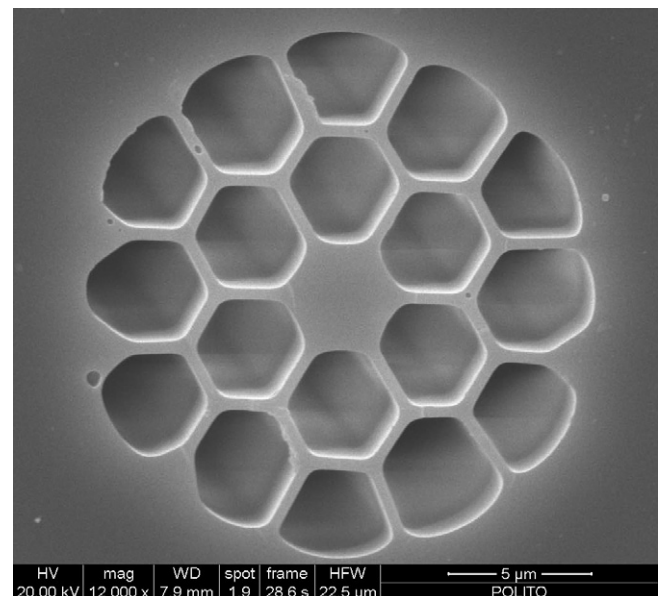


Fig. 1. SEM image of the borosilicate PCF.

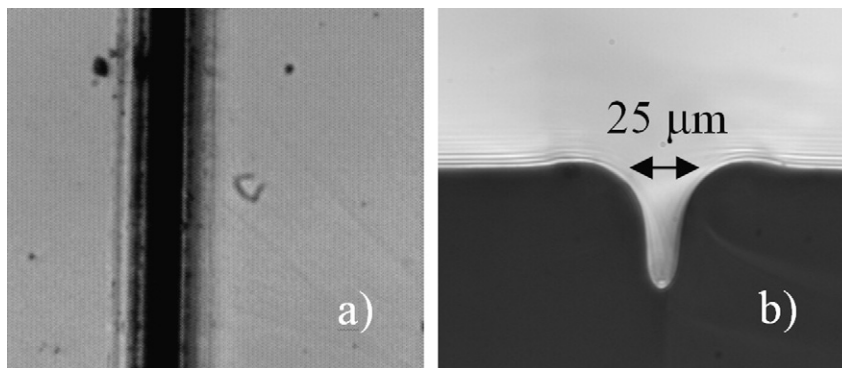


Fig. 2. Microscope image of groove fabricated in borosilicate glass using CO₂-laser ablation; (a) top view, (b) lateral view showing the depth profile of the trench.

low loss single mode waveguides, can be fabricated in only a few seconds using a CW CO₂ laser by etching channels on either side of what becomes the core. This technique is however limited as the smallest feature size attainable is $\sim 10\ \mu\text{m}$. To overcome this limitation, a second laser can be added with a much shorter wavelength that can in turn lead to a smaller feature size [14,15]. A laser such as pulsed (ns) frequency doubled Nd:YAG laser ($\lambda = 0.532\ \mu\text{m}$) may be used. Typically at this wavelength the absorption of optical glasses is low at room temperature but can increase significantly at high temperature [16].

Although heat transport in borosilicate samples is radically different to pure silica based glasses, by optimizing the process using a CO₂-laser only, we produced samples with high quality grooves without cracking. The walls of the groove were found to be almost vertical with almost no protrusions on the surface as shown in Fig. 2b. The processing of the borosilicate glass was performed with a writing speed of 50 mm/s. With smooth wall surfaces and a well defined region light will be guided if the refractive index in the ridge (n_{guide}) is higher than the surrounding material (n_{air} and n_{buffer}) as shown in Fig. 3. This is the first step towards forming ridge waveguides in such glasses. In the future the aim is to heat the glass with the CW CO₂ laser to just below its ablation threshold; the temperature is then raised to the ablation point by the short wavelength laser to form finer features.

2.3. UV-absorption and refractive index control by thermal poling

The technique for material engineering described in this section is based on thermal poling. Thermal poling consists of applying a high voltage for a period of time with the sample at an elevated temperature. The sample is then allowed to cool with the field applied [17]. During the poling process, a dc electric field is recorded in the sample due to a space-charge distribution located at an ion depleted layer near the anodic surface [17]. The result is the creation of an effective second order susceptibility in the glass making its refractive index sensitive to an external applied field, opening up the possibilities for developing high-speed electro-optical switches and modulators. Poled glass also allows second harmonic generation, a process forbidden in centro-symmetric (un-poled) amorphous materials. The induced optical nonlinearity in poled bulk silica glasses is of the order of $\sim 1\ \text{pm/V}$ [18] which is much lower than the nonlinear coefficient of the commonly used material, LiNbO₃. The challenge is to use glass as a nonlinear material to achieve high nonlinearity in a reproducible and controllable manner. A natural way to pursue this task is to seek various vitreous systems to create a second order optical nonlinearity (SON) artificially by the poling process. More recent studies include telluride [19], boro-phosphate, [20] bismuth-borate [21] and chalcogenide glasses [22].

The SON distribution in thermally poled borosilicate glass was recently investigated by An and Fleming [23], reporting also compositional and structure changes near the anode region of poled glass. Additionally, enhanced stability of the SON in these glasses has also been demonstrated [24].

Here we show that thermal poling also has the potential of changing the UV-absorption, and consequently the refractive index, providing a novel method for refractive index engineering for manufacturing planar optical waveguides. Previous work on poling soda-lime glasses has shown a decrease in refractive index [25] or an increase in refractive index due to an accumulation of ions buried below the anode surface [26]. For the case of poled borosilicate

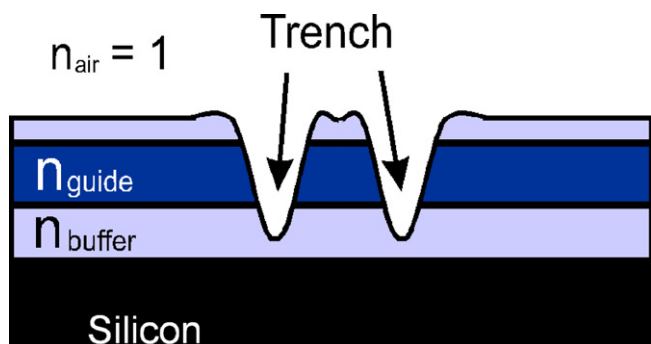


Fig. 3. Design of waveguides through laser ablation.

samples, Kramers–Kronig calculations were performed based on the data of the change in the UV-absorption spectrum resulting in a positive index change of the order of 0.01 at 1550 nm for the measure data. Therefore, with the present borosilicate glass system, we expect a positive refractive index change providing a simple method for waveguide fabrication.

Borosilicate samples from Schott (Duran), 2.5 mm thick, were poled at 280 °C in air atmosphere by applying up to 4.0 kV through pressed-on stainless-steel electrodes for 140 min. The voltage was increased in steps of 500–1000 V, a procedure typically employed for soda-lime glass [27], due to the high ionic conductivity. Also, a sample of the same glass, but with a thickness of 200 μm , was poled using corona poling [28] in order to avoid cracking which often occurs during cooling of the thin samples when using pressed-on electrodes. Here the stainless-steel anode was replaced with a NiCr wire, placed 2 mm above the glass sample. Thermal poling was performed at 280 °C with an applied voltage of 3 kV. Absorption spectra of the samples were measured in the range 200–700 nm. Poled 2.5 mm thick samples were also heat treated up to 500 °C, in 30 min intervals and in steps of 50 °C, in order to study the thermal stability of the absorption change. Changes in absorption were measured after each heating step.

The measured absorbance spectra of the poled 2.5 mm thick glass sample after the completion of the poling process, showed a red shift ($\Delta\lambda = 34$ nm) in the UV-absorption edge compared to an un-poled sample, as shown in Fig. 4. Besides the large shift of the apparent absorption edge, there are also indications of a weak absorption peak located at or above 350 nm (3.5 eV), as indicated on the long-wavelength side of the main absorption peak in Fig. 5. Thermal annealing experiments performed on poled samples did not remove the induced absorption, even at temperatures up to 500 °C, where the build-in electric field

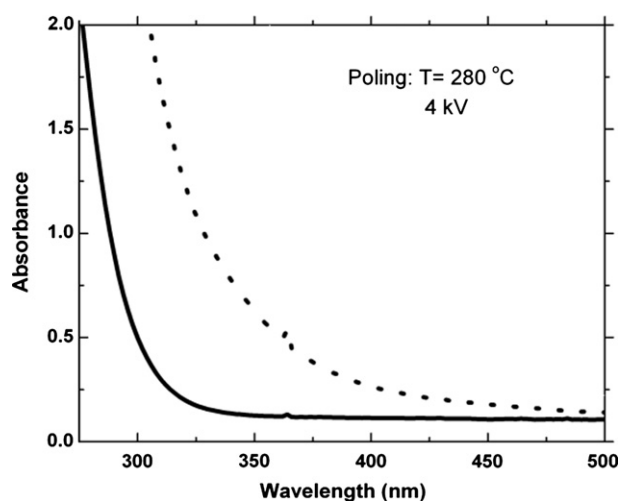


Fig. 4. Optical absorbance of un-poled (thick solid line) and poled (dotted line) 2.5 mm thick borosilicate glass sample. Poling conditions: 280 °C, 4 kV, 140 min.

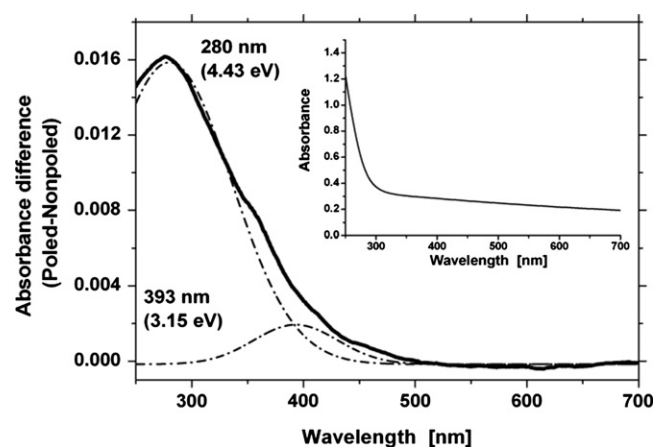


Fig. 5. Spectra of the absorption difference due to corona thermal poling of the 200 μm sample showing an induced absorption peak near 280 nm (inset shows the absorption spectra of the reference sample).

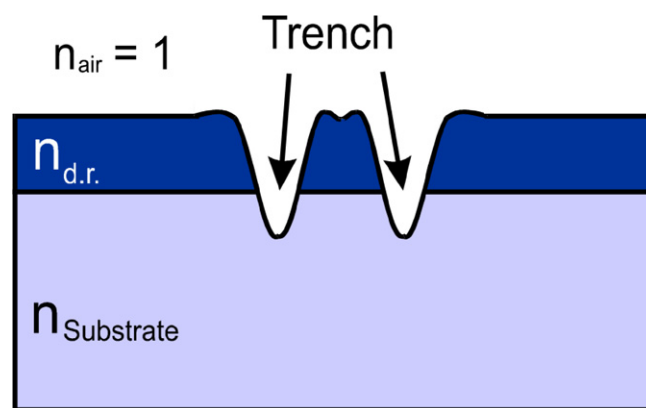


Fig. 6. Waveguide fabrication by a combined process of laser ablation and thermal poling. The higher refractive index of the poled region ($n_{d.r.}$) provides the guiding for the waveguide.

is removed instantaneously. Applying the same thermal treatment as above to an un-poled sample did not result in significant absorption changes. This indicates that the thermally stable absorption change is induced by thermal poling, i.e. the combination of the electric field and temperature resulting in a depletion of mobile ions near the anode.

To infer the depth of the depletion region in the poled sample, a scanning electron microscope (SEM) inspection was used in conjunction with an energy dispersion X-ray spectrometer (EDS). The sample was investigated in the poled region under the anode. The EDS measurement indicates a depletion region of ~ 18 μm . Further, to verify if the depletion region of the poled sample was contributing to the shift of the absorbance edge, the optical absorbance spectrum of the sample was measured after successive HF (20%) etching of the poled glass, removing the depletion region in a controllable manner. It was observed that when the depletion region was completely removed, the shift in the optical absorbance spectrum was no longer observed confirming that the absorption change is located in the

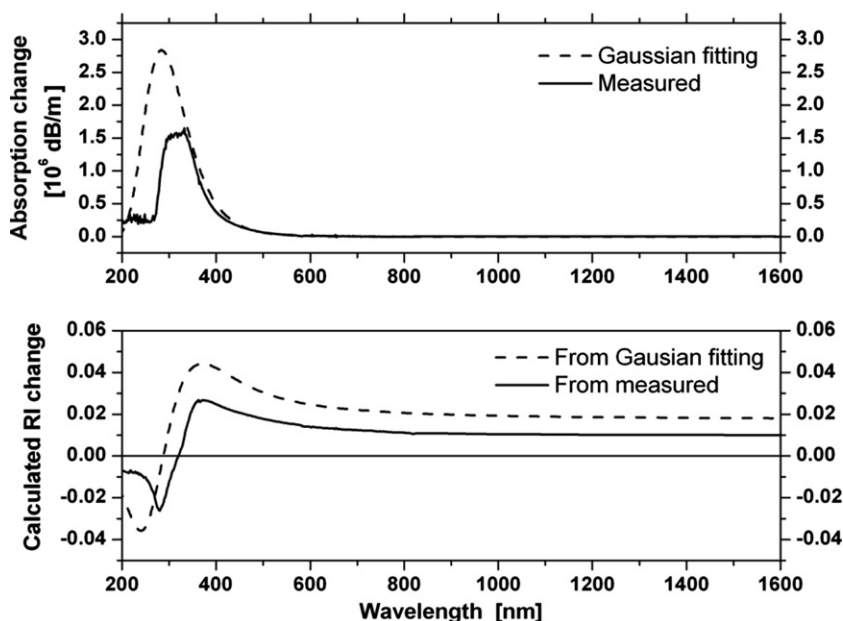


Fig. 7. Kramer–Kronig calculations based on the measured absorption change, limited at shorter wavelengths by the resolution of the spectrophotometer (solid line), and absorption change simulated by fitting a Gaussian absorption peak at 280 nm (dotted line). Top graph shows measured and simulated absorption change while bottom graph shows corresponding calculated refractive index change.

depletion region. Using the 200 μm thick sample attempts were made to identify the possible absorption peaks at shorter wavelengths, not possible using the thicker 2.5 mm sample. The result is shown in Fig. 5, where a peak located near 280 nm is clearly seen. We speculate that the change of the glass structure after poling could be related partly to an oxygen vacancy defect as is expected in silica glass. Non-bonding oxygen hole centers in silica have an absorption peak near 258 nm (4.8 eV) [29]. A possible explanation for the absorption change can also be tentatively correlated to the boron–oxygen-hole-center (BOHC) which is known to have an absorption peak near 280 nm. Using this value when fitting a Gaussian function to the main peak of Fig. 5, an additional smaller absorption peak near 390 nm provided an even better fit to account for absorption changes above 350 nm (Fig. 5). In the literature a defect associated to this wavelength has been ascribed to an oxygen vacancy defect [29]. To get an estimate of the refractive index change due to the change in UV-absorption Kramer–Kronig calculations were performed on the measured data for the 2.5 mm thick sample, as shown in Fig. 4. As the sample thickness limits the resolution at lower wavelengths calculations were also performed on spectra where the absorption change is simulated by fitting a 280 nm peak as shown in Fig. 5. The results of the Kramer–Kronig calculations are shown in Fig. 7. Further work is required to clarify the underlying mechanism for the large absorption change and to determine the effect on the refractive index to explore the future potential for using thermal poling for waveguide fabrication. The striking feature related to the optical absorption spectrum is that the change is also stable at high temperatures. We are investigating the material properties in order to understand

refractive index modification for the combined process of using laser ablation and thermal poling for waveguide fabrication, schematically shown in Fig. 6.

3. Conclusions

In this work, we have presented the use of three different processing techniques which can potentially be used to manufacture low cost optical waveguides and fibers using commercially available material. The material we have chosen to work with is traditional borosilicate glass, while the processing techniques are; rod and tube stacking for photonic crystal fiber fabrication, dual laser ablation processing for planar waveguide fabrication, and thermal poling, which could potentially be used for refractive index engineering of planar optical waveguides. The results of this work opens new possibilities for a broad range of potential low cost photonic devices that can be made by using traditional glass systems.

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References

- [1] P. Russell, *Science* 299 (2003) 358.
- [2] V. Treanton, L. Celebi Ozcan, R. Kashyap, L. Martinu, in: *Proceedings of Photonics North 2006*, June 2006, Quebec.
- [3] P.-Y. Balme, M. Fokine, C.M.B. Cordeiro, I.C.S. Carvalho, in: *Brazilian MRS Meeting, SPB Mat, Florianopolis, October 2006, Brasil*, p. D557.
- [4] T. Konishi, T. Matsumoto, T. Araki, T. Tsuchiya, S. Todoroki, S. Inoue, *Appl. Surf. Sci.* 223 (2004) 238.
- [5] (a) J. Warnock, D.D. Awschalom, *Phys. Rev. B* 32 (1985) 5529;
(b) J. Warnock, D.D. Awschalom, *Appl. Phys. Lett.* 48 (1986) 425.
- [6] A.F. Craievich, O.L. Alves, L.C. Barbosa, *J. Appl. Crystallogr.* 30 (1997) 623.
- [7] (a) C. Strohhofer, A. Polman, *Appl. Phys. Lett.* 81 (2002) 1414;
(b) M. Xian-Geng, P. Ming-Ying, C. Dan-Ping, Y. Lv-Yun, J. Xiong-Wei, Z. Cong-Shan, Qiu Jian-Rong, *Chinese Phys. Lett.* 22 (2005) 615.
- [8] R. Oven, P.R. Young, *IEEE Microw. Wireless Comp. Lett.* (2005) 125.
- [9] E.F. Chilcice, C.M.B. Cordeiro, L.C. Barbosa, C.H. Brito Cruz, *J. Non-Cryst. Solid.* 352 (2006) 3423.
- [10] M.A. van Eijkeleborg, M.C.J. Large, A. Argyros, J. Zagari, S. Manos, N.A. Issa, I. Bassett, S. Fleming, R.C. McPhedran, C.M. DeSterke, N.A.P. Nicorovici, *Opt. Express* 9 (2001) 319.
- [11] V.V.R.K. Kumar, A. George, J. Knight, P. Russell, *Opt. Express* 11 (2003) 2641.
- [12] G.D. Maxwell et al., *Electron. Lett.* 31 (1995) 95.
- [13] T. Nagata, M. Kamata, M. Obara, *Proc. SPIE* 5448 (2004) 992.
- [14] L.Ç. Özcan, V. Tréanton, R. Kashyap, L. Martinu, in: *Proceedings of the Bragg Gratings, Photosens. and Poling of Waveguides*, 1–4 July 2005, Sydney, Australia.
- [15] V. Tréanton, L. Çelebi-Özcana, F. Guay, R. Kashyap, L. Martinu, *Engineering of waveguides and other micro-structures in dielectrics*, in: P. Mathieu (Ed.), *Photonics North 2006. Proc. of SPIE*, Vol. 6343, 2006, pp. 6343121–634318.
- [16] R. Kashyap, V. Tréanton, L. Çelebi-Özcana, L. Martinu, *Dual laser fabrication of planar lightwave circuits*, in: P. Mathieu (Ed.), *Photonics North 2006. Proc. of SPIE*, vol. 6343, 2006, pp. 63431H1–63431H6.
- [17] R.A. Myers, N. Mukherjee, S.R.J. Brueck, *Opt. Lett.* 16 (1991) 1732.
- [18] X.C. Long, R.A. Myers, S.R.J. Brueck, *Opt. Lett.* 19 (1994) 1819.
- [19] K. Tanaka, A. Narazaki, K. Hirao, *J. Opt. Soc. Am. B* 19 (2002) 54.
- [20] M. Guignard, V. Nazabal, F. Smektala, H. Zeghlache, A. Kudlinski, Y. Quiquempois, G. Martinelli, *Opt. Express* 14 (2006) 1524.
- [21] O. Deparis, F.P. Mezzapesa, C. Corbari, P.G. Kazansky, K. Sakaguchi, *J. Non-Cryst. Solids* 351 (2005) 2166.
- [22] M. Guignard, V. Nazabal, J. Troles, F. Smektala, H. Zeghlache, Y. Quiquempois, A. Kudlinski, G. Martinelli, *Opt. Express* 13 (2005) 789.
- [23] H. An, S. Fleming, *Appl. Phys. Lett.* 89 (2006) 181111.
- [24] O. Deparis, C. Corbari, P.G. Kazansky, K. Sakaguchi, *Appl. Phys. Lett.* 84 (2004) 4857.
- [25] W. Margulis, F. Laurell, *Appl. Phys. Lett.* 71 (1997) 27.
- [26] A.L.R. Brennand, J.S. Wilkinson, *Opt. Lett.* 27 (2002) 906.
- [27] F.C. Garcia, I.C.S. Carvalho, E. Hering, W. Margulis, B. Lesche, *Appl. Phys. Lett.* 72 (1998) 3252.
- [28] A. Okada, K. Ishii, K. Mito, K. Sasaki, *Appl. Phys. Lett.* 60 (1992) 2852.
- [29] L. Skuja, *J. Non-Cryst. Solids* 239 (1998) 16.