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High contrast glasses for all-solid fibers fabrication

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ABSTRACT

We present composition development of borosilicate glasses for fabrication of high refractive index contrast, all-solid photonic crystal fibers. An oxide system composed of SiO_2–B_2O_3–Al_2O_3–Li_2O–⊕ Na_2O–K_2O was adjusted to match thermal properties of selected highly nonlinear, lead bismuth gallium silicate glass. A high difference of refractive index of 0.376 is achieved at a wavelength of 1550 nm. We proved experimentally that the developed pair of glasses enables to draw optical fibers, and we propose a design of a photonic crystal fiber structure for broadband supercontinuum generation.

1. Introduction

All-solid glass photonic crystal fibers are an alternative approach to the designing of fiber structures, one which allows to extend engineering of their propagation properties beyond what is achievable with “classic” air-hole structures. In the all-solid glass design, air holes of the photonic lattice of a PCF are replaced by another type of glass. Novel structures can hence be designed and fabricated, which would be difficult or impossible by conventional air holes approach. This includes coaxial rings [1], all solid fibers [2], birefringent fiber structures [3] and other sub micrometer structures [4], which would be challenging to fabricate due to air pressure fluctuations during thermal processing. Many novel all-solid glass fiber designs developed with chalcogenide [2], tellurite [5] or other glass types with high nonlinearity for applications in frequency conversion. Here the high refractive index contrast is essential to provide strong optical guiding [6]. Recently many phosphate glasses are also used in all-solid photonic lattices due to the feasibility to incorporate high concentration of rare earth ions for lasing applications [7]. Additionally the all-solid design prevents guided light from air interaction near air holes in conventional PCFs.

In order to fabricate an all-solid microstructured fiber, the materials constituting the latticemust have similar thermal properties. Several parameters have to be considered, such as thermal expansion coefficient, drawing temperature range, and as for all glasses suitable for fiber drawing - crystallization resistance. Successful matching of both materials provides an additional degree of freedom in fiber dispersion engineering, by allowing manipulation with the difference of the refractive indices of the two glasses [8]. There are potentially many types of glasses within which glass-pairs for fabricating all-solid fiber microstructures could be found, including silica [9], chalcogenide [2,10], tellurite type glasses [5,6,11], as well as other types of soft glasses [1,8]. The possibility to join different types of glasses opens up new opportunities of possible applications, as in the work of Tuan et al. where tellurite and phosphate glasses were used for nonlinear applications [12].

The goal of this work is to study the feasibility to fabricate all-solid photonic crystal fibers with maximum contrast of refractive index, incorporating silicon oxide based glasses with high concentration of heavy metal oxides. This approach opens new path for all-solid structures allowing for the use of wide selection of multicomponent glasses with strong nonlinearities. Up to date the highest refractive index contrast was reported in tellurite-phosphate fiber with the difference of 0.49 at 1.54 μm [12], and

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Table 1
Composition of investigated glasses.

Glass codename	UV-701	UV-702	UV-703	UV-704	UV-705	UV-706	UV-707	UV-708	UV-709	UV-710	UV-711	UV-712
Mass concentration [%]												
SiO_2	54	53	50	48.5	58.5	56	55	53	55	53	52.5	58
B_2O_3	28	31	34	36	25	27.5	28	30	27	28	30	24
Al_2O_3	1	1	1	0.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Li_2O	7	7	8	9	7	8	5.5	6.5	8	5	9	7.5
Na_2O	6	6	5	6	4	3	4	3	3.5	5	2	3.5
K_2O	4	2	2	–	4	4	6	6	5	7.5	5	5.5

0.336 in a step-index fiber using tellurite and germanium-tellurite glasses [6]. In all-solid all-chalcogenide fiber, Toupin et al. reported 0.37 at 1.55 μm [2]. In order to maximize the difference in refractive index values of glasses for drawing of all-solid photonic crystal fibers, we consider two types of oxide glasses. As the high refractive index glass we used the modified lead-bismuth-gallium-silicate glass labeled as PBG81 [13]. As the low refractive index glass we chose borosilicate glass type with composition in a SiO_2–⊜ B_2O_3–Al_2O_3–Li_2O–Na_2O–K_2O system. Previous research confirmed that these glasses have thermal expansion coefficient close to the lead-bismuth-gallium-silicate glass and can be easily modified by changing the ratio of the used components [14].

2. Glass composition design and synthesis

Borosilicate test glasses were synthetized by conventional melt-quenching technique. Grinded quartz glass, boric acid, aluminum oxide, lithium carbonate, sodium carbonate and potassium nitrate, all with analytic grade purity, were used as raw materials. Proper weight compositions were mixed to obtain homogenous powder and then melted in corundum crucible. Weights of substrates were adjusted to obtain 100 g glass batches from each melt. Batches for preliminary melting were melted in 1100–1270 °C for at least 4 h with several mechanical stirrings, to obtain good homogeneity of the samples. The melts were poured into preheated graphite forms and annealed to room temperature at a cooling rate of 0.5°/min. After annealing, the glass bars were cut and polished to obtain proper samples for characterization measurements. For the glass chosen for further processing, an increased volume of 1000 cm^3 was melted in a platinum crucible with addition of a bubbling process during melting for reduction of hydroxyl group concentrations. During the synthesis, the platinum tube was inserted into the glass melt in the furnace. The purified air was delivered by the Parker Balston zero air generator HPZA-30000 accompanied with FT-IR Purge Gas Generator 75-62. In the result the glass melt was rinsed by air purified from hydrocarbons and water contamination. The compositions of studied glasses are summarized in Table 1.

3. Characterization of synthesized glass

After annealing all the synthesized glasses were characterized to determine their rheological properties. Thermal expansion coefficient in the range of 20 and 300 °C (α_{20}^{300}), transformation temperature (T_g) and Dilatometric softening point (DSP) were obtained by a BÄHR Thermoanalyse GmbH DIL801 dilatometer. Viscosity curves were obtained by probe observation technique in a Leitz Heat Microscope. In this method the viscosity unit was logarithm from viscosity in Poise (1P = 0.1 kg m^{-1} s^{-1}). Specific viscosities were assigned to the shape of the sample during the heating. Characteristic shapes were: ovalization of the sample ($\log\eta = 9.0$), sphere creation ($\log\eta = 6.0$), hemisphere creation ($\log\eta = 4.0$) and spread of the sample ($\log\eta = 2.0$). The resistance towards crystallization was determined by 2 h tempering of the polished glass samples at a temperature of 10 °C above the sphere creation temperature ($\log\eta = 6.0$). After cooling, the samples were checked under a polariscope for crystal growth on the glass surface. Measurement results are presented in Table 2.

Confirmation of thermal compatibility was achieved by stacking a PBG81 glass plate between two plates of the UV series glass (see Table 2), and joining them at the hemisphere creation temperature of PBG81 ($\log\eta = 4.0$, 680 °C) for 30 min. After annealing, polished cross section was observed under microscope with a polarization attachment. Microscope images of the different borosilicate glasses are shown at Fig. 1. From the difference in colors, the stress induced by difference of the thermal expansion can be estimated [15]. The best result was observed for UV-706 and UV-710 glasses. In the case of UV-706 glass there was no internal stress between the two glasses, despite of a slight difference in the thermal expansion coefficients. Based on these results, for further use we choose the glass labeled UV-710, as it had very good crystallization resistance, acceptable thermal expansion coefficient difference with PBG81 glass and similar temperatures for fiber drawing. Material dispersions of the selected PBG81 and UV-710 glasses were measured in a Michelson interferometer to verify difference in refractive indices. The measurements were carried in the range of 400–1700 nm wavelengths (Fig. 2). The refractive index for the sodium line was equal to 1.511 and 1.887 for the UV-710 and PBG81 glasses, respectively. Measured transmission showed that borosilicate glass UV-710 has shifted spectral window to the shorter wavelengths comparing to PBG81 glass and its transmittance is higher in general. Both glasses show high transmission in the range of 600–2700 nm. The Sellmeier coefficients obtained for UV-710 glass were: B1 − 1.2, B2 − 0.105503321, B3 − 1.3, C1 − 0.007039263, C2 − 0.023826792, C3 − 113.8818986, and for PBG81: B1 − 2.01188143,

Table 2
Rheological properties of synthesized borosilicate and reference lead-bismuth-silicate glasses.

	Property	UV-701	UV-702	UV-703	UV-704	UV-705	UV-706	UV-707	UV-708	UV-709	UV-710	UV-711	UV-712	PBG81
Dilatometric	α_{20}^{300}[10^{-6} K^{-1}]	93.0	80.3	83.3	84.2	74.4	79.3	77.1	77.9	82.9	77.8	80.9	82.8	81.7
	T_g [°C]	491	495	491	495	492	493	490	490	492	487	489	490	484
	DSP [°C]	522	524	515	521	522	523	526	516	523	524	516	519	514
Viscosity	$\log\eta = 9.0$ [°C]	545	550	585	580	620	600	580	600	590	590	600	610	570
	$\log\eta = 6.0$ [°C]	650	660	660	660	720	660	680	670	660	680	650	680	640
	$\log\eta = 4.0$ [°C]	700	710	705	700	750	700	730	740	700	720	720	730	680
	$\log\eta = 2.0$ [°C]	840	940	840	840	920	940	910	910	840	850	920	840	745
Crystallization presence		+	+	+	+	+	+	–	–	+	–	+	+	–