Role of ion diffusion in direct femtosecond laser writing in tellurite glass

G.K. Alagashev[1,*], **M.P. Smayev**[1], **A.A. Gulin**[2], **A.G. Okhrimchuk**[1,3]

[1]*Mendeleev University of Chemical Technology of Russia*
[2]*N.N. Semenov Federal Research Center for Chemical Physics RAS*
[3]*Prokhorov General Physics Institute of the Russian Academy of Sciences, Dianov Fiber Optics Research Center*

[*]*E-mail: alagashevgrigory@gmail.com*

Waveguide devices based on soft glass with a large nonlinear refractive index are promising for integral nonlinear photonics and mid-IR photonics, in particular, for generating a mid-IR supercontinuum [1]. Direct femtosecond laser writing makes it possible to create such devices. However, designing waveguides with specified characteristics in such glasses and calculation of the waveguide parameters are difficult due to the complex refractive index profile. The latter circumstance is apparently related to the fact that the change in the refractive index is caused not only by a change in the density of the glass (as, for example, when recording waveguides in a quartz glass), but also by the mutual diffusion of chemical elements from and into zone of impact by the laser beam (the laser plasma zone) [2].

In this work we investigated laser writing in the volume of glass with the composition of $70TeO_2$-$22WO_3$-$8Bi_2O_3$. Femtosecond laser beam focused by a lens with NA=0.85 at the repetition frequencies in the range of 50 – 1000 kHz. In order to facilitate the numerical simulation of the process and understanding the modification mechanism, the writing was made without scanning the sample with respect to the laser beam waist, and with a different number of pulses and at different repetition rates. The spatial distribution in the refractive index change in the modification region was measured using quantitative phase microscopy (QPm). Figure 1 shows the plot of the maximum variation in the transmitted light phase, caused by the change in the refractive index in the modification region, against number of laser pulses.

The spatial distribution of the metal oxides in the modification region was investigated by of time-of-flight secondary ion mass spectrometry (ToF-SIMS). A significant change in the concentrations of Bi_2O_3, WO_3, and TeO_2 in the region of the laser action and in its vicinity was found. In particular the yield of bismuth oxide ions decreases in the region of the waist of the laser beam. However the spatial resolution of the method turned out to be insufficient to associate the distribution of concentration changes with the phase profile. Therefore numerical calculations of the thermal diffusion of ions were undertaken. Diffusion was modeled using coupled heat and diffusion equations:

$$\rho C_p(T)\frac{\partial T}{\partial t} + \nabla \cdot \left(-k(T)\nabla T\right) = F(t) \qquad (1)$$

$$\frac{\partial C}{\partial t} + \nabla \cdot \left(-D(T)\nabla C - CD_T(T)\nabla T\right) = 0 \qquad (2)$$

The temperature dependences for the heat capacity (C_p) and thermal conductivity (k) of glass in the range of 300 – 950 K were previously measured for glass with a similar composition. The temperature dependence of the diffusion coefficients is taken to satisfy the Arrhenius law:

$$D(T) = D_0 \exp\left(-E_a/RT\right) \tag{3}$$

where R is the universal gas constant, E_a is the diffusion activation energy. Thermal diffusion coefficient reads as:

$$D_T(T) = D(T)Q/RT^2 \tag{4}$$

where Q is the heat of transfer [3]. The impact of laser pulses was simulated through the heating $F(t)$, with a spatial distribution in the form of a generalized normal distribution. We suppose that the change in refractive index is proportional to the change in the relative concentration of glass components. The shape of the experimental dependence of the phase on the number of pulses was approximated by the calculated dependence of the concentration change on the number of laser pulses under varying parameters E_a and Q. Good agreement between theory and experiment was obtained for pulses with the highest energy E_p = 90 nJ (Fig. 1). For energies of 50 and 70 nJ and for less than 10 pulses the model predicts significantly lower values of the concentration change than it is necessary to explain the phase change. The calculations performed indicate that the redistribution of chemical elements due to diffusion makes a significant contribution to the change in the refractive index, but at the same time, it is necessary to take into account other factors (for example the change in density due to deformation) in order to explain the change in the refractive index at low heating.

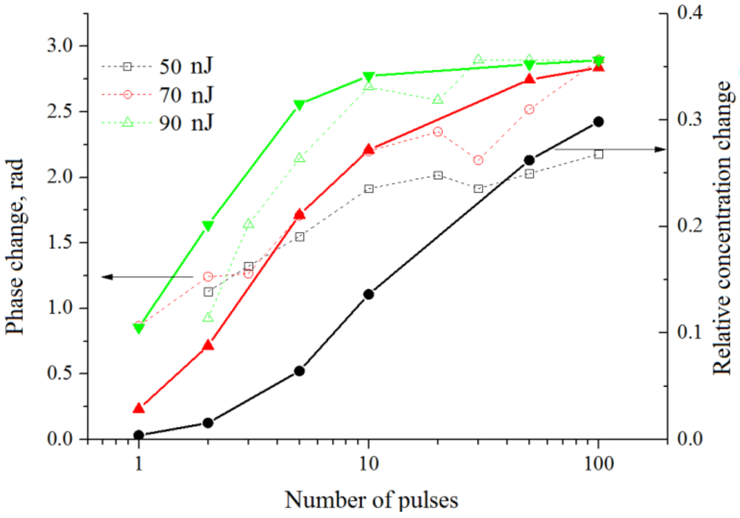

Fig.1 Comparison of the measured variation of the optical phase of radiation transmitted through the modified regions (dashed line) and the simulated ion concentration (solid lines) at a pulse repetition rate of 1 MHz. Q = 104 J/mol, $E_a = 7\cdot10^4$ J/mol, $D_0 = 10$ m^2/s, $C(0) = 2.5\cdot10^3$ mol/m^3.

The research was supported by the Russian Science Foundation, grant # 18-19-00733.

References

[1] A.G. Okhrimchuk, A.D. Pryamikov, et al, *J. Light. Technol*. **38**, 1492–1500 (2020).
[2] T. Gretzinger, T. T. Fernandez, et al, *Opt. Lett.* **45**, 3369 (2020)
[3] P. Shewmon, *Diffusion in Solids* (1963).