Laser-induced optical nonlinearity in a Li-rich glass

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Abstract. The selective crystallization of a photosensibilized lithium silicate glass after a light emitting diode (280 nm) and a nanosecond laser (355 nm) UV irradiation and subsequent heat treatment was studied. Using a focused beam of the laser allows successive drawing regions in which the formation of silver nanoparticles after 500 °C heat treatment of the glass co-doped with silver and cerium ions takes place. It is shown that this treatment is a necessary step for the growth of sodium metasilicate crystals under the second thermal treatment of the glass at 600 °C, while these regions demonstrate second optical harmonic generation of 1064 nm nanosecond laser radiation.

1. Introduction
Formation of a given pattern of the second order optical nonlinearity in transparent materials is of interest, first of all because of the possibility to provide quasi-phase-matched generation of optical harmonics in nonlinear media which, by different reason, are not capable of providing phase synchronism at required wavelength. An example of this is, e.g., periodically poled lithium niobate crystal[1]. Another problem relates to the formation of periodic second order nonlinearity in initially centrosymmetrical glasses which does not possess the second-order nonlinearity. To solve this, optical poling [2] and periodic thermo-electric poling [3] of glasses were proposed. The latter technique requires the formation of periodic anodic electrode to be used for poling at elevated temperatures. That is why there is an interest to search for other (simpler) techniques which could provide prescribed pattern of the second order optical nonlinearity in glassy media. For this, a possibility of optical recording such patterns could look attractive. The approach we consider in this paper supposes using photosensitive glasses, which optically initiated nanocrystallization, contrary to spontaneous formation of crystallites in glasses under thermal treatment for, e.g., nonlinear optical absorbers [4], could provide formation on optically nonlinear glass-ceramics pattern. In the experiments we used a foturan[5] like glass. Foturan lithium-silicate glasses were designed for the formation of relief structures...
by means of hydrofluoric acid etching of UV-irradiated regions of these glasses after thermal processing [6]. These glasses are photosensitive due to their doping with Ag+ and Ce3+ ions. Under UV irradiation the reaction Ce3+ hv +Ag+ → Ce4+ + Ag0 takes place, subsequent and thermal processing of the glass first results in silver atoms clustering and then in the glass crystallization, the silver clusters behaving as the crystallization nuclei. The type of crystals formed in a glass depends on the glass composition and structure in accordance with general rules [7]. In the foturan glass, the growth of lithium metasilicate microcrystals (LMS), Li₂SiO₃, takes place. Being non-centrosymmetrical, LMS crystallites should possess quadratic optical nonlinearity. Here we present the studies of the crystallization of a synthesized foturan-like glass and show that the local laser irradiation of the glass with UV nanosecond laser allows “drawing” optically non-linear glass regions.

2. Experiments and results

In the experiments, we used synthesized glass which composition is presented in Table 1. 1 mm thick polished plates of the glass were irradiated either with light emitting diode (LED) at 280 nm wavelength or the 3rd harmonic of a Litron laser (6 ns pulses, maximal pulse energy 14 mJ at 1064 nm and 0.7 mJ at 355 nm wavelength). Both LED and laser exposing resulted in similar transformation of optical absorption spectra. The irradiated samples were annealed at the temperature of 500 °C for 1 h and then at 600 °C for 10 min - 1 h. The influence of the first thermal treatment on optical absorption spectrum of the glass plates is illustrated with figure 1b.

| Component | SiO₂ | Li₂O | Al₂O₃ | K₂O | Na₂O | ZnO | Ag₂O | CeO₂ | Sb₂O₃ |
|-----------|------|------|-------|-----|------|-----|------|------|-------|
| Weight %  | 75.55 | 10.44 | 5.33  | 5.74| 1.17 | 1.13| 0.236| 0.085| 0.33  |

We also locally exposed the glass with a unfocused to 120 μm spot laser beam at 355 nm wavelength measured optical absorption of the irradiated spots after the first thermal treatment (figure 2a). Prepared samples were characterized with optical microscopy, microRaman spectroscopy (figure 2b) and X-ray diffractometry (figure 3). Finally, we checked the presence of 532 nm radiation (the second harmonic generation (SHG) of the nanosecond laser radiation at the wavelength of 1064 nm) in a light beam transmitted through the sample at normal incidence and measured the dependence of the second harmonic intensity in the transmitted light on the incidence angle of the fundamental beam—figure 4.

![Figure 1](image1.png)

**Figure 1.** (a) Transformation of optical absorption spectra under successive UV exposition and (b) after UV exposition (curve 2) 1 h anneal of the irradiated glass sample at 500 °C.
3. Discussion

The appearance of the left wing in the cerium optical absorption peak at 280 nm after the irradiation and its growth with the increase of the exposition (figure 1a) indicates the formation of neutral silver atoms in the glass via taking electrons from Ce³⁺ ions by Ag⁺ ions. This process saturates because of limited concentrations of these entities in the glass. First annealing at 500° C results in clustering of silver atoms and in subsequent formation of silver nanoparticles in the subsurface layer of the glass, which thickness corresponds to the penetration depth of exposing UV irradiation. The formation of silver nanoparticles is reflected in appearance of optical absorption peak at 415 nm, which coincides with the wavelength of surface plasmon resonance in silver nanoparticles[8]. This absorption also resulted in yellowish coloration of the specimens. The amplitude of the absorption peak, and, respectively, the number of nanoparticles depends on the UV exposition. We verified this by locally irradiating the specimens with UV laser beam unfocused to ~ 120μm spot at different laser intensity and annealing them at 500° C for 1 h. Optical microscopy showed that the size of the colored spot formed after this treatment corresponded to the size of the irradiation spot. Measurements of local absorption spectra shown in figure 2a, demonstrate the dependence of the optical density of the irradiated regions after such treatment on the exposition.

![Figure 2](image_url)

**Figure 2.** (a) Influence of the UV exposition on optical absorption spectra after the first thermal treatment and (b) Raman spectra of virgin glass and UV exposed glass after the first and the second thermal treatment.

In the Raman spectra of the UV-irradiated and annealed samples (figure 2b) one can see the increase of the signal in the range 2700-3700 cm⁻¹, which can be attributed to the luminescence of atomic silver clusters, Agₙ, n=2-4,[9,10] and a small peak at 962 cm⁻¹, possibly indicating the glass pre-crystallization. Probably, silver atomic clusters formed in parallel with the formation of silver nanoparticles during the thermal treatment at 500° C, for the luminescence of a virgin glass sample was essentially weaker. The second annealing has resulted in the appearance of narrow lines in the Raman spectrum of the corresponding specimen (indicated with arrows in figure 2b), which indicates the formation of a crystalline phase in the glass. Positions of these lines coincide with ones of orthorhombic lithium metasilicate, Li₂SiO₃[11]. However, due to relatively “soft” second thermal treatment of the glass, which was used to avoid strong scattering of light in the SHG experiments, only two lines were registered with assurance, and we used X-ray diffractometry to reliably identify the crystalline phase. The diffractometry returned a set of lines perfectly corresponding to orthorhombic lithium metasilicate (see figure 3).

Increasing the duration of the second heat treatment led to the growth of the diffraction peaks as shown in figure 3. The size of the crystalline grainsevaluated in accordance with the diffraction peaks width is about 30-35 nm. Besides, detailed studies of the X-ray diffraction spectra allowed identifying
diffraction peaks corresponding to both Li$_2$SiO$_3$ and crystalline silver (see inset in figure 3). The latter confirmed the formation of silver nanoparticles after the first thermal processing of the UV-exposed glass and preservation of the nanoparticles under the second thermal treatment. This corresponds to the situation when the nanoparticles behave as nuclei in the glass crystallization.

We were sure that the low symmetry of the grown nanocrystals of orthorhombic lithium metasilicate allows SHG, and chose a specimen that was 40-min secondary heat-treated to characterize SHG. This choice was based on two criteria: low light scattering and high crystalline phase content. The appearance of the second optical harmonic radiation in a light beam passed through the sample confirmed the ability of lithium metasilicate nanocrystals to generate the second harmonic. Figure 4 shows a monotonic decrease in the SHG intensity with an increase in the angle of incidence of the fundamental beam on the sample surface. This allows concluding that there is no oriented crystallization of Li$_2$SiO$_3$ during the second heat treatment and, as a consequence, powder-like SHG by the glass matrix – nanocrystal system. The observed angular dependence of the SHG intensity is due to an increase in the reflection of waves of both the fundamental and second harmonics with an increase in the angle of incidence of light.
4. Conclusions
Finally, to form a two-dimensional distribution of optical nonlinearity in the synthesized glass, we used a procedure similar to the traditional one for foturan glasses to form a 2D pattern resistant to chemical etching. Silver nanoparticles formed in the near-surface region of UV-irradiated and heat-treated glass specimens behaved as nuclei of orthorhombic Li$_2$SiO$_3$ nanocrystals that grew to 35 nm in size during the second heat treatment. Exposure of the glass to a focused UV laser beam ensured local reduction of silver and, accordingly, 2D “drawing” nanocrystals-containing glass regions. The low symmetry of these nanocrystals provided their second order optical nonlinearity which allowed the second optical harmonic generation by the regions of the glass which contained the nanocrystals. Angular dependence of the second harmonic signal evidenced a random distribution of nanocrystals in the glass subjected to UV irradiation.

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