Conference materials
UDC 53.043
DOI: https://doi.org/10.18721/JPM.183.113

Thermal poling of photosensitive glasses containing Ag^{+} and Ce^{3+} ions

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Abstract. We present the results on the crystallization of photo-thermo-refractive glass under thermal poling and ultraviolet (UV) irradiation followed by heat treatment. Poling was carried out at a temperature of 300 °C and a voltage of 400–1000 V. A femtosecond laser with a wavelength of 343 nm was used as UV sources. The studies were carried out using optical microscopy, optical absorption and Raman scattering. It is shown that in the subanode layer of the glass after poling, subsequent UV irradiation and heat treatment, crystallization of glass is completely suppressed. After the poling and the heat treatment cesium ions are also recharged in this layer $Ce^{3+} \rightarrow Ce^{4+}$. The mechanisms of the crystallization suppression and ion recharge in the poled region of the glass are discussed.

Keywords: photosensitive glass, thermal poling, UV irradiation, heat treatment, crystallization

Funding: The study was funded by the Ministry of Science and Higher Education of Russian Federation, project FSRM-2023-0009.

Citation: Moroz A.Yu., Chistikov I.E., Melehin V.G. Kaasik V.P., Thermal poling of photosensitive glasses containing Ag^{+} and Ce^{3+} ions, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 18 (3.1) (2025) 77–80. DOI: https://doi.org/10.18721/JPM.183.113

Материалы конференции
УДК 53.043
DOI: https://doi.org/10.18721/JPM.183.113

Термическая поляризация фоточувствительных стекол, содержащих ионы Ag^{+} и Ce^{3+}

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Аннотация. Представлены результаты исследования кристаллизации фото-терморефрактивного стекла при термическом полинге и ультрафиолетовом (УФ) облучении с последующей термообработкой. Полинг проводился при температуре 300 °C

и напряжении 400–1000 В. В качестве источников УФ излучения использовалась 3-я гармоника фемтосекундного лазера с длиной волны 343 нм. Исследования проводились методами оптической микроскопии, оптического поглощения и Рамановского рассеяния. Показано, что в прианодном слое стекла после полинга, последующего УФ облучения и термообработки кристаллизация стекла полностью подавляется. После полинга и последующей термообработки в этом слое происходит также перезарядка ионов цезия $Ce^{3+} \rightarrow Ce^{4+}$. Обсуждаются механизмы подавления кристаллизации и перезарядки ионов в поляризованной области стекла.

Ключевые слова: фоточувствительные стёкла, термический полинг, УФ облучение, термическая обработка, кристаллизация

Финансирование: Работа выполнена в рамках Государственного задания FSRM-2023-0009.

Ссылка при цитировании: Мороз А.Ю., Чистиков И.Е., Мелехин В.Г., Каасик В.П. Термическая поляризация фоточувствительных стекол, содержащих ионы Ag^+ и Ce^{3+} // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2025. Т. 18. № 3.1. С. 77–80. DOI: https://doi.org/10.18721/JPM.183.113

Introduction

Photocrystallized glasses [1] are used in various fields of optics, such as holography, photonics, sensors, laser technology (see [2, 3] and references therein). Under the influence of UV radiation in the absorption band of trivalent cerium, its charge exchange occurs, and an electron is captured by a silver ion: $Ce^{3+} + h\nu + Ag^+ \rightarrow Ce^{4+} + Ag^0$ [1]. Subsequent heat treatment at 500 °C leads to the formation of silver clusters, which are the crystallization centers of the glass occurring under heat treatment at 600 °C. With local excitation by UV radiation and subsequent heat treatments, local photothermoinduced crystallization of the glass occurs, which is used to create various 2D and 3D structures, such as Bragg gratings for lasers and holographic optical elements [2]. An important factor is also the difference in the rate of chemical etching of the crystalline and amorphous phases in such glasses, which makes it possible to create relief structures at the surface and inside photo-thermo-refractive glasses, e.g. microfluidic chips [3]. A common method of modifying glasses is also thermal poling, the essence of which lies in placing a glass plate between electrodes (flat capacitor configuration) and heating to a temperature at which noticeable ionic conductivity appears (~ 300 °C), with subsequent application of voltage to the electrodes [4]. As a result, the composition and structure of the subsurface layer of glass changes, and the layer itself acquires a set of new properties, e.g. the second-order optical nonlinearity [5]. The aim of this work is to study the effect of thermal poling on photothermally induced crystallization of the glass and the processes of charge recharging of cerium ions.

Experiments and results

In the experiments, we used synthesized alumina-lithium-silicate glass with the following composition (in weight % of oxides): 75.5% of SiO_2; 10.44% of Li_2O; 5.33% of Al_2O_3; 5.74% of K_2O; 1.17% of Na_2O; 1.13% of ZnO; 0.236% of Ag_2O; 0.085% of CeO_2; 0.33% of Sb_2O_3. Transition temperature of this glass is T_g = 480 °C. It should be mentioned that in the synthesized glass cerium state is Ce^{3+} [6]. For poling, the glass plate was placed between two electrodes, one (cathode) completely covering the glass surface, and anode only partially. Then the structure was heated to temperature of 300 °C, after which a DC voltage of 400–1000 V (depending on the experiment) was applied to the electrodes. In Fig. 1, *a* we demonstrate differential (minus the spectrum of the initial glass) absorption spectra of the poled glass and the glass poled and subsequently annealed at 500 °C. In the spectra, we observe appearance of an absorption band near 245 nm, which is the charge transfer band of Ce^{4+} [7, 8]. The intensity of this band after poling is weak (see curve 1 in Fig. 1, *a*), but the anneal results in ~ 5-fold increase of the intensity

(see curve 2 in Fig. 1, *a*). This behavior can be apparently associated with a leftward shift in the equilibrium of the following oxidization process: $4Ce^{4+} + 2O^{2-} \leftrightarrow 4Ce^{3+} + O^2$.

Oxidization occurs both during poling due to the recombination of non-bridging oxygens with the formation of O_2 after the alkali ions have gone deep into the glass [9], and evidently during heat treatment in air. With increasing temperature, the rate of oxygen diffusion increases and the process of cerium oxidation activates, as a consequence, the intensity of the 245 nm Ce^{4+} band increases.

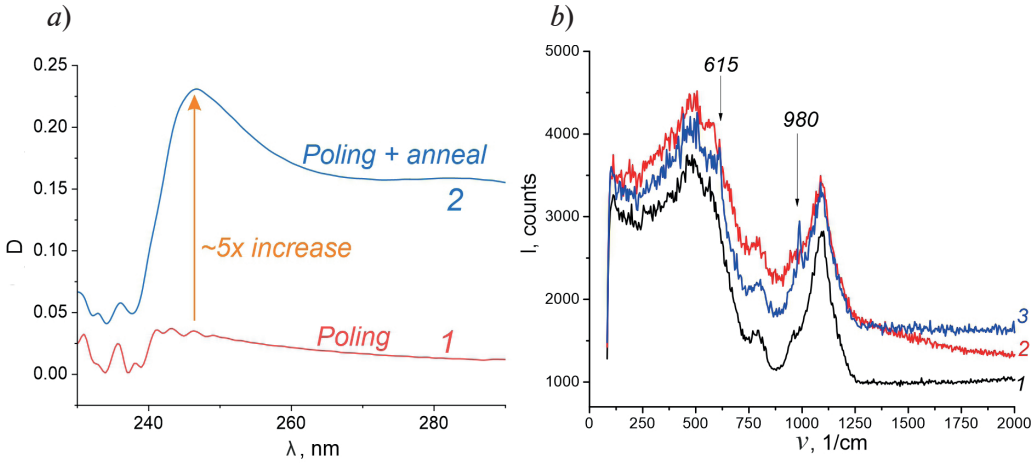

Fig. 1. Differential optical absorption spectra of the glass after poling under 800 V (*1*) and after poling under 500 V followed by anneal at 500 °C (*a*); Raman spectra of the initial glass (*1*), glass after poling and subsequent anneals at 500 and 600 °C (*2*), glass after poling, UV irradiation and subsequent anneals at 500 and 600 °C (*3*) (*b*)

When poled glass is subjected to UV irradiation and conventional crystallization procedure [6], the samples become opaque due to the formation of crystals which scatter the light. Raman spectra (Fig. 1, *b*) clearly demonstrate appearance of the peaks at frequencies of 615 cm^{-1} and 980 cm^{-1}, corresponding to lithium metasilicate, Li_2SiO_3 [8] in the specimen, which was poled, UV-irradiated and annealed. We also performed depth-scan via Raman spectroscopy by varying the distance between the objective lens and the sample surface and studied depth-dependence of intensities of the "glass" peak at ~ 1080 cm^{-1} and the "crystal" peak at ~ 980 cm^{-1}. Using a 530 nm wavelength and a 100x objective lens gave us a depth resolution about one micron. The results are shown in Fig. 2. We see the absence of crystals in a ~ 1 μm-thick subsurface layer. This is due to the fact that during poling lithium ions migrate into the glass under the action of the electric field and the subsurface region is depleted of these ions. Also, depth-scan demonstrated that the crystallites are not uniformly distributed at μm-scale (see "crystal" intensity line in Fig. 2).

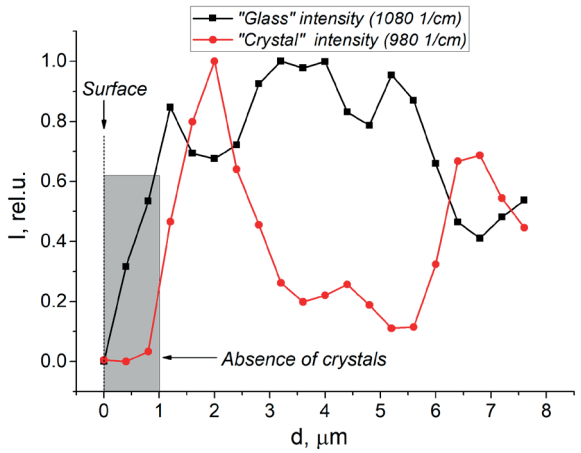

Fig. 2. Depth-dependence of normalized intensities of Raman peaks at ~ 1080 1/cm ("glass" peak) and at ~ 980 1/cm ("crystal" peak)

This nonuniformity, in particular the appearance of a second peak on the 980 1/cm line in parallel with the decline on the 1080 1/cm line may be due to the redistribution of reduced silver atoms during the first thermal treatment (500 °C) of the samples.

We etched the specimen in a 4% hydrofluoric acid solution, which showed that the surface of the poled region of the glass, unlike the regions without polarization, is not sensitive to the etching. This indicates a change in the composition of the near-surface layer of the polarized region, and that it completely lacks lithium metasilicate crystals, which are easily soluble in the etchant used.

Conclusions

We demonstrated that thermal poling of the photo-thermo-refractive glass results in the complete suppression of crystallization in the subsurface ~1 μm-thick layer, but does not affect the crystallization of deeper regions of the glass. Thus, thermal poling provides an additional tool to control crystallization of the photosensitive glass.

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Received 12.08.2025. Approved after reviewing 03.09.2025. Accepted 04.09.2025.