

doi: 10.17586/2226-1494-2020-20-4-515-519

ABSORPTION CHARACTERISTICS OF SILVER ION-EXCHANGED LAYERS IN CHLORIDE PHOTO-THERMO-REFRACTIVE GLASS

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Article info

Received 16.05.20, accepted 20.06.20
 Article in English

For citation: Semaan R., Marasanov D.V., Sgibnev Ye.M., Nikonorov N.V. Absorption characteristics of silver ion-exchanged layers in chloride photo-thermo-refractive glass. *Scientific and Technical Journal of Information Technologies, Mechanics and Optics*, 2020, vol. 20, no. 4, pp. 515–519 (in English). doi: 10.17586/2226-1494-2020-20-4-515-519

Abstract

Subject of Research. The paper considers effect of chloride in composition of photo-thermo-refractive glass on the spectral properties of silver nanoparticles formed in ion-exchanged layers after heat treatment. **Method.** Glasses based on $\text{Na}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}$ doped with antimony oxide Sb_2O_3 , cerium oxide CeO_2 and a variable chloride content (0–1 mol%) were synthesized for the study. Silver ions were introduced by the low-temperature Na^+-Ag^+ ion exchange method into the synthesized glasses. For this purpose, glass samples were immersed in a mixture of 0.1 $\text{AgNO}_3/99.9\text{NaNO}_3$ (mol%) nitrates at the temperature of 320 °C for 15 minutes. After the ion exchange glasses were irradiated with ultraviolet radiation and heat-treated at the temperature of 500 °C for 3 hours to achieve the growth of silver nanoparticles. **Main Results.** Spectrum properties of chloride photo-thermo-refractive glasses with silver nanoparticles in ion-exchanged layers are studied. It is found that the presence of chloride in the photo-thermo-refractive glass matrix results in a long-wavelength shift of the absorption band of silver nanoparticles. That may be attributed to the growth of the mixed AgCl/NaCl shell on silver nanoparticles. The formation of silver nanoparticles in ion-exchanged layers occurs both in the irradiated and unirradiated regions of the glass. **Practical Relevance.** The results can be used to create Bragg gratings inside photo-thermo-refractive glass for input and output radiation (pump and signal) into the waveguide structures formed by the ion exchange method, and to create monolithic integrated optical elements on a single substrate, that is very essential for integrated optics.

Keywords

low-temperature ion exchange, photo-thermo-refractive glass, silver nanoparticles, chloride

УДК 535.343.2

doi: 10.17586/2226-1494-2020-20-4-515-519

ИССЛЕДОВАНИЕ АБСОРЦИОННЫХ ХАРАКТЕРИСТИК СЕРЕБРЯНЫХ ИОНООБМЕННЫХ СЛОЕВ В ХЛОРИДНОМ ФОТО-ТЕРМО-РЕФРАКТИВНОМ СТЕКЛЕ

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Информация о статье

Поступила в редакцию 16.05.20, принята к печати 20.06.20
 Язык статьи — английский

Ссылка для цитирования: Семаан Р., Марасанов Д.В., Сгибнев Е.М., Никоноров Н.В. Исследование абсорционных характеристик серебряных ионообменных слоев в хлоридном фото-термо-рефрактивном стекле // Научно-технический вестник информационных технологий, механики и оптики. 2020. Т. 20. № 4. С. 515–519 (на англ. яз.). doi: 10.17586/2226-1494-2020-20-4-515-519

Аннотация

Предмет исследования. В работе исследовано влияние введения хлоридов в состав фото-термо-рефрактивного стекла на спектральные свойства наночастиц серебра, сформированных в ионообменном слое в результате термообработки. **Метод.** Для исследования были синтезированы стекла, представляющие собой матрицу на основе $\text{Na}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}$, легированные оксидом сурьмы Sb_2O_3 , церия CeO_2 и переменным содержанием

хлоридов (0–1 мол.%). Серебро вводилось методом низкотемпературного $\text{Na}^+ - \text{Ag}^+$ ионного обмена, для чего образцы стекла погружались в смесь нитратов $\text{AgNO}_3/\text{NaNO}_3$, содержащем 0,1 мол.% AgNO_3 при температуре 320 °C в течение 15 мин. Для формирования наночастиц серебра стекла после ионного обмена облучались ультрафиолетовым излучением с последующей термообработкой при температурах 500 °C длительностью до трех часов. **Основные результаты.** В работе изучены спектральные свойства хлоридного фото-термо-рефрактивного стекла, легированного оксидом сурьмы Sb_2O_3 , церия CeO_2 , и переменным содержанием хлоридов с наночастицами серебра в ионообменных слоях. Обнаружено, что с увеличением концентрации хлора в матрице фото-термо-рефрактивного стекла выявлен длинноволновый сдвиг полосы поглощения наночастиц, связанный с ростом смешанной оболочки AgCl/NaCl на наночастицах серебра. Формирование наночастиц серебра в ионообменных слоях происходит как в облученной, так и необлученной области стекла. **Практическая значимость.** Результаты работы могут быть использованы для создания брэгговской решетки внутри фото-термо-рефрактивного стекла для ввода и вывода излучения (накачки и сигнала) в волноводные структуры, образованные ионообменным методом, для создания монолитных интегральных оптических элементов на одной подложке, что очень важно для интегральной оптики.

Ключевые слова

низкотемпературный ионный обмен, фото-термо-рефрактивное стекло, наночастицы серебра, хлор

Introduction

Currently, the development of plasmon silver nanostructures is of great interest in the field of miniaturization and integration of optical devices, such as microresonators, plasmon waveguides, converters, and other passive elements [1, 2]. Silver nanoparticles can be precipitated in a glass matrix like photo-thermo-refractive glass [3], which is a promising widely used material due to its high mechanical strength and chemical resistance. It can be classified as a polyfunctional material combining the properties of several monofunctional materials such as the photosensitive, photorefractive, laser, luminescent, and plasmonic ones [4]. Photo-thermo-refractive (PTR) glass was designed on the basis of photosensitive glasses in the sodium–aluminum–zinc silicate system. It was developed by Corning Inc. in 1977, and was called “polychrome glasses” [5]. In Russia, these glasses appeared a little later and were called “multi-color glasses”. PTR glass changes its refractive index after an exposure to the near ultraviolet (UV) radiation followed by thermal treatment at the temperatures close to the glass transition one (T_g) [6]. This change results from the precipitation of nanocrystalline $\text{AgBr}-\text{NaF}$ phases in the fluoride PTR glasses on the silver nanoparticles and $\text{AgCl}-\text{NaCl}$ in chloride PTR glasses. In contrast to fluorine-containing PTR glasses, the formation of a crystalline phase in chloride PTR glasses leads to a local positive change in the refractive index in the region irradiated with ultraviolet radiation followed by heat treatment compared to the region without irradiation up to 1500 ppm [6]. Silver ions can be introduced into the glass in a variety of ways, for example, low temperature ion-exchange [7], which is the process of substituting one kind of alkali cations (usually Na^+) in glass for another one (Li^+ , K^+ , Rb^+ , Cs^+) or transition metal ions (Ag^+ , Cu^+ , Tl^+) from a salt melt. The objective of this work is to study the effect of chloride introduction into the PTR glass on the spectral properties of silver nanoparticles formed by the $\text{Na}^+ - \text{Ag}^+$ ion-exchange method.

Experimental

Chloride PTR glasses were synthesized in a system of $\text{Na}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}$ with reduced fluorine concentration and variable batch concentration of Cl

(0–1 mol%) doped with CeO_2 and Sb_2O_3 . These dopants are responsible for the process of photo-thermo-induced crystallization and the precipitation of crystalline sodium chloride and silver nanoparticles. The glass synthesis was carried out in Gero-electric furnace in air atmosphere using the platinum crucibles, the melts being homogenized with platinum stirrer. The synthesized glasses were annealed and cooled down to room temperature with a pre-set program. After the synthesis, planar polished samples were prepared with a thickness about 1 mm. Silver ions were introduced into the synthesized glasses by the $\text{Na}^+ - \text{Ag}^+$ low-temperature ion-exchange (IE) method. The samples were immersed in a bath with a melt of 0.1 $\text{AgNO}_3/99.9$ NaNO_3 (mol%) nitrate mixture at the temperature of 320 °C for 15 minutes. Then UV-irradiation was performed using a Kimmon He-Cd laser IK3501R-G model. Subsequent heat treatment (HT) was carried out at the temperature of 500 °C for 3 hours. The low-temperature ion exchange process and heat treatment of the studied samples were carried out in a muffle furnace. Absorption spectra were measured in the spectral range of 200–800 nm on a Perkin-Elmer Lambda 650 double-beam spectrophotometer (USA). Calculation of the effective optical size of silver nanoparticles was performed according to the Mie Theory [8] with the following equation:

$$d = \frac{2v_F}{\Delta w},$$

where d is a mean diameter of nanoparticles, v_F is Fermi velocity (1.39×10^8 cm/s for silver [9]), and Δw — full width at half maximum (FWHM) of the absorption band in the angular frequency unit.

Results and discussion

In order to study the effect of chloride on the formation of silver nanoparticles in the PTR ion exchanged layers, four samples of the glass were prepared with Cl = 0, 0.5, 0.75, 1 mol%.

Fig. 1 demonstrates the absorption spectra of the samples without chloride (Cl = 0 mol%). The absorption band centered at 310 nm is related to the absorption of Ce^{3+} ions in the virgin glass spectrum [10]. A long-wavelength shift of the UV absorption edge was observed after the IE process. The shift results from the $4d^{10} \rightarrow 4d^9 5s^1$

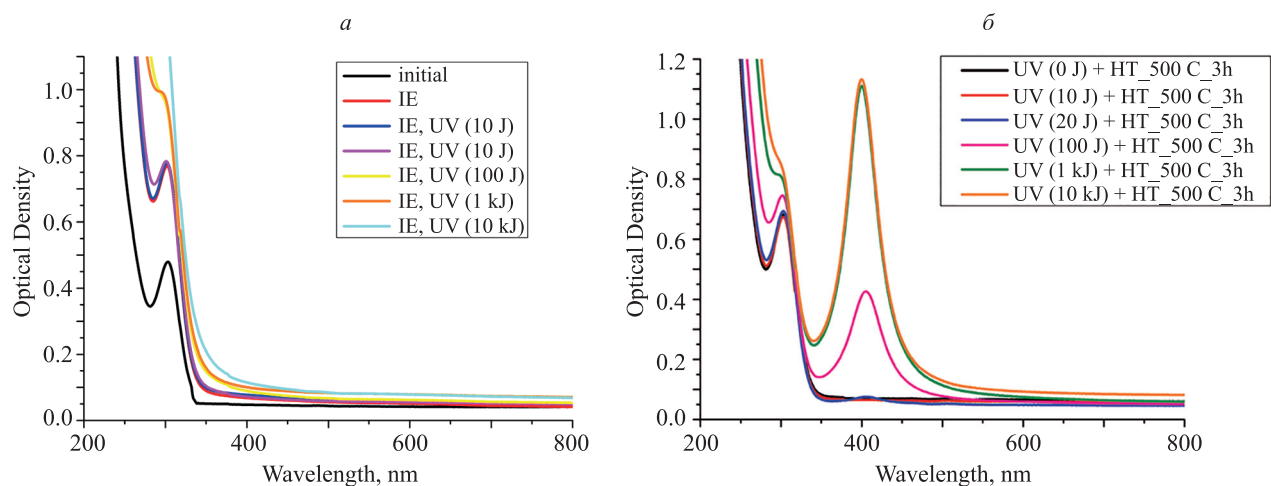


Fig. 1. Absorption spectra of PTR glass samples without chloride (Cl = 0 mol%): initial glass (black line), after IE (red line) and after UV irradiation (a). After IE, UV irradiation and subsequent HT (b)

absorption transitions of Ag^+ ions [11]. After UV irradiation, a disappearing of the absorption band at 310 nm occurs due to the transformation of Ce^{3+} to Ce^{4+} as a result of photoionization [12].

In PTR glass without chloride a wide absorption band, centered at 410 nm, is formed after IE, UV irradiation, and subsequent HT, which is associated with the formation of silver nanoparticles. The diameter of the silver nanoparticles was calculated according to the Mie Theory, and was found to be 4 nm. As the UV irradiation dose increases, the optical density of the absorption band of nanoparticles grows. Irradiation with a dose of 1 kJ leads to saturation and a further growth in the absorption amplitude is not observed.

Fig. 2 demonstrates the absorption spectra of PTR glasses sample with chloride (Cl = 1 mol%). As seen in Fig. 2, a, the presence of chloride does not affect the absorption spectra of the PTR glass without heat treatment, while (Fig. 2, b) it leads to the long-wavelength shift

of the absorption band of nanoparticles from 410 nm to 440 nm compared to the case without chloride. This shift is related to the growth of mixed silver and sodium chloride shell AgCl-NaCl around the nanoparticle in the irradiated region of the glass [6, 13]. Also, the formation of silver nanoparticles occurs in the unirradiated region of the glass, but their optical density is lower due to the lack of additional electrons for silver reduction. With the increase of the UV irradiation dose the optical density of the absorption band of nanoparticles grows. Not shown absorption spectra of the samples with Cl = 0.5%, 0.75 mol% are similar and behave in the same way.

Fig. 3 clearly shows the long-wavelength shift of the absorption band of nanoparticles after ion exchange, UV irradiation, and heat treatment due to the addition of chloride in the PTR glass matrix, which is equal to 30 nm. This shift may be attributed to the high refractive index of the NaCl/AgCl shell ($n_{\text{shell}} = 2.3$) compared to refractive index of the glass bulk ($n_{\text{PTR}} = 1.49$) [6].

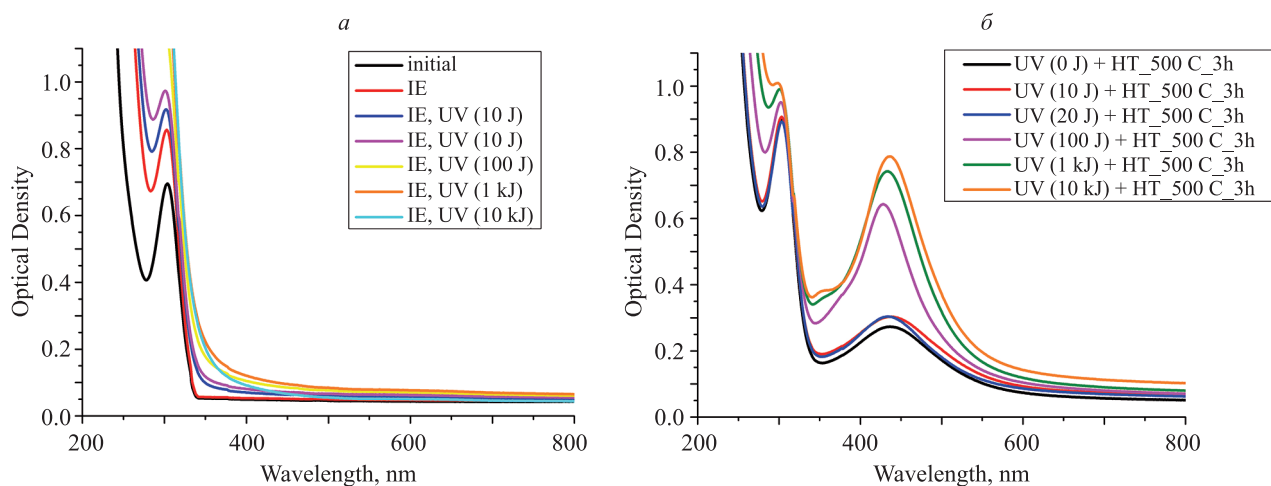


Fig. 2. Absorption spectra of PTR glass samples with chloride (Cl = 1 mol%): initial glass (black line), after IE (red line) and after UV irradiation (a). After IE, UV irradiation and subsequent HT (b)

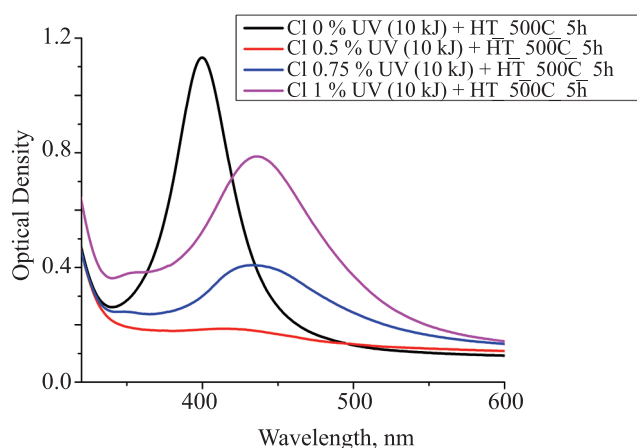


Fig. 3. Absorption spectra of PTR glass samples after ion exchange IE, UV irradiation (10 kJ) and heat treatment ($T = 500\text{ }^{\circ}\text{C}$, $t = 5\text{ h}$) without chloride (black line) and with (0.5, 0.75, 1 mol%) chloride

Conclusion

The paper considers the effect of chloride in the ion-exchanged PTR glass on the spectral properties of silver nanoparticles formed inside the glass. It was shown that the incorporation of chloride into the PTR glass matrix affects the kinetics of silver nanoparticle formation in $\text{Na}^+ - \text{Ag}^+$ ion exchanged layers. The formation of silver nanoparticles with a shell was not detected in glasses without chloride. The addition of the chloride in the PTR glass matrix leads to formation of a shell consisting of mixed silver and sodium chlorides around the silver nanoparticle, which leads to a constant long-wavelength shift (30 nm) of the nanoparticle absorption bands. The diameter of nanoparticles in the glass without chloride is 4 nm. Silver nanoparticles were detected only after heat treatment in the ion-exchanged layer of PTR glass with/without chloride. UV irradiation affords additional electrons to reduce silver ions to silver atoms, and therefore, to obtain higher concentrations of silver nanoparticles. The results can be used to record Bragg gratings in PTR waveguide structures.

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