

The effect of UV irradiation on the refractive index modulation in photo-thermo-refractive glasses: Mechanisms and application

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ABSTRACT

It is shown experimentally that in photo-thermo-refractive glasses the transformation of charged silver subnanosized molecular clusters to neutral state by UV irradiation results in the increase of glass refractive index. The increment of the refractive index reaches $\Delta n = 0.76 \cdot 10^{-4}$. Computer simulation has shown that the polarizability of neutral molecular clusters is by 20–40% larger than of charged ones. The reason of this is the increase of electron density and volume of electron density surfaces during the transformation of molecular cluster to the neutral state. The transition molecular cluster from the ground state to the excited state also results in the increase of its polarizability.

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1. Introduction

Local modulation of the refractive index of glasses and other transparent optical materials is used for recording of holograms, optical waveguides and other elements of integrated optics. In glasses without sensitizers local modulation of refractive index can be obtained by focused IR femtosecond laser [1–6], or electron beam irradiation [7,8]. Several mechanisms of material modification were proposed for glasses: strained bond restructuring, molecular rearrangement, and kinetics of melting and solidification [9–13]. During femtosecond laser irradiation of glasses the refractive index change of $\Delta n = (1-5) \cdot 10^{-3}$ can be obtained. In the case of electron irradiation the refractive index change is caused by the destruction of glass network chemical bonds by fast electrons and by the field migration of positive metal ions into the irradiated zone [8,14]. The refractive index modulation in this case can reach $\Delta n = 0.04-0.01$ [8]. By these methods optical waveguides and digital phase holograms can be fabricated in glasses.

Photo-thermo-refractive (PTR) silicate glasses are glass systems which are doped by Ag, Ce and Sb ions [15]. Generally they are used for 3D holograms recording and also as a base for the developing of

new materials for photonic devices [16–21]. During holograms recording local refractive index modulation is produced by the following complex procedure [18,21]. At first the interference field is produced in PTR glass bulk by summarizing of two beams of continuous UV laser, which radiation wavelength matches the absorption band of Ce^{3+} ions ($\lambda = 300-330$ nm). Photoionization of cerium ions in the nodes of interference fringes produces free electrons in these local areas. Some part of these free electrons is trapped by Ag^+ ions and positively charged silver molecular clusters (MCs) Ag_n^+ , transforming them to neutral state, and another part is trapped by Sb^{5+} ions forming $[\text{Sb}^{5+}]$ complexes [19]. During the subsequent thermal treatment at $T = 300-400$ °C $[\text{Sb}^{5+}]$ complexes loose electrons and they are trapped by the remained Ag^+ ions and charged silver MCs in the irradiated areas. Then glasses are treated at temperatures above glass transition temperature T_g ($T_g = 490-495$ °C). Thermal diffusion of Ag atoms, halides and sodium ions during this treatment transforms neutral silver MCs to spherical silver nanoparticles with halogenide shells on their surfaces [22,23]. As a result of spatial redistribution of mentioned glass components the spatial modulation of glass refractive index takes place. In the nodes of interference fringes refractive index decreases by $\Delta n = (2-9) \cdot 10^{-4}$ [21,24,25], and the phase hologram is formed.

The detailed investigation of refractive index change in PTR glasses under continuous UV irradiation and of mechanisms of this

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effects, to our opinion, were not performed. The only exception is the work [26], in which the refractive index change in PTR glass after UV irradiation with low doses (less than 600 mJ/cm²) was measured by interferometric method. The measured increment of refractive index was $\Delta n = 5 \cdot 10^{-6}$, but the nature of this effect was not discussed in that work.

In the present work we experimentally demonstrate that local refractive index modulation in silver-containing PTR glasses during low-intensity continuous UV irradiation is sufficient for optical devices fabrication (optical waveguides, holograms, etc.). The role of the subsequent thermal treatment of PTR glass is discussed. By methods of density functional theory we explain the observed effects.

2. Materials and methods

PTR glasses based on the Na₂O–ZnO–Al₂O₃–Si₂O–NaF–NaCl system and doped with Ag₂O (0.12 mol.%), photosensitizer – CeO₂ (0.07 mol.%) and reducer – Sb₂O₃ (0.04 mol.%) were synthesized in ITMO University. As-prepared the glass is transparent in a spectral range of 350–1500 nm and has the refractive index of 1.52 in a spectral range of 400–800 nm. The glass transition temperature T_g was measured with STA6000 (Perkin–Elmer) differential scanning calorimeter, its magnitude being found to be 494 °C (Fig. 1). It must be noted, that during the glass synthesis some part of Ce ions change the valence state from IV to III, and some part of Sb ions change the valence state from III to V. The samples to be investigated were prepared in the form of the plane-parallel polished plates 1 mm thick.

For optical waveguides fabrication the group of samples were irradiated during 10 min through the masks with the gap of 0.8 mm by UV mercury lamp with the radiation band matching the absorption band of Ce³⁺ ions ($\lambda = 305$ –315 nm). The diameter of curved waveguide was 8 mm, the lengths of straight waveguides was 10 mm. For waveguide modes excitation semiconductor lasers with $\lambda = 405$ and 650 nm were used. For the measurements of refractive index modulation in the other group of samples the volume holograms were recorded with the use of continuous He–Cd laser ($\lambda = 325$ nm) Kimmon IK3501R-G. Laser power density during hologram recording was 0.75 mW/cm², irradiation dose was 6 J/cm². For hologram recording the standard optical scheme with the interference of two splitted laser beams was used [24,25]. The period of the written grating was 810 nm. The thickness of written hologram was approximately 400 μ m. The refractive index change was measured with the use of He–Ne laser ($\lambda = 633$ nm) and semiconductor laser ($\lambda = 532$ nm). For the definition of refractive index modulation Δn Kogelnik formulae were used by the matching of calculated and experimental angle selectivity contours. The value of Δn was calculated using the following expression [24]:

$$\varphi = \frac{\pi \Delta n H}{\lambda \cos \theta}, \quad (1)$$

where θ is Bragg angle (in our case $\theta = 12.40$ deg.), H is the effective thickness of hologram. The value of φ can be defined from the measured diffraction efficiency η using the following expression:

$$\varphi = k\pi \pm \arcsin \sqrt{\eta}, k = 0, 1, 2, \dots, \quad (2)$$

taking into account the shape of angle selectivity contour.

Thermal treatment of the samples was performed at $T = 350$ –400 °C during 1 h in a muffle furnace (Nabertherm) with program control. Optical density spectra of the glass samples were measured using Lambda 650 (Perkin–Elmer) spectrophotometer. Luminescence and excitation spectra were recorded by LS-55 spectrofluorimeter (Perkin–Elmer). Spectral measurements were performed at room temperature.

3. Computer simulation

In order to elucidate the possible source of the refractive index change, the static dipole polarizabilities of neutral and positively charged silver clusters in their ground state were calculated using response theory based on the time-dependent density functional theory (TDDFT). In recent years a number of experimental [27] and theoretical [28–30] investigations have been reported on the static electric dipole polarizability of neutral silver MCs. On the other hand, Tiggesbäumker et al. [31] have studied experimentally single charged silver MCs of medium size and analyzed their polarizabilities using the sum rule approach. However, to our knowledge, there is no first-principles comparison of the static polarizabilities for subnanosized neutral and cationic silver MCs yet.

In our calculations at the first step, the cluster geometries at the ground state were fully optimized within the Amsterdam Density Functional (ADF) program suite [32] using the Perdew–Becke–Ernzerhof gradient-corrected functional (PBE) and Slater-type orbitals basis set of triple-zeta quality (TZ2P). Then, ground-state polarizability calculations were performed using linear response theory as implemented in the DALTON program package [33] employing the Becke's three-parameter hybrid functional (B3LYP) and effective core potential basis set (SBKJ/C ECP) proposed by Stevens and coworkers [34]. As shown by Labello et al. [35], this basis set could be utilized to achieve a good performance for efficient polarizability calculations on transition metal clusters at the Hartree-Fock level of theory. The mean (isotropic) total polarizability α has been calculated from the polarizability tensor as: $\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$.

By analogy with the Stark (electroabsorption) spectroscopy, the combination of TDDFT with an external static field allowed us to study polarizability of MC in the excited states [36]:

$$E_{exc}(F) = E_{exc}(0) - \Delta\mu F - 1/2\Delta\alpha F^2, \quad (3)$$

where E_{exc} is the excitation energy in presence and without of an external electric field F , $\Delta\mu$ is the dipole moment change and $\Delta\alpha$ is the difference between ground and excited state isotropic polarizabilities, often referred to as the excess polarizability. The calculations of excited-state properties were carried out in ADF program. The excess polarizability $\Delta\alpha$ upon excitation from the ground state to the first unrelaxed (Franck–Condon) dipole allowed excited state of neutral silver tetramer (Ag₄), as an example, have been obtained at the previously optimized ground-state geometry. Polarizability value was evaluated by calculating the excitation energy at zero-field and five different field strengths in the range from 1×10^{-4}

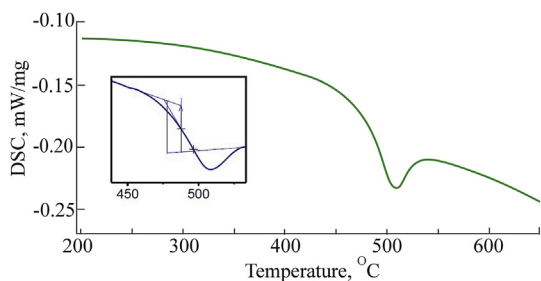


Fig. 1. DSC-plot for samples glass transition measurement. Inset: Part of DSC-plot near T_g . Thin curves describe the method of T_g definition.

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