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Volume Bragg gratings in chloride photo-thermo-refractive glass after femtosecond laser bleaching

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Abstract: We report on the optical properties of volume Bragg gratings in chloride photo-thermo-refractive glass after femtosecond laser bleaching. We show experimentally that irradiation of the gratings with femtosecond laser pulses can expand their transmission into the whole visible range without dramatic decrease of diffraction efficiency. The mechanism of glass bleaching is considered and modulation of refractive index is described in terms of the coupled wave theory for mixed volume Bragg gratings.

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References and links
1. Introduction

Photo-thermo refractive (PTR) glass is a promising optical material for fabrication of volume Bragg gratings (VBGs) and other diffraction optical elements [1–5]. It possesses unique optical properties, high mechanical, chemical, and optical damage resistance. Purely phase holograms recorded in the glass are transparent in wide spectral range and can possess diffraction efficiency up to 99% [4, 5]. It is worth noting that such an incredible performance is caused mostly by the refractive index modulation which can reach values up to \(1 \times 10^{-3}\) [6]. Also high homogeneity of the glass allows fabrication of gratings with large apertures (up to 35x35 mm\(^2\)) and thickness (up to 20 mm). Even larger modulation of refractive index is possible in fused silica (\(4 \times 10^{-3}\)) and LiNbO\(_3\) (\(2 \times 10^{-3}\)), which are also suitable for special applications [7, 8].

Mechanism of hologram recording in this material is based on photo-thermo-induced crystallization process [4, 5]. It is initiated by local refractive index decrease in the UV exposed areas of the glass. Unfortunately, negative refractive index change limits classic PTR glass functionality in the area of wave guiding applications.

We have recently proposed, synthesized and characterized a novel PTR glass composition, which provides positive refractive index change [9, 10]. X-ray diffraction analysis revealed the precipitation of the NaAgCl nanocrystalline phase which is responsible for the positive refractive index change with magnitude of as high as \(8.7 \times 10^{-4}\) [9, 11]. It has been shown that this glass open a way to fabricate the volume mix type Bragg gratings, which possess both refractive index and absorption coefficient modulation. Additional advantage of this type of material is a small - in comparison with the classic PTR glass - size of the crystalline phase that suppresses scattering and improves performance of the gratings with a period smaller than 400 nm [12]. Recently, it was shown that this glass allows fabrication of the mixed volume Bragg gratings, i.e. posses both refractive index and absorption modulation [12]. Unfortunately, the diffraction efficiency of such mixed gratings is limited in agreement with the coupled wave theory [13]. It is caused by decrease of diffraction efficiency with increase of absorption for sinusoidal VBGs [14]. Thus, strong absorption in the visible and near IR range discards this advantage.

Since the modulation of the absorption in the grating fringes originates from the strong surface plasmon resonance of silver nanoparticles (AgNPs) [9, 12], it can be suppressed by photodestruction of the AgNPs. This process was studied extensively during last two decades in different glass matrix including classic PTR glass [15–19]. We have recently shown that the absorption can be significantly reduced by means of the intense femtosecond laser radiation.
without noticeable effect on the NaAgCl volume fraction [11, 20]. In addition it have been demonstrated that fluorescent silver nanoclusters remain in the glass volume after femtosecond bleaching of the AgNPs [11].

In this paper, we examine how the femtosecond laser bleaching affect performance of the VBGs in the chloride PTR glass. In particular, the diffraction efficiency, modulation of the refractive index and the absorption coefficient inside the gratings fringes were measured before and after bleaching.

2. Experimental

For this work silicate glass based on Na₂O-ZnO-Al₂O₃-SiO₂ system with 1.46 mol% concentration of chlorine doped with CeO₂, Sb₂O₃ and Ag₂O was used. The glass was synthesized at ITMO University in fused silica crucible at 1500°C in the environment air. Stirring with a Pt thimble was used to homogenize the liquid. After melting, the glass was cooled down to 500°C, then annealed at glass transition temperature \( T_g = 494°C \) for 1h, and cooled down to room temperature with a rate of 0.15 K/min. Polished sample had size 50x20x1.35 mm. Schedule for the VBGs preparation was equal to that of the previous work [12]. We recorded a series of holograms utilizing horizontally polarized UV radiation (325nm) of the He-Cd laser (TEM00, Kimmon) in the exposure range of 1-12 \( J/cm^2 \). The transmission gratings were recorded using symmetrical transmission optical scheme, i.e. that the grating vector and the surface normal are mutually perpendicular. The angle between recording beams at the sample surface was \( 2\theta = 25° \). Thus the grating period was equal to 750 nm. 8 gratings with size 5x5 mm with different exposure were recorded on glass sample.

Following thermal treatment was conducted in the programmable muffle oven (Neibotherm). Samples were processed close to the glass transition temperature 546°C during 20 hours. This regime allows to achieve maximum refractive index modulation amplitude (RIMA) and absorption index modulation amplitude (AIMA) [12].

Optical density spectra were measured using spectrophotometer (Lambda 650, PerkinElmer) at 200-900nm spectral range with 1 nm step. Characterization of the recorded VBGs was carried out through measurements of the grating selectivity contours at wavelength of the He-Ne laser (632.8 nm).
nm). The angular selectivity contour represents intensity dependence on the deviation of the incidence angle of readout laser radiation from the Bragg conditions in the zeroth or the first order of diffraction. All measurements of the angular dependences were performed at the wavelength of He-Ne laser with horizontal polarization. Although it was far enough from the plasmon resonance of the AgNPs, the absorption was noticeable, i.e. the gratings at this wavelength are still of mixed type. Smaller wavelengths cannot be used due to the strong absorption.

Finally, bleaching of the VBGs was done by Ti:Sapphire femtosecond laser (Integra-C-3.5, Quantronix) with regenerative amplifier, with maximum pulse energy of 3.5 mJ, pulse duration of 120 fs and wavelength of 400 nm. In average 3000 laser pulses with energy 1.4 µm focused to spot with diameter 50 um were used for the bleaching of VBGs.

In addition, pump-probe femtosecond laser system with similar parameters was used to estimate shape modification during laser bleaching of AgNPs. To cover the spectral range of interest in one measurement we employed a multi-color pump-probe setup. The detailed description of the setup can be found elsewhere [21]. The setup consists of 1kHz Ti:Sapphire amplified system delivering pulses with duration of 150 fs at 780 nm fundamental wavelength. As a pump light we used a 390 nm second harmonic generated in BBO crystal. To probe the photoresponse in a broad range we employed a white-light continuum generated in the sapphire crystal. The independent control of polarization of pump and probe beams with half-waveplates allowed us to perform co- and cross polarized measurements of pump induced absorption changes in the sample. By measuring the differential absorption spectra between the intensive pump pulse and the weak probe at different delay times we were able to reveal the full picture of relaxation dynamics in our samples in the requested spectral range.

3. Results and discussions

In order to estimate the ablation threshold and rate of optical density change in highly absorbing chloride PTR glass we performed femtosecond pump-probe measurements. The dependence of optical density on the energy and polarization of the femtosecond pump pulses presented in Fig. 1(a) demonstrates that a single pump pulse produces optical anisotropy in the sample. This anisotropy manifests itself as different change in the optical density at wavelength 550 and 600 nm when probe and pump pulses are co- and cross-polarized. This is because when the pump pulse wavelength is close to the surface plasmon resonance of AgNPs, the shape of nanoparticles becomes elliptical at small exposure (compared with [16,17]). It is worth noting, however, that it remains unclear at what extent the modification of the silver core shape affects on distribution of crystal phase around each nanoparticle. However, it is out of scope for the present article.

Figure 1(b) shows optical density spectra of chloride PTR glass with recorded VBG before and after full femtosecond laser bleaching of the sample. Before the bleaching glass possess high absorption (>100 cm⁻¹) at whole UV and visible spectral range. It mostly related with...
surface plasmon resonance band absorption at 450 nm wavelength. Inset to Fig. 1(b) shows optical density spectrum for relatively short thermal treatment duration (10 hours at 546°C) when AgNPs concentration is rather low. One can see that laser bleaching of the VBG results in a considerable decrease of optical density over the visible spectral range.

The process of photodestruction of metallic nanoparticles is well-known for different types of glass [16,22]. The absorption of ultrashort pulse energy leads to local heating and explosion of the metallic particle [23]. However, the particle species cannot move far from the origin due to limited space. Figure 2 shows that initially metallic nanoparticle is surrounded by NaAgCl shell with larger refractive index [9,11]. The femtosecond bleaching transforms AgNPs into closely spaced silver clusters, which can be bought back and restore the nanoparticle via thermal treatment within several minutes [11,16].

Since absorption caused by plasmon resonance in AgNPs is absent, we assume that after the bleaching procedure a grating become purely phase modulation. It has been previously revealed that VBGs in chloride PTR glass are of mixed type, i.e. in the glass volume both absorption and refractive index are modulated [12]. According to the coupled wave equations (1-3) the coupling constant ($\chi$) responsible for the energy transfer between reference (R) and signal (S) wave consists of RIMA ($n_1$) and AIMA ($a_1$) thus elimination of the one leads to the natural decrease of the coupling efficiency. Coefficients $\Gamma$, $c_R$ and $c_s$ are described in detail by Collier [24].

\[ c_R R' + \alpha R = -i \chi S \]  
\[ c_s S' + (\alpha + i \Gamma) S = -i \chi R \]  
\[ \chi = \frac{\pi n_1}{\lambda} - \frac{i a_1}{2} \]  
\[ \eta_1(\theta) = \frac{\exp(-2\alpha T/\cos \theta)}{z_0} \left[ \frac{\theta^2 + z_0}{2} \cosh \left( \frac{\sqrt{2\alpha T} \cos \psi_0}{\cos \theta} \right) - \frac{\theta^2 + z_0}{2} \cos \left( \frac{\sqrt{2\alpha T} \sin \psi_0}{\cos \theta} \right) \right] \]  
\[ + \sqrt{\frac{2\alpha T}{\sin \psi_0}} \sin \psi_0 \sin \left( \frac{\sqrt{2\alpha T} \cos \psi_0}{\cos \theta} \right) - \sqrt{\frac{2\alpha T}{\sin \psi_0}} \cos \psi_0 \sin \left( \frac{\sqrt{2\alpha T} \sin \psi_0}{\cos \theta} \right) \]  
\[ z_0 = \theta^2 + 4 \left( \frac{\pi n_1}{\lambda} \right)^2 - \left( \frac{i a_1}{2} \right)^2 + \left( \frac{8\alpha_1}{\lambda} \frac{\pi n_1}{2} \right)^2 \]  
\[ \theta = \frac{4\pi n_0 \sin \theta_b}{\lambda} (\sin \theta - \sin \theta_b) \]  
\[ 2\psi_0 = \arccos \left\{ \frac{\phi^2 + 4 \left( \frac{\pi n_1}{\lambda} \right)^2 - \left( \frac{i a_1}{2} \right)^2}{z_0} \right\} \]  
where: $n_1$ is RIMA, $a_1$ is AIMA, $\lambda$ is reconstruction wavelength, $T$ is hologram efficient thickness, $\theta$ is angle of reconstruction, $\alpha$ is absorption coefficient, $\theta_b$ is Bragg angle, $n_0$ is refractive index of the material.

Since the first order diffraction selectivity contour looks similar for both phase and amplitude-phase holograms with the same coupling, its analysis does not allow one to distinguish RIMA and AIMA contributions to the coupling constant. On the other hand, the contour shape in the zeroth diffraction order depends on both coupling constant and AIMA magnitude. Thus, the comparison of the gratings before and after bleaching was made through the analysis of the zeroth order. Measured angular selectivity contours for VBGs in chloride PTR glass are presented at Fig. 4.
One can observe from Fig. 3(a) that the shape of the zero diffraction order contour before bleaching is asymmetric relative to Bragg angle, which directly points out at mixed nature of the grating [12, 14, 25]. After the bleaching procedure the contour becomes symmetric as shown at Fig. 3(b). These factor indicates that there is no modulation of the absorption in the grating anymore and it became purely phase. The change of the contour shape indicates decreasing of the coupling constant, i.e. the modulation became lower as it was expected.

Further analysis includes the estimation of the RIMA and AIMA [12–14, 25]. The calculation of these parameters was carried out by fitting of the contours obtained in the experiment with those predicted by the theory (Fig. 4, red curves). Equation 4 describes diffraction efficiency dependence on the reference wave incidence angle for mixed and pure phase gratings. In case of pure phase gratings $a_1$ was set to zero.

Since we know the gratings period and readout wavelength along with thickness and refractive index of the sample, the only variables are the modulation amplitudes of the absorption coefficient and refractive index.

![Fig. 3](image-url)  
(a) Experimental angular selectivity contours before (a) and after (b) femtosecond laser bleaching.

![Fig. 4](image-url)  
(a) RIMA before and after laser bleaching of VBGs. (b) Difference of RIMA before and after laser bleaching (curve with squares) and AIMA before laser bleaching (curve with circles)
The performed fitting of the experimental results allows us to evaluate RIMA magnitude for each grating in the exposure range of 1-12 J/cm$^2$ before and after bleaching (Fig. 4(a)). Saturation of the RIMA value at the exposures approximately above 6 J/cm$^2$ indicates that the volume fraction of the crystalline phase along with the NP concentration is the same. Thus, we utilized all available silver and chlorine in the grating fringe. Also it is clear that values of RIMA decreased after bleaching for all exposures. However, the magnitude of this decrease depends on the exposure. Maximum value of the refractive index modulation is reduced from $8.6 \times 10^{-4}$ down to $5.1 \times 10^{-4}$, i.e. it becomes almost two times lower after bleaching. One can see from Fig. 4(b) the difference in the RIMA before and after bleaching and the AIMA vs exposure shows similar dependence on the exposure. It indicates that additional RIMA, which is lost during the bleaching process, is inflicted by the presence of the AgNPs in the grating fringes and the value is determined by their concentration. Even though the fall of the RIMA magnitude at the maximum is significant, its value was still sufficient to enhance diffraction efficiency from 25% to 86% for 1 J/cm$^2$ UV exposure.

4. Summary

In conclusion, we have demonstrated that although the femtosecond laser bleaching of chloride PTR glass with VBGs results in decrease of refractive index modulation magnitude from $8.6 \times 10^{-4}$ to $5.1 \times 10^{-4}$, it is still sufficient for VBGs operation. We demonstrated that after the bleached gratings become purely phase one, which is capable to achieve high diffraction efficiency at optimal recording conditions and appropriate sample thickness. The transmission range of the VBGs expanded considerably in visible opening avenues towards using them for high-power laser applications. Moreover, small size of the crystalline phase in combination with absence of absorption in the visible region boosts the performance of such gratings at the small periods.

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