Gradient of refractive index (GRIN) effect in photo-thermo-refractive glass

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Received 22 October 2014; revised 12 January 2015; accepted 15 January 2015; posted 16 January 2015 (Doc. ID 225471); published 23 February 2015

Photo-thermo-refractive (PTR) glass is a photosensitive multicomponent silicate glass containing photosensitive agents such as cerium and silver. Photoinduced crystalline phase precipitation results in refractive index variations in exposed areas of PTR glass, which has been successfully used for phase hologram recording. Photosensitivity being the result of the partial absorption of the exposing radiation by cerium ions, it results in a gradient of refractive index (GRIN) along the exposure beam propagation. This GRIN is a parasitic effect that deteriorates the parameters of some types of volume Bragg gratings because of the beam deflection they produce. In this paper, the evolution of GRIN is investigated as a function of the dosage of UV exposure and the thermal treatment duration. We show that GRIN is a deterministic process that can be easily modeled and predicted using basic optics and glass science equations.

OCIS codes: (300.1030) Absorption; (160.5335) Photosensitive materials.
http://dx.doi.org/10.1364/AO.54.001587

1. Introduction

Photo-thermo-refractive (PTR) glass is a multicomponent silicate glass that undergoes a refractive index change (RIC) after UV exposure and thermal treatment [1,2]. Based on this photosensitivity, high-efficiency volume Bragg gratings have been recorded in this glass [3] and successfully used for laser beam control [4]. One of the very promising laser applications is ultrashort pulse stretching and compression by means of chirped volume Bragg gratings (CBGs) [5]. These gratings have a period that is linearly chirped along the beam propagation direction. Due to this variation in period, different spectral components of a pulse incident on the grating along the Z direction are reflected by different parts of the grating along its thickness. The optical path length difference between the different spectral components leads to a wavelength-dependent group delay. A stretched pulse being launched to the same grating from the opposite direction would be compressed to its original state [5]. Detailed studies of the principles of pulse stretching and compression by a single volume diffractive grating with a variable period and their use for chirped-pulse amplification can be found in [5–10]. Using this technology, stretching of ultrashort pulses with widths exceeding 100 to 1000 ps and high-efficiency re-compression to near-transform-limited pulse duration has been demonstrated.

There are multiple parameters that will influence the quality of the beam diffracted by volume Bragg gratings and more precisely on CBGs through the generation of sidelobes [11,12]. One of these effects is the one studied in this paper, i.e., the gradient of refractive index or GRIN. Actually, CBGs are fabricated by holographic recording of plane parallel fringes with linearly increasing period in the Z direction (Fig. 1).

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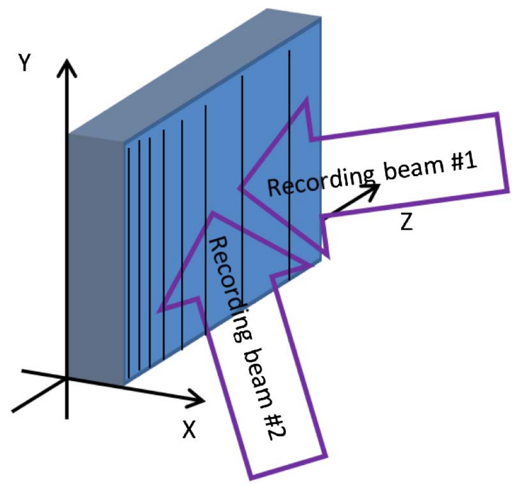

Fig. 1. Geometrical configuration of a holographically recorded CBG.

The recording beams propagate in the X–Z plane and are collimated in this plane (Fig. 1). The angle between the recording beams in plane X–Z determines the average period of the grating. The angles of divergence and convergence of the recording beams determine the spatial chirp of the grating period. The photosensitive process is triggered by absorption of UV radiation by cerium ions. Therefore, it appears a gradient of absorbed dosage that will be converted into a GRIN along the X direction of the CBGs (Fig. 1). This GRIN then produces a mirage effect. Due to the different beam paths of each spectral component, each of them will be deflected to a different place, finally impacting the quality of the diffracted beam. More precisely, Moser and Havermeyer have shown that GRIN will result in the elongation of the beam in the vertical direction after diffraction on a CBG [12]. The authors have also shown that it is, however, possible to compensate this effect by pressing the CBG and deforming it. Actually, GRIN results in a vertical tilt of the grating vector along the CBG's thickness that can be expressed in a term of a radius of curvature (R_{GRIN}) that is equal to

$$R_{\mathrm{GRIN}} \approx \frac{1}{\mathrm{GRIN}}. \tag{1}$$

Therefore by pressing it, is possible to mechanically warp the glass and create a physical deformation of the glass which equivalent radius of curvature will compensate the one of the GRIN. However, pressing induces other parasitic effects, such as depolarization due to the mechanically induced birefringence. Thus, mitigating, and not compensating this effect implies understanding the mechanisms of GRIN in PTR glass as well as what are the controlling parameters. In this paper, we therefore present a thorough study of the origin of GRIN as well as of the parameters that control its amplitude.

2. Experimental

To experimentally study GRIN, five Gaussian stripes with increasing dosages of 0.3, 0.6, 0.9, 1.2, and 1.5 $\mathrm{J/cm^2}$ were recorded in several 6 mm thick PTR glass plates. Exposure was carried out using a HeCd laser at 325 nm, 4 mW, $FW1/e^2$ of 0.55 mm. Stripes were obtained by scanning the PTR glass sample in the laser beam at constant speed, this speed controlling the dosage of UV exposure. The PTR glass samples were doped with 0.01 mol. % of cerium oxide. Due to absorption of cerium at 325 nm, these samples exhibited a gradient of absorbed dosage that resulted in a GRIN through the thickness of the glass that could be detected and measured after thermal development. These glass samples were then heat-treated using a classical heat-treatment schedule that allows achieving high RIC with low losses, i.e., for 100 min at 485°C (nucleation) followed by a second heat treatment at 515°C for 30, 60, and 90 min.

To characterize the lateral gradient of average refractive index (GRIN) in these samples, a specific procedure was implemented. It is based on a custom liquid-cell shearing interferometer that was developed a few years ago [13]. Samples were cut into pencil-like geometries, parallel to the y–z plane, with thickness of ~2 mm (Fig. 2, right) and double-side polished to flatness of $\lambda/2$ at 633 nm. These samples exhibit a laterally varying refractive index (GRIN) resulting from gradual attenuation of actinic radiation in the glass plate (Fig. 2).

These samples were then inserted inside the shearing interferometer and a typical interferogram is shown in Fig. 3. Along the width of the interferogram, the fringe shift linearly increases (or decreases) according to the magnitude of the GRIN. A specific program was developed in order to locally analyze the fringe shift and therefore to locally extract the RIC dependence on dosage as defined by the Gaussian profile [13]. Then, by extracting the evolution of the maximum RIC versus sample position and knowing the aperture size, the evolution of the RIC on the glass thickness could be obtained

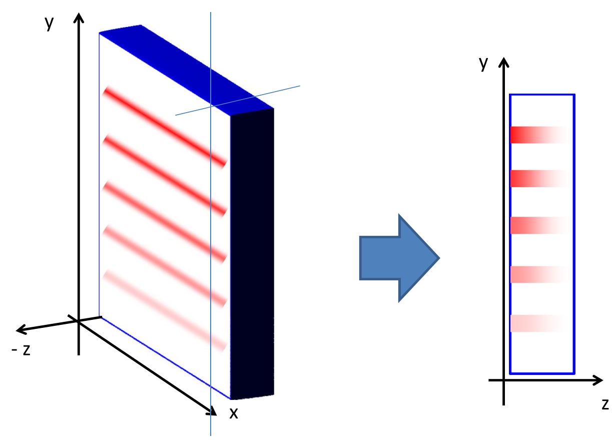

Fig. 2. Scheme of the geometry of the samples exposed to UV stripes in Z direction with different dosage that was used for studying gradient of average refractive index (GRIN) in PTR glass.

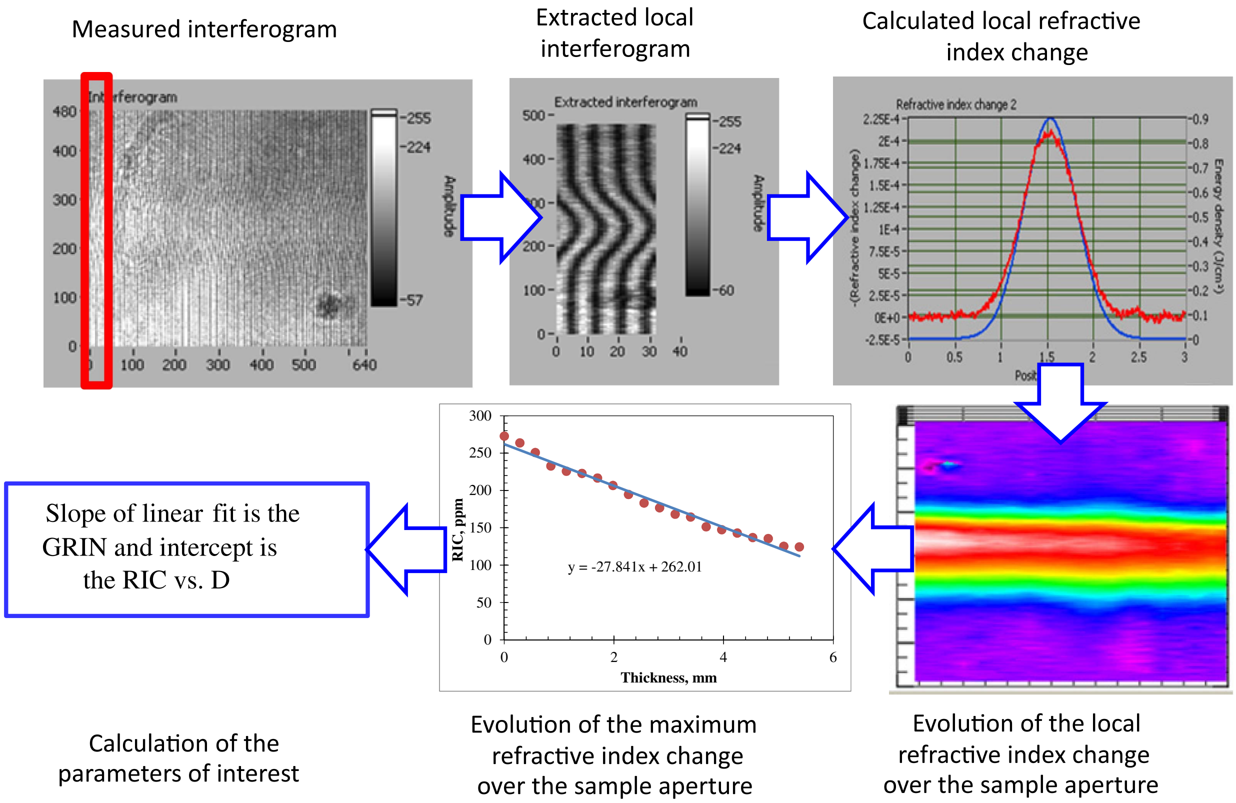

Fig. 3. Description of the procedure used for studying GRIN in PTR glass.

(Fig. 3). Fitting of this curve with a linear function allowed extracting two parameters: the slope gave the GRIN while intercept gave an accurate value of the RIC at the dosage of UV exposure.

3. Experimental Study of the Parameters Influencing GRIN

The previously described experimental procedure was used to analyze the evolution of the gradient of induced refractive index (GRIN) in a PTR glass plate resulting from the attenuation of the exciting UV radiation in PTR glass. The evolution of GRIN on dosage of UV exposure and on thermal treatment duration was studied in glasses containing 0.01 mol.% of cerium oxide. Figures 4(a) and 4(b) show the dependence of GRIN and of the maximum refractive index at the front face of the exposed sample on dosage of UV exposure for different thermal treatment durations at 515°C.

One can see that while maximum RIC monotonically increases with an increase of either the dosage of UV exposure or the thermal treatment duration, GRIN shows a maximum for a dosage between 0.3 and 1 J/cm^2 when the thermal treatment duration is longer than 60 min at 515°C.

It is also seen that the curves of GRIN versus dosage after 71 and 102 min at 515°C intercept at 0.6 J/cm^2, proving that GRIN is a complex function of dosage of UV exposure and thermal treatment duration. Another way to present these data consists in combining Figs. 4(a) and 4(b) and plot GRIN versus maximum RIC (Fig. 5). In first approximation, GRIN appears to be an independent function of dosage and thermal treatment duration, but more generally a function of the maximum RIC. For maximum RIC below 500 ppm, GRIN is linearly increasing with an increase of the maximum RIC.

Then GRIN reaches a maximum in the 500–700 ppm region before quickly decreasing when maximum RIC saturates. Moreover, for a given RIC, GRIN cannot be severely modified by changing the dosage or the thermal treatment procedure.

In order to understand if this process is a deterministic one, a model of GRIN based on the measured photosensitivity curve was developed. For each GRIN measurement, the RIC measured at the front face of the glass corresponds to the RIC that can be achieved for a given incident dosage of UV exposure and thermal treatment temperature and duration. Using this data allowed extracting the dependence of the RIC on dosage of UV exposure for each thermal treatment (Fig. 4(a)). Then, these curves were modeled using a hyperbolic function (Fig. 4(a)), as it was shown that such function perfectly describes the dosage dependence of RIC in PTR glasses [13,14]:

$$\Delta n(D,t,T) = \frac{\Delta n(0.9\ \mathrm{J/cm^2},t,T)(0.9+\varepsilon(t,T))D}{0.9(D+\varepsilon(t,T))}. \quad (2)$$

The two controlling parameters $\Delta n(0.9\ \mathrm{J/cm^2},t,T)$ and $\varepsilon(t,T)$ were then extracted for further modeling (Table 1).

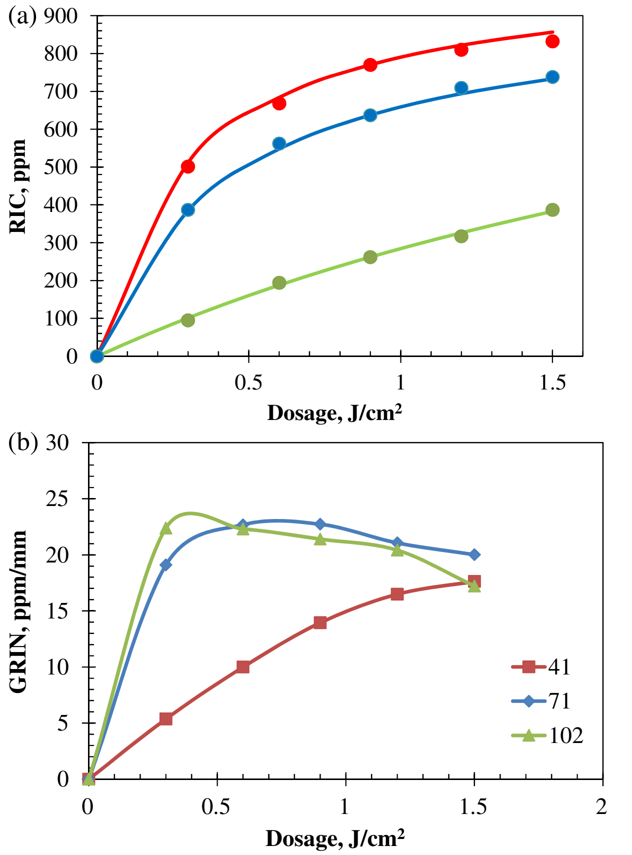

Fig. 4. (a) Refractive index change dependence on dosage of UV exposure at 325 nm. Points refer to experimental data and continuous curves to the hyperbolic fit. The green curve refers to a sample developed for 30 min at 515°C, blue curve to a sample developed for 60 min at 515°C, and red curve to a sample developed for 90 min at 515°C. (b) Evolution of the GRIN on dosage of UV exposure for different durations (in minutes) of thermal treatment at 515°C.

Absorption at 325 nm in the characterized glass is equal to $\alpha = 0.74\ \mathrm{cm}^{-1}$. It is therefore possible to calculate the distribution of dosage ($D(z)$) through the glass thickness z:

$$D(z) = 0.9 \cdot 10^{-\alpha z}. \tag{3}$$

Combining Eqs. (2) and (3) allows calculating the dependence of the refractive index throughout the glass sample and therefore to model the GRIN. The measured and calculated GRIN are overlapped in Fig. 5. Agreement between theory and experiment is fair, proving that GRIN is not only determined by the glass absorption but by a combination of the glass absorption and photosensitivity curve.

Table 1. Parameters Extracted from the Fit of the Refractive Index Change Versus Dosage Using an Hyperbolic Function

Parameters	30 min	60 min	90 min
$\Delta n(0.9\ \mathrm{J/cm^2}, t, T)$	262	637	770
$\varepsilon(t, T)$	3.39	0.44	0.30

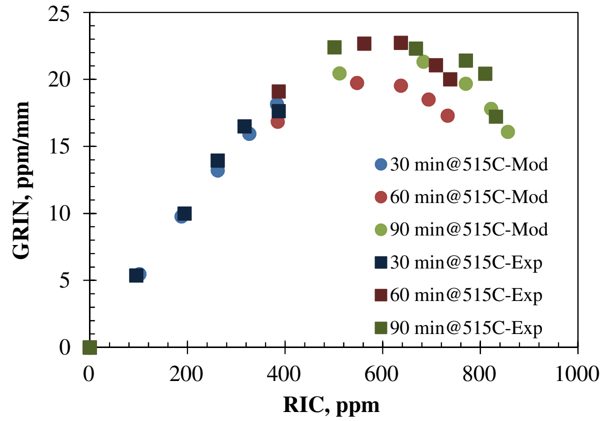

Fig. 5. Evolution of the GRIN on maximum refractive index change in PTR glass. Circles refer to measured data and squares to modeled data.

The shapes of the GRIN dependence on RIC were further studied and explained. First of all it was shown that for a RIC below 500 ppm, GRIN is almost a linear function of the RIC. This can be easily explained by the fact that for low RIC, the dependence of RIC on dosage is close to being linear. This feature for the case of 400 ppm RIC is illustrated in Fig. 6. Therefore, whatever the dosage of UV exposure and the associated thermal treatment schedule, GRIN will always be proportional to the gradient of dosage of UV exposure through the glass thickness. For higher RIC above 600 ppm, GRIN tends to decrease with an increase of the RIC. This effect is due to the appearance of a saturation of the dependence of RIC on dosage which results in a lower decrease of the refractive index throughout the PTR glass thickness and therefore a lower GRIN (Fig. 7).

4. Development of a Model for GRIN

Due to the high impact of GRIN on volume Bragg gratings properties, a model of GRIN was developed.

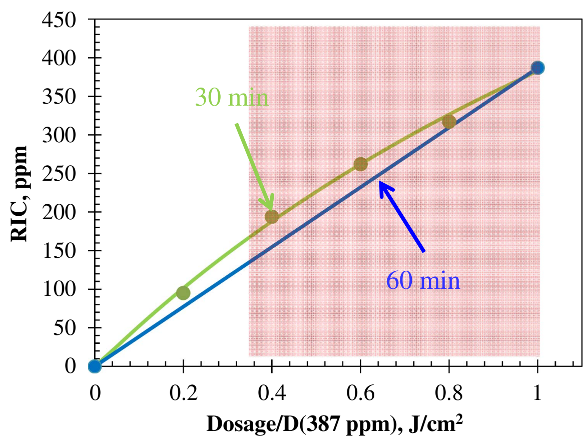

Fig. 6. Dependence of the refractive index change (RIC) on normalized dosage in a UV-exposed PTR glass after development for 30 and 60 min at 515°C. For a 400 ppm refractive index change, the dependence of RIC on dosage is close to being linear whatever the thermal treatment duration. Points are experimental data and lines their associated exponential fits.

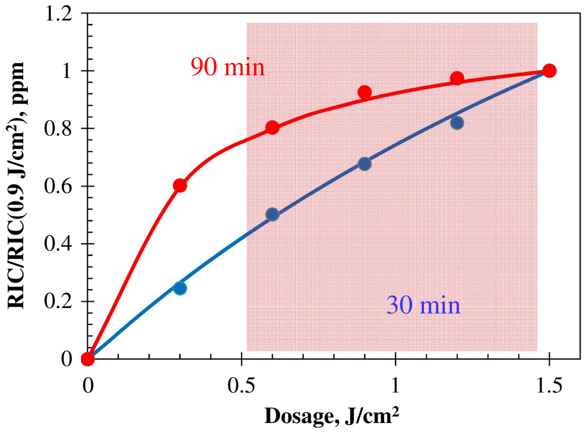

Fig. 7. Dependence of the normalized refractive index change (RIC) on a UV-exposed PTR glass after development for 30 and 90 min at 515°C. Due to saturation GRIN decreases with an increase of the refractive index change. Points are experimental data and lines their associated exponential fits.

This model allows predicting GRIN for any dosage of UV exposure followed by any thermal treatment temperature and duration. Previously it was shown that the dependence of the photoinduced RIC on UV dosage and thermal treatment duration and temperature can be fully modeled using simple equations [13,14]. First it was shown that the refractive index dependence ($\Delta n(D, t, T)$) on dosage (D) follows an hyperbolic function shown in Eq. (2), where $\Delta n(0.9\ \mathrm{J/cm^2}, t, T)$ and $\varepsilon(t, T)$ are two parameters that are time and temperature dependent. We have shown that the first parameter ($\Delta n(0.9\ \mathrm{J/cm^2}, t, T)$) follows the JMAK equation [14]:

$$\Delta n(0.9\ \mathrm{J/cm^2}, t, T) = \Delta n_{\max}(0.9\ \mathrm{J/cm^2}, T)(1 - \exp(-K(T)t^{1.5})), \tag{4}$$

where $\Delta n_{\max}(0.9\ \mathrm{J/cm^2}, T)$ is the RIC at saturation and follows a linear dependence on temperature:

$$\Delta n_{\max}(0.9\ \mathrm{J/cm^2},\ T) = 5.22(T°\mathrm{C} - 460) + 777, \tag{5}$$

and $K(T)$ is a thermodynamic parameter that follows a Boltzmann law:

$$K(T) = K_0 \times \exp\left(\frac{E_K}{RT}\right). \tag{6}$$

The second parameter $\varepsilon(t, T)$ follows an exponential function:

$$\frac{1}{\varepsilon(t, T)} = \exp(\beta(T)t), \tag{7}$$

while $\beta(T)$ is a thermodynamic parameter that follows a Boltzmann law:

$$\beta(T) = \beta_0 \times \exp\left(\frac{E_\beta}{RT}\right). \tag{8}$$

To perform the GRIN modeling, the kinetics parameters ($K_0, \beta_0 \ldots$) were supposed to be identical for all glass melts and equal to the one presented in [14] (even if it is known that there are some fluctuations of the refractive index kinetics from melt to melt). Using linear combinations of the set of equations from (3) to (8), simple equations that describe the dependence of GRIN on PTR glass and processing parameters could be extracted. First, at constant dosage (0.9 J/cm^2) and temperature (515°C) of development, GRIN can be expressed as

$$\mathrm{GRIN}(\alpha, t) = \frac{\Delta n(0.9, t)}{L}\left(\frac{\varepsilon(t)(1 - 10^{-\alpha L})}{0.9 \times 10^{-\alpha L} + \varepsilon(t)}\right). \tag{9}$$

From this equation, it can be shown that the shape of the dependence of GRIN on RIC has very low dependence on the absorption at 325 nm, the only changing parameter being the amplitude of the GRIN. The dependence of GRIN amplitude at maximum on the absorption at 325 nm is shown in Fig. 8. One can see that GRIN is linearly increasing with the cerium concentration.

Dosage of UV exposure is another way to control the GRIN. At constant absorption (0.73 cm^{-1} at 325 nm) and temperature of development (515°C), the dependence of GRIN on dosage can be expressed as

$$\mathrm{GRIN}(D, t) = \frac{\Delta n(D, t)}{L}\left(\frac{\varepsilon(t)(1 - 10^{-\alpha L})}{D \times 10^{-\alpha L} + \varepsilon(t)}\right). \tag{10}$$

From this equation, it can again be shown that the shape of the dependence of GRIN on RIC has no dependence on the dosage of UV exposure, the only changing parameter being the amplitude of the GRIN. We plotted in Fig. 9 the dependence of GRIN amplitude at maximum on the dosage of UV exposure. One can see that GRIN is decreasing with an increase of the dosage of UV exposure. This result is easily explained by the fact that increasing the dosage results in a higher saturation of the dependence of RIC on dosage that minimizes the refractive index decrease through the glass thickness.

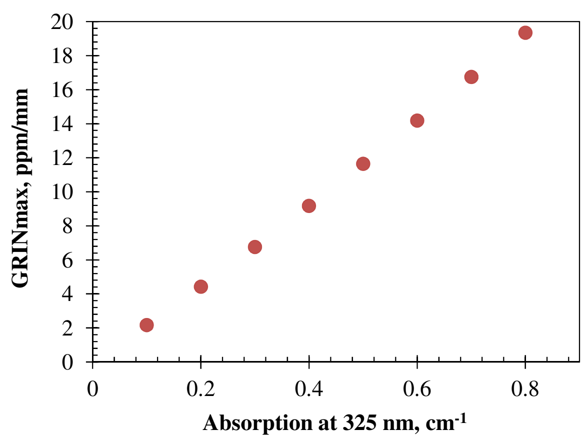

Fig. 8. Dependence of GRIN amplitude at maximum on the absorption at 325 nm.

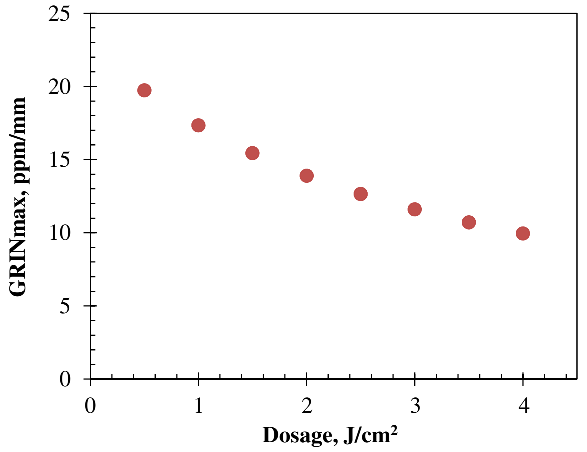

Fig. 9. Dependence of GRIN amplitude at maximum on the dosage of UV exposure.

Finally, the third controlling parameter is the temperature of thermal treatment. At constant absorption ($0.73\ \mathrm{cm}^{-1}$ at 325 nm) and dosage of UV exposure ($0.9\ \mathrm{J/cm}^2$), the dependence of GRIN on temperature of thermal treatment can be expressed as

$$\mathrm{GRIN}(T,t) = \frac{\Delta n(0.9,T,t)}{L}\left(\frac{\varepsilon(t,T)(1-10^{-\alpha L})}{D\times 10^{-\alpha L}+\varepsilon(t,T)}\right). \tag{11}$$

From this equation, it can again be shown that both the shape and the amplitude of the dependence of GRIN on RIC will depend on the temperature of thermal treatment. The dependence of GRIN on RIC for different temperatures of thermal treatment was plotted in Fig. 10. One can see that GRIN amplitude is decreasing with a decrease of the thermal treatment temperature and that saturation and decrease of GRIN on RIC appears faster. This result can be explained by the fact that maximum refractive index at saturation that can be achieved in PTR glass linearly depends (in first approximation) on the temperature of thermal treatment; the lower the thermal treatment temperature, the lower the RIC at saturation [14,15].

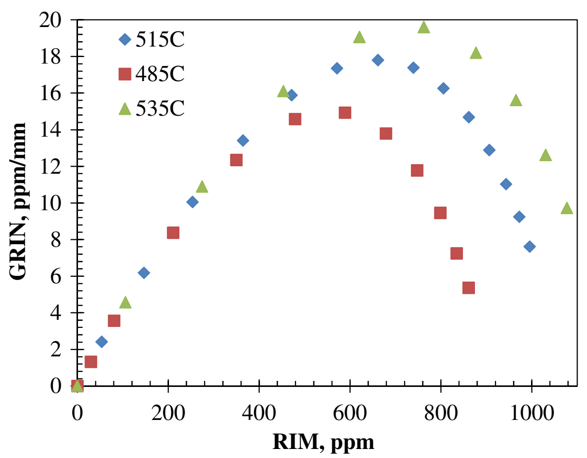

Fig. 10. Dependence of GRIN on refractive index change for different temperatures of thermal treatment.

In conclusion, we have seen that four main parameters will influence the level of GRIN, i.e., the cerium concentration and its associated absorption at 325 nm, the dosage of UV exposure, the temperature of thermal treatment, and the thermal treatment duration.

5. Conclusions

A detailed study of the GRIN in PTR glass was presented. GRIN was shown to be a deterministic process that combines the effect of absorption of cerium ions and the resulting gradient of dosage with the dependence of the RIC on dosage. GRIN can be controlled by several parameters (cerium concentration, dosage of UV exposure, thermal treatment duration and temperature), but for a given cerium concentration, GRIN is more generally dependent on the RIC. Finally, a model that allows predicting GRIN for any combination of the previously cited parameters was developed.

The work was partially supported by Navy contracts NN00024-09-C-4134 and N68335-12-C-0239 and HEL JTO contract W911NF-10-1-0441. The authors want to thank Larissa Glebova for providing PTR glass, Karima Chamma for preparing the PTR glass samples, and Vadim Smirnov for the very fruitful discussions.

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