Change of self-focusing behavior of phosphate glass resulting from exposure to ultraviolet nanosecond laser pulses

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Abstract: The self-focusing characteristic of 355 nm, 3.3 ns pulses propagating through phosphate glass samples is found to significantly change during repeated exposure. The results indicate this change is related to the formation of color centers in the material as well as the generation of a transient defect population during exposure to the laser pulses. A model is used to fit the experimental data and obtain an estimated range of values for the modified linear and nonlinear indices of refraction.

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References and links

1. Introduction

Self-focusing is typically caused by the nonlinear term of the index of refraction ($n_2$) and becomes significant under exposure of materials to intense laser pulses, typically with ultrashort pulses. Various methods have been developed to perform the measurement of $n_2$ such as the z-scan method [1]. The theory of self-focusing was well understood [2, 3] soon after the advent of high power lasers and experimental confirmation of related effects were extensively studied thereafter. This process is a considerable limiting factor in the operation of high power or intensity laser systems, such as in large aperture laser systems for inertial confinement fusion, and in long distance fiber communication applications. In particular, self-focusing can cause laser-induced damage of the material but also contributes to the lowering of the threshold of other nonlinear processes, such as stimulated Raman and Brillouin scattering.

Phosphate and silicate glasses are some of the most important optical materials in high power laser systems [4]. Silicate glasses are most often used in the manufacturing of optical elements that require transparency in the ultraviolet (UV) spectral region. On the other hand, phosphate glasses are used in a variety of optical components but most commonly as a host material for doping ions for color filters or gain medium after doping with a lasant ion (such as neodymium). A characteristic behavior of phosphate glasses is the formation of color centers under exposure to ultraviolet light, commonly referred to as solarization [5]. High energy photons cause the release of electrons and holes, which are subsequently trapped by precursors in the matrix, leading to the formation of electron and hole defect centers. These defect centers cause a red-shift in the UV absorption band from about 300 nm to above 400 nm. It has been previously reported that defects can increase the second-order optical nonlinearity and change the refractive index in silica glasses implemented via a combination of thermal poling and defect generation such as via exposure to x-ray, electron-beam or UV laser irradiation [6–8].

The motivation for this work is to investigate if transient defects (in addition to permanent defects) formed in optical materials during exposure to high power laser pulses can significantly affect beam propagation. The formation of transient defects in various technologically important optical materials under such excitation conditions is well documented in the literature but their role in beam propagation (in addition to transmission loss) has not been explored. Such effects become increasingly important as the repetition rate of high power lasers is continuously increased in order to generate higher output average laser power. As a result, defect generation and accumulation (especially when the lifetime of the generated defects is on the same order or larger than the inverse of the repetition rate of the laser) become increasingly important. Phosphate glasses are known to create defects under UV exposure [5] and therefore, they represent a good model medium to study the relevant possible phenomena.

In this work, we investigate the propagation of small beam, 355 nm laser pulses in two phosphate glasses as a function of the beam average intensity and material exposure to these laser pulses. A fused silica sample was also used as reference. The results suggest a change of the beam self-focusing behavior in phosphate glasses, which is attributed to a change of the refractive index that is directly related to the population of transient and residual defects in the material. These transient defects in phosphate glasses can increase the nonlinearity by orders of magnitude. This work provides new knowledge on the behavior of these materials under high power UV excitation that can be of importance in their application under relevant excitation conditions for high power laser applications or in optical and optoelectronic devices.

2. Experimental design

The experimental system is shown in Fig. 1. It involves a Nd:YAG laser system operating at 355 nm (third harmonic) having about 3.3 nanosecond temporal duration at half width at half maximum (HWHM). The laser power and the pulse repetition rate were computer controlled.
and were adjusted as needed for the execution of the experiment. The repetition rate was set at 0.2 Hz to allow any thermal energy deposited in the location of laser exposure to diffuse in the material before the arrival of the next pulse. The laser beam was focused using a nominally 1-meter focal length lens. Fused silica plates were used to divert part of the beam first to an energy meter for pulse-to-pulse energy measurement and thereafter to the reference arm of our diagnostic instrumentation. The samples are positioned at the focal point of the beam. The beam profile at the output of the sample was recorded using a CCD camera after the output plane was imaged on the camera using a 6.5 X magnification lens system. In this arrangement, 1 pixel on the CCD camera captures the image of about 1 µm² on the output surface of the sample. The reference arm is configured using identical instrumentation to record the beam profile at the same location along the beam propagation path without the presence of the sample.

The two CCD cameras recording the input and output beam profiles were calibrated using the following two steps: In the first calibration step, an energy meter was positioned at the location of the sample. Subsequently, 20 pulses were recorded by the reference (input) CCD camera along with the corresponding values of the energy of the pulses as recorded by the energy meter. This enabled the correlation of the counts recorded by the reference CCD to the energy recorded by the energy meter (counts per unit energy), thus the energy reaching the sample. This also enabled the estimation of the fluence at each location within the beam profile recorded by the reference camera. In the second calibration step, the sample was removed and 20 pulses were simultaneously recorded by the two CCD cameras capturing the (same) beam profile at the sample location. This step was repeated for various laser pulse energies covering the entire range of energies used in the experiments. This enabled the calibration of the second camera in terms of counts per unit energy (using the first camera as reference) and subsequently the estimation of the fluence at each location within the beam profile recorded by the output CCD camera. This configuration enabled us to monitor a) the energy and spatial profile of the input beam, b) the relative intensity of the output beam compared to the input (transmittance) and, c) the beam profile and its modification due to propagation inside the sample. These parameters also allow us to evaluate the peak intensity of the output beam if there was no distortion by its propagation inside the sample, which is referred to as “reference peak fluence”. The beam profile had a nearly Gaussian shape with a beam radius at 1/e of peak intensity of about 48 µm. The beam-to-beam stability exhibited modulation in both, the spatial dimensions of the beam and at the location of the center of the beam. Since the profiles of all pulses were recorded by the two CCD cameras, we were able to monitor the effect of these variations in the experimental data as discussed later.

Fig. 1. Schematic depiction of the experimental system. Images show in gray scale the entrance and exit beam images at equi-distant planes from the lens corresponding to the exit plane of the sample in the presence of self-focusing.
Samples from three materials were used in this work. The first two were phosphate glasses, referred to as LHG-8 and LG-770, manufactured by Hoya and Schott, respectively. Detailed information on these materials is provided in Ref. 9. These materials are used as laser glasses in the main amplifiers of the National Ignition Facility laser [4] using an Nd-doping density of $4.2 \times 10^{20}$/cm$^3$. However, in order to avoid the absorption of the Nd doping ions at the excitation wavelength of 355 nm, the doping with Neodymium ions was replaced by Lanthanum ions, which leads to a transparent material with minimal absorption (of about 2%) at 355 nm. In addition, the LHG-8 glass was doped with Copper at about 0 – 1 mole% (< $2.7 \times 10^{20}$/cm$^3$) with the Cu$^{2+}$ oxidation state dominating the absorption characteristics of the material. As a result, the UV absorption edge is located in the 300-350 nm range with about 5% absorption at 355 nm while a second broad absorption band located in the near infrared range is due to the Cu$^{2+}$ ions [9]. The samples were cut to about 4-mm thick sections so that their thickness is more than an order of magnitude smaller than the Raleigh range (which is estimated to be about 5.9 cm) to achieve a nearly collimated propagation of the focused beam through the sample. In addition, a fused silica sample was used as a reference material under similar excitation conditions. The literature value for the nonlinear refractive index in fused silica is $3.6 \pm 0.64 \times 10^{-7}$ cm$^2$/GW [10] while the corresponding values for the LHG-8 and LG-770 samples are $3.13 \times 10^{-7}$ cm$^2$/GW and $2.85 \times 10^{-7}$ cm$^2$/GW, respectively [4].

3. Experimental results

Figure 2 shows the spatial profiles of the transmitted pulses through sample LG-770. The first profile was obtained prior to exposure of this site to any 355 nm laser pulses (first exposure pulse on a pristine site of the material). The second profile was obtained after this site was previously exposed to 300 pulses of about the same energy. This pre-exposure was used in order to saturate the solarization of this site prior to performing this set of measurements. It must be noted that the laser beam pointing fluctuations result in exposure (and solarization) of an area of the sample over a radius that is about twice the size of the beam radius. Specifically, the beam center position is reproducible with an rms uncertainty of 60 µm determined by recording 300 pulses.

![Fig. 2. The fluence profiles of the transmitted pulses through sample LG-770 averaged along a 2 µm section that transverses the central region of the digitized image of the beam for a pristine and a pre-irradiated site under similar excitation conditions.](image-url)

The profiles shown in Fig. 2 represent the average value (expressed in J/cm$^2$) along a 2 µm in width section (2 pixels) spanning through the central region of the digitized image of
the beam profile. These two profiles were selected because their input beam profiles (as recorded by the reference CCD camera) were practically identical. The profile of the pulse that propagated though the pristine site was indistinguishable (within experimental error which is on the order of a few µm in beam diameter) from that of the reference profile. The input energy for this pulse was 980.4 µJ, corresponding to a peak fluence of about 11 J/cm². The measured losses due to reflection and absorption in the sample were about 9% indicating that the energy of the pulse after passing though the sample was about 892 µJ. In comparison, the pulse that propagated through the pre-irradiated site with 300 pulses of about the same fluence (on the order of ≈950 ± 100 µJ) was 917.7 µJ while the losses were about 14.7% indicating that the output energy was about 783 µJ. The higher losses in the latter case may be attributed to the enhanced absorption at 355 nm due to the solarization of the sample after its pre-exposure to the laser pulses. Although the transmitted energy in the second case was more than 10% lower, the beam profile exhibits a self-focusing behavior with the peak fluence of about 16 J/cm².

This effect could be attributed to a change in the linear index of refraction, thus creating a waveguide leading to the focusing of the beam. To address this issue, we performed interferometry measurements to assess the change of the linear index of refraction \( \Delta n_0 \) of the material due to the localized exposure to the UV pulses and ensuing solarization. The experiments were performed using a high sensitivity in house-built interferometric microscope system having lateral resolution of 4 µm using a laser operating at 514 nm. The experimental results suggested that \( \Delta n_0/n_0 \approx 10^{-6} \) at maximum for the experimental conditions used in this experiment. This change of \( n_0 \) is too small to support the change of the beam propagation behavior exemplified in Fig. 2, as will be discussed in more detail later. In addition, the area of solarization and increased \( n_0 \) was found to be larger than the beam spot, which is anticipated due to the beam spatial movement (discussed earlier).

![Fig. 3. Intensification (ratio of the measured peak fluence over the reference peak fluence) as a function of the output energy and reference peak fluence (open circles) obtained from a pre-irradiated site (open circles) and corresponding measured transmission (solid circles) in sample LG-770. Solid line represents the fit to the data using the self-focusing model below.](image)

The self-focusing effect can be quantified in terms of the ratio of the measured peak fluence over the estimated reference fluence as defined earlier (which represent the peak fluence at the transmitted energy if there was no self-focusing involved). We will refer to this
peak fluence ratio as “Intensification” to quantify the self-focusing strength. Figure 3 shows the beam intensification as a function of the output energy and output reference peak fluence from a pre-irradiated site in sample LG-770. The experimental error in these data represents mostly the error in the CCD cameras (the error in determining the energy as obtained from the energy meter and the corresponding total detected signal by the CCD cameras) and the error in the estimation of the peak fluence. It must be noted that the peak fluence was estimated by averaging over a square area of 5X5 pixels in the digitized image of the beam profile as recorded by the CCD camera (corresponding to an area of about 25 µm²) at the position of observed peak fluence.

Figure 3 also shows the measured transmission of the laser pulses as a function of the laser pulse energy. These measurements were performed starting with the highest energy pulses and subsequently decreasing the laser pulse energy. Therefore, the observed increase in transmission as the laser pulse energy was decreased cannot be attributed to solarization of the sample (which would have led to lower transmission for the lower energy pulses in the as executed sequence of measurements). In addition, the measured transmission at higher laser pulse energies is significantly lower than that at lower laser pulse energies. For comparison, the measured absorption (using a conventional spectrophotometer) at 355 nm due to solarization (produced using a large aperture laser having a square, nearly flat-top beam profile with dimensions of about 1 cm X 1 cm) was found to be on the order of a few percent. As a result, the decrease of the transmission with increasing laser pulse energy may be attributed to the formation of transient defects during laser exposure. This, in turn, results in the appearance of a transient absorption that is dependant on the laser pulse energy (intensity). It should be noted that the additional induced absorption observed in Fig. 3 corresponds to a very small imaginary part of the refractive index, less than 10⁻⁶ in the most severe case. This estimate was arrived at by setting the relative change in transmission to 2 k (Im(n)/n₀) z.

The results of the experiments using the Cu-doped LHG-8 glass were very similar to those observed in the LG-770 glass. The results shown in Fig. 4 obtained using this material demonstrate the build up of the self-focusing behavior with the number of exposure to 355 nm pulses. Specifically, while the input laser pulse energy was kept constant to a measured average of 980 µJ per pulse, the ratio of the measured over the reference peak fluence (intensification) is plotted as a function of the number of exposure pulses. The as measured transmission is also plotted in the same graph. It can be appreciated that as the intensification increases due to self-focusing, the transmission loss due to the formation of color centers (solarization) increases. This suggests a direct relationship between the materials parameters governing the self-focusing process and the density of defect centers.

The measured data are affected by instrumentation errors in recording the laser pulse energy and beam profiles (as discussed earlier) as well as the beam pointing stability. Specifically, the effect of exposure to even the first few pulses is significant and can be detected as a loss of transmission. However, as the center of the beam moves around covering an area that has a diameter about twice that of the each individual laser pulse, some of the pulses will be transmitted though areas of material that exhibit lower solarization leading to slightly lower values of absorptivity (higher transmission). The same mechanism also contributes to the spread in the data of the intensification, but to a higher degree due to the nonlinearity of the process. The presence of the copper doping ions in this material does not seem to affect to a measurable degree the change of the self-focusing parameters in phosphate glass. Further increase of the laser input pulse energy above the range used in these experiments leads to laser induced damage.

As mentioned earlier, the literature value of the nonlinear index of refraction of fused silica is slightly higher than that of the phosphate glasses. For this reason, we also tested fused silica using the same excitation conditions as those used for the study of the phosphate glass
but no measurable self-focusing was detected. This indicates that no other extrinsic effects (such as self focusing in air, abnormal laser beam characteristics etc) are responsible for the experimental observations presented in this work. Therefore, it appears that the main contributor to the self-focusing effect observed in phosphate glasses is the color centers (or a sub-population of the color centers) formed during the solarization process.

4. Modeling

The results discussed above indicate the involvement of both, a steady state defect population (giving rise to what is commonly referred to as solarization) and a transient defect population, which is manifested as an increased transmission loss (absorptivity) with increasing laser intensity/fluence. Such defects can induce changes in both the linear and the nonlinear indices of refraction. It was mentioned earlier that the solarization causes a change on the linear index of refraction of about $10^{-6}$. Since the change of the refractive indices is proportional to the density of defects, which is expected to follow the beam energy distribution, such changes can lead to self-focusing behavior of the laser beam even when only the linear index is affected. The experimental results shown in Fig. 3 can be used to obtain information about the underlying mechanisms. The slowly varying envelope of the self-focusing electric field $E$ can be described by the non-linear Schrodinger equation:

$$\frac{i}{\partial z} E + \frac{\nabla^2}{2k} E - \frac{k}{2n_0} \left( \frac{r}{a} \right)^2 E - \frac{kn_2}{n_0} |E|^2 E = 0$$

(1)

where $z$ is the distance propagated, and the units of $E$ are chosen so that $|E|^2$ is the laser intensity. Here $n_0$ is the linear refractive index of the medium, $k = 2\pi n_0/\lambda$ is the wavenumber, $\lambda$ the wavelength, $\Delta n_0$ is the magnitude of induced linear index, $a$ the 1/e intensity radius and $n_2$ is the induced nonlinear coefficient. Since we don’t know the relative strength of the linear vs. nonlinear indices, we analyzed cases of pure $\Delta n_0$, of pure $n_2$, and mixed effect. We employed the method of moments [11] to describe the degree of intensification due solely to $n_2$ of a Gaussian beam as a function of laser intensity. The theory predicts:
in terms of the laser intensity \( I \) or fluence \( \phi \) and pulselength \( \tau \). In this expression \( a \) is the initial \( 1/e \) beam radius and \( z_R \) is the Raleigh range \( ka^2 \). The experimental observations were modeled using this expression with \( a = 48 \mu m \), \( \tau = 3.3 \) ns, \( n_0 = 1.47 \) and \( z = 4 \) mm. The results are shown in Fig. 3. Note that \( z_R = 59.9 \) mm so diffractive spreading is not significant during the propagation of the beam inside the sample.

The situation in which self-focusing is due solely to \( \Delta n_0 \) was treated using the waveguide model of ref [12]. This gives the intensification as:

\[
\text{Intensification} = \frac{1}{1 + \left( \frac{a}{z_R} \right)^2 \frac{n_0 I}{2n_0^2} \left( \frac{z}{a} \right)^2} = \frac{1}{1 + \left( \frac{a}{z_R} \right)^2 \frac{n_0 \phi}{2n_0^2 \tau} \left( \frac{z}{a} \right)^2} \tag{2}
\]

The resulting fit of the data was essentially indistinguishable from the fit shown in Fig. 3. Finally, we used a generalization [13] of Eq. (2) that accounts for self-focusing of an already converging beam to treat the case in which both indices contribute. This model leads to the necessary relationships between \( \Delta n_0 \) and \( n_2 \) to be consistent with the data.

In using either Eq. (2) or Eq. (3), it is necessary to account for the entire population of defects present during the laser irradiation that contribute to the nonlinear focusing. Specifically, solarization is associated with a residual (steady-state) population of defects which is the result of the generation of a larger population of defects during the laser pulse followed by partial annihilation of this population via recombination afterward. Typically the recombination rate of the defects rapidly increases with defect density. As a result, there is an initial rapid increase of the residual population with increasing number of pulses which thereafter saturates as the population reaches a high enough density so that recombination ultimately balances the new defects generated during the laser pulse. However, the optical nonlinearity experienced during the pulse can be influenced by both the steady state and transient defect populations. Experiments have verified that the density of generated defects increases monotonically as a function of the laser fluence [14] as one would expect. Furthermore, such transient defects can contribute to both \( \Delta n_0 \) and \( n_2 \) during the laser pulse. Both the experimental results and Eqs. (2) and (3) average this effect over the duration of the laser pulse. Accordingly, in Eq. (2), we assume that \( \Delta n_0 \) and \( n_2 \) are themselves a function of intensity or fluence.

Comparison of the model fits shown in Fig. 3 to the experimental data indicate a good representation of intensification observed in our measurements. The corresponding values of either solely \( \Delta n_0 \) or solely \( n_2 \) as a function of input laser fluence, assuming generation of transient defects as necessary for the best fit in Fig. 3, is given in Fig. 5. When both indices contribute, their values lie between the limiting cases of the two curves shown. Thus the maximum induced \( n_2 \) is on the order of a few times \( 10^{-5} \) cm\(^2\)/GW and the induced \( \Delta n_0/n_0 \) is on the order of \( 10^{-4} \).

The background \( n_2 \) in the solarized sample at low intensity is several times (≈8) larger than that for LG770 or fused silica and its increase is attributed to the presence of color centers (solarization). For reference, the accepted value of \( n_2 \) for fused silica is \( 3.6 \times 10^{-7} \) cm\(^2\)/GW and that of LG770 is \( 2.8 \times 10^{-7} \) cm\(^2\)/GW. Despite the increased self-focusing with laser pulse energy, the observed increased absorption is only on the order of a few percent. Consequently, the theoretical model assumes for simplicity no change in absorption while the beam transverses the sample, which would only introduce small changes in the estimated values.
Since the value of $n_2$ shown in Fig. 5 is derived from a fit to the observed intensifications in Fig. 3, we estimated the uncertainties in the derived values using a bootstrap method in which pseudo data sets are created with the same statistical deviations from the fit intensification as were observed experimentally and then refit these pseudo data sets. This method suggests that the nonlinearity at the highest fluences to be well determined with less than about a 5% standard deviation. The theoretical value at the lowest fluences is less well determined since the observed differences of intensification from unity are much more relatively uncertain there. A similar conclusion is obtained for the value of $\Delta n_0$. Thus, the general shape of the curves in Fig. 5 with the upper values more or less fixed is well established from the experimental observations.

5. Discussion

The results demonstrate the strong effect of the transient population of defects on the propagation (and self focusing) of the laser beam. The measurement of the $n_0$ in the solarized material ($\Delta n_0/n_0 \approx 10^{-6}$) is about two order of magnitude smaller to the peak required value to fully account for the self focusing behavior as shown in Fig. 5 ($\Delta n_0/n_0 = 1.2 \times 10^{-4}$). As the change of $n_0$ is generally proportional to the induced absorption [8], the comparison of the transient absorption component (about 6-10% transmission loss) with the steady state component (about 3-5% transmission loss) does not support an additional change of the $\Delta n_0/n_0$ by the transient defects of two orders of magnitude. This may indicate that the main contributor to the self-focusing behavior is the non-linear index of refraction $n_2$. As discussed earlier, the data fit shown in Fig. 5 suggest that the $n_2$ of the solarized material is about 8 times higher than the pristine material ($=25 \times 10^{-7}$ cm$^2$/GW). A change by another factor of 20 due to the presence of the transient defects is suggested by the fit to the experimental data shown in Fig. 5. Resonance phenomena may play an important role in such process. We must also consider that the transient defects are probably different from the steady state defects as they may represent a short lived state of the photo-excited electrons and holes which are subsequently trapped by precursors in the matrix to form the color centers (solarization). Thus, the transient defects may be capable of inducing a higher change of the $n_2$ (associated in the nonlinear polarization generated in the medium) compared to the steady state defects.
Additional experiments are required in order to resolve the relative contribution of the linear and the nonlinear index of refraction and the underlying mechanisms. The effects discussed in this work are of importance in high power laser applications. Transient defects are known to form in other optical materials under exposure to high power UV laser pulses and therefore, the behaviors discussed in this work may not be unique to the phosphate glasses but may be present in other materials currently used in high average power or high peak intensity UV laser systems.

The maximum value of $n_2$ of $\approx 550 \times 10^{-7} \text{cm}^2/\text{GW}$ shown in Fig. 5 is essentially identical to the value for Cu$^{2+}$-doped germano-silicate glass fibers [15] exhibiting high resonant nonlinearity. Various such ion-doped fibers have been developed for all optical switching applications [15–17]. The phosphate glass samples used in this work demonstrate analogous nonlinear behavior but the change of the nonlinearity is introduced via the formation of long-lived or transient defects via exposure to UV laser pulses. It is therefore a material whose nonlinearity can be locally increased merely via exposure to UV irradiation, not requiring a change in stoichiometry (via doping with impurity ions as in the case of germano-silicate glass fibers). Furthermore, the defects formed due to UV exposure can be annealed via heating. Therefore, it is possible to generate three dimensional re-writable $n_2$ structures in bulk material where the solarization via a focused or properly spatially shaped beam can be used to induce localized increases of the $n_2$ while heating can be used to reverse such changes, even locally. One efficient method to produce such local heating may be via doping the material with an absorbing ion, such as the Cu-doped sample used in our experiments. In this case, a proper dose of localized exposure to a near infrared laser beam (to excite the absorption band of the Cu$^{2+}$ ions) can deliver the localized heating. Other all-optical methods to anneal the point defects are also possible without using heating. Furthermore, the entire material can be solarized and then use localized heating (or another method to locally anneal the defects) to imprint locally decreased $n_2$.

6. Conclusion

We demonstrated that “solarized” phosphate glass irradiated by nano-second laser pulses undergoes large transient changes in optical properties, which we attribute to the generation of residual and transient defects. The optical effect of the transient defects is considerably larger than the effect related solely to steady state “solarization”. This results in induced changes in refractive index that cause induced beam self-focusing. This effect is potentially important for the operation of powerful, high rep rate pulsed laser systems. Analogous mechanisms could also be used to “write” dispersive structures and 3-dimensional reversible memory and optical circuits.

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