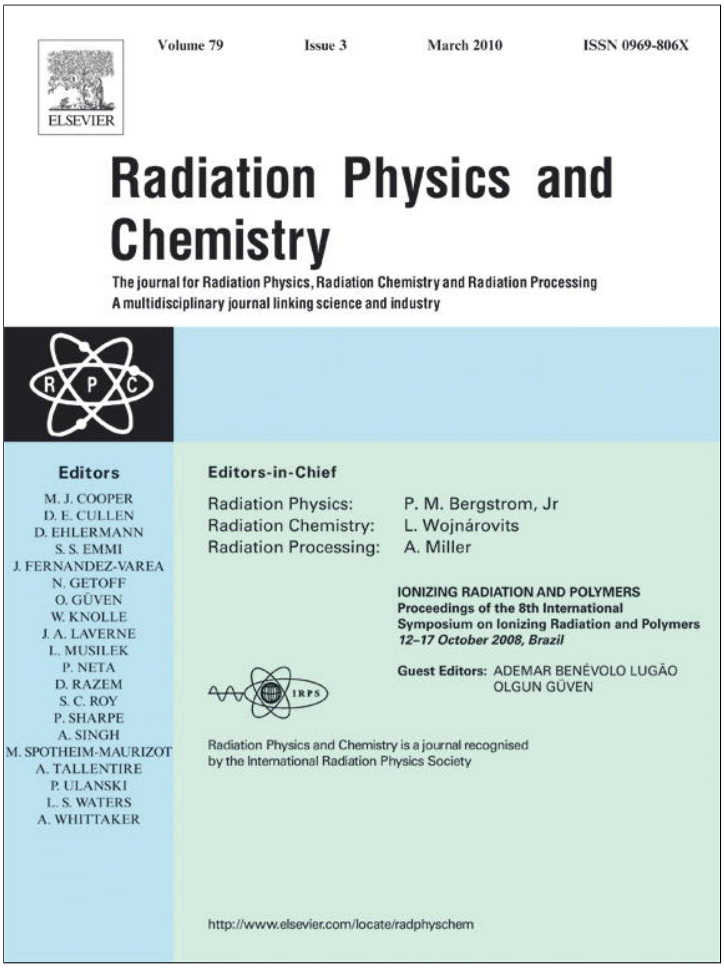

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Production of color centers in PMMA by ultrashort laser pulses

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ABSTRACT

We report here the creation of color centers in commercial, transparent PMMA samples by ultrashort pulses from a Ti:Sapphire laser emitting at 800 nm, with spatial control. Although the 800 nm photon energy is not sufficient to ionize the polymer, the centers are created following a multiphotonic absorption that causes the ionization. We propose that the free electrons quivering motion on the pulse electric field displaces atoms from its equilibrium positions, creating free radicals and double bonds that coalesce into color centers. The absorption and emission spectra of the centers were measured, but a dose-like curve could not be built due to the presence of damages created along with the centers that scatter the excitation and emission lights due to the commercial sample's poor optical quality.

1. Introduction

There are a number of emerging applications in which polymeric materials are utilized in optical devices that operate in radiation filled environments. In such devices the polymer optical absorbance is the most critical property for its performance, and since ionizing radiations are known to create color centers in these materials (Clough et al., 1996), the study of these centers' optical properties is crucial to develop and build the devices. This examination is also important because color centers are known to modify the mechanical properties of the polymer (Lu et al., 2001).

Color centers have been traditionally created in solid samples by ionizing radiations, but in the last years it has been demonstrated that these centers can be created in crystals and glasses (Courrol et al., 2008a, 2004, 2006) by high-intensity, femtosecond laser pulses centered around 800 nm. Although this wavelength is not in the ionizing radiation region of the electromagnetic spectrum, the very short time scale of the laser pulses increases the probability of multiphotonic absorption processes occurrence leading to the sample ionization (Keldysh, 1965). The free electrons quivering motion creates vacancies via collision, and after electrons capture, the color centers are formed. This only happens around the laser focus, where the laser intensity is high enough to initiate the process, conferring the ability to machine structures inside the material (Davis et al., 1996). An additional advantage of this process is the nonthermal interaction arising from the ultrashort pulse duration, that allows the machining of heat sensitive materials (Mendonca et al., 2008; Scully et al., 2002; Sowa et al., 2005, 2006), to create optical devices (Eldada and Shacklette, 2000).

In this work we report the study of the formation mechanisms and of the optical properties of color centers created inside commercial, transparent PMMA samples, by ultrashort laser pulses.

2. Experimental setup

Color centers were created in commercial, transparent PMMA samples, by irradiation with ultrashort laser pulses. A Ti:Sapphire CPA laser system (Quantronix Odin seeded by Femtolasers Rainbow) was used to generate a train of 330 μJ, 40 fs pulses, centered at 800 nm with 30 nm of bandwidth, at 1 kHz repetition rate, in a beam with a $M^2 < 2$ and a maximum peak power of 8.25 GW. The beam was focused by a 25.4 mm focal length lens to a calculated radius of 10 μm, and the samples were placed in the focused beam in such a way that the beamwaist (laser focus) was inside the sample, and no ablation occurred at its surfaces. The samples were fixed to a translation table controlled by a computer that performed sinusoidal movements in x and y directions (Fig. 1) with amplitudes of 1 and 5 mm, respectively, during 5 min. These orthogonal oscillatory movements were done with different frequencies, creating Lissajoux figures of color centers, building up volumetric colored regions inside the samples, as schematized in Fig. 1. In each sample several irradiations were done with different pulse energies, and for each pulse energy a new region of the sample was chosen.

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The color centers' absorption spectra were measured by a Cary 17D dual beam spectrometer. To determine the emission of the color centers, each volumetric region was individually excited by the second harmonic from the ultrashort pulses laser (Femtolasers Rainbow), centered at 443 nm, and the emission spectra were measured at 90° by a CCD spectrometer (Newport OSM).

3. Results and discussion

The results obtained in various samples were similar, and this work reports the results for a sample irradiated with 148, 207, 253, 296 and 327 μJ pulse energies, shown in Fig. 2. In this figure, the color centers created by the laser pulses can be observed as greenish regions, and the black spots represent damages created by the laser, that are absent at the lowest irradiation energy. During irradiation, the ultrashort pulses generate a supercontinuum (Brodeur and Chin, 1998) and scattering spots inside the PMMA samples can be observed as shadows and diffraction centers in this white light beam, evidencing that these commercial grade PMMA samples do not have a good optical quality, which interfere with the color centers' production. The scattering centers are probably microbubbles remaining from the polymerization process.

The absorption spectra of a PMMA sample before and after the irradiation by the ultrashort pulses are shown in Fig. 3. The creation of color centers is confirmed by the presence of an absorption band in the visible region, similar to that obtained when PMMA is subjected to gamma irradiation (Clough et al., 1996). Color centers in PMMA are created as a consequence of polymer degradation, according to the following sequence: the acrylate chemical group is excited by ionizing radiation and undergoes a homolytic scission from the main chain followed by a hydrogen abstraction that leads to the formation of a double bond. This process occurs without scission of the polymer main chain. The isolated double bond does not absorb in the visible region, but the propagation of the degradation process produces conjugated double bonds. The energy of these electronic $\pi\rightarrow\pi^*$ transitions is shifted to lower values according to the number of conjugated double bonds, originating absorption bands in the visible spectrum. In the present case, although the 800 nm photons have 1.55 eV of energy and, in principle, are not able to ionize the polymer atoms, the pulses' high intensity resulting from their short duration increases the probability of multiphotonic ionization processes (Keldysh, 1965), and consequently electrons are freed from atoms by the ultrashort pulse leading edge via a multiphotonic absorption process. These free electrons then oscillate in the pulse electric field, and by collisions create more free electrons and shift atoms from their places, forming double bonds and free radicals. The association of these free radicals and double bonds usually acts as non-permanent color centers. The increment in number of these $\pi\rightarrow\pi^*$ electronic transitions increases the formation of color centers in the yellow and orange regions. Thus, color centers can be created without ionizing radiation, appearing only at positions where the laser is focused to high intensities, allowing their formation with spatial control.

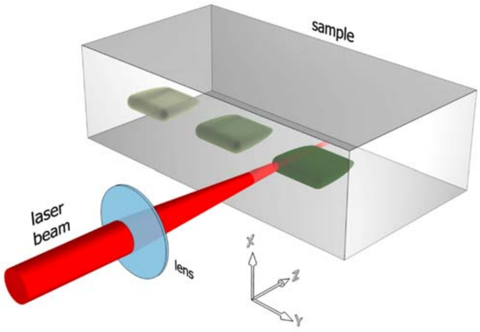

Fig. 1. Scheme of the PMMA samples irradiation by ultrashort pulses. The sample was moved in sinusoidal oscillations in *x* and *y* directions, with different frequencies and amplitudes of 5 and 1 mm, respectively. The greenish regions represent the color centers formed at different pulse energies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

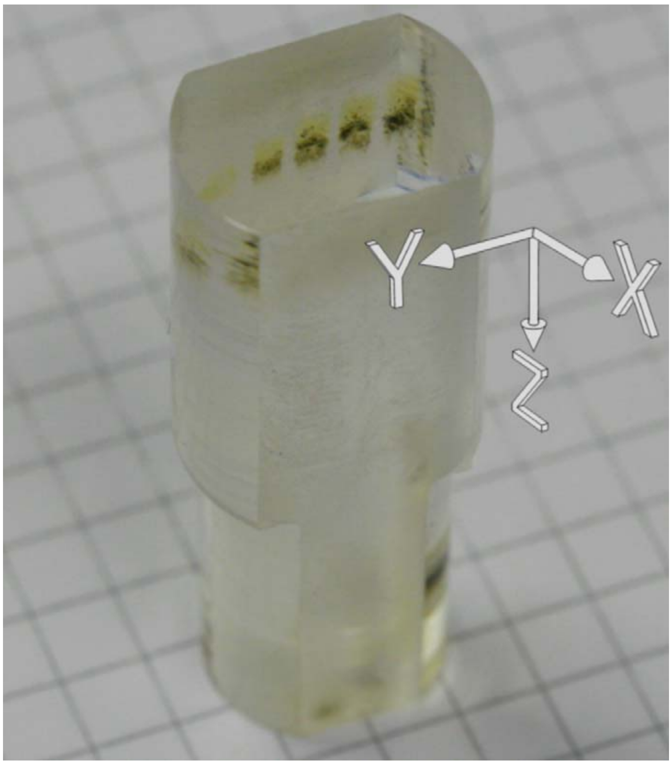

Fig. 2. PMMA sample showing the color centers (greenish regions) created under irradiation with 148, 207, 253, 296 and 327 μJ ultrashort pulses, from left to right. The laser beam propagated in the *z* direction, and the sample was moved in the *xy* plane (according to the axis shown in Fig. 1) for each irradiation energy. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

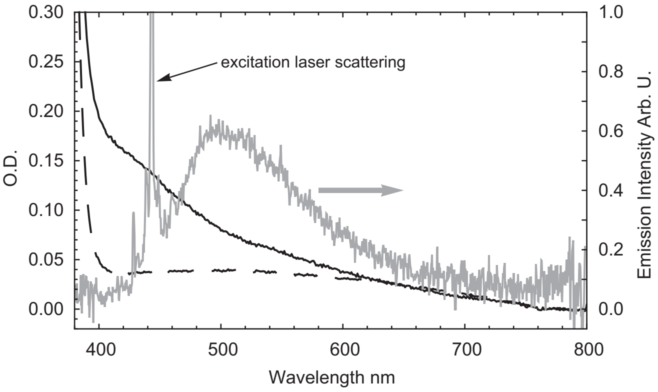

Fig. 3. Dashed line: absorption spectrum of a transparent PMMA sample. Continuous black line: absorption spectrum of color centers created by ultrashort pulses in the transparent PMMA sample. Continuous gray line: color centers emission spectrum under excitation by laser pulses at 443 nm. The emission spectra scale is at the right.

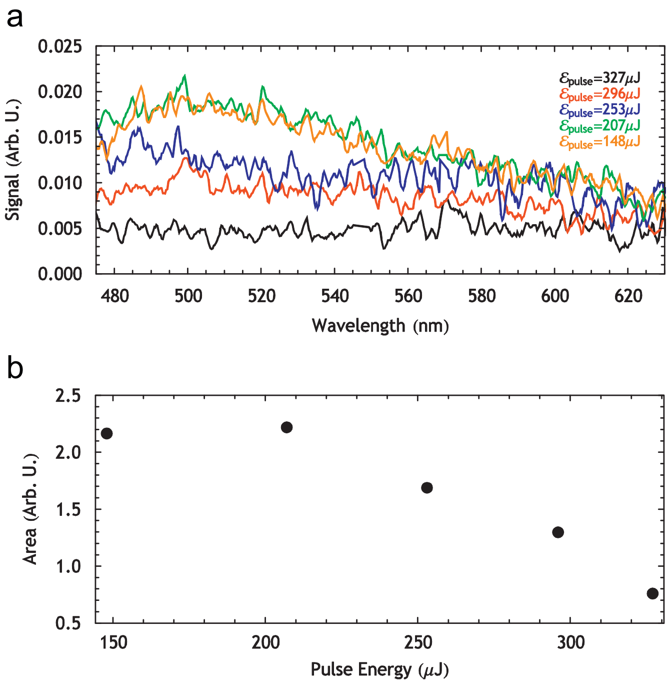

Fig. 4. Emission spectra of color centers created at various pulse energies (a), and color center emission spectrum area in the range 475–635 nm as a function of the pulse energy (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3 also shows a representative emission spectra of the centers created by the laser pulses. The excitation laser scattering is observed at 443 nm, and a broad emission band extending from 420 to 650 nm is observed. The intensity increase that starts before 780 nm is the excitation laser fundamental emission, which is much broader than the second harmonic.

In order to determine how the color centers' density depends on the pulse energy, the emission spectra were measured for the various color centers' regions shown in Fig. 2, and the results are shown in Fig. 4a. The emission spectra areas between 475 and 635 nm were calculated and plotted as a function of the pulse energy (Fig. 4b), in order to establish a dose-like curve for the creation of the color centers (Courrol et al., 2008b). Contrarily to what is expected, the emission spectra areas decrease as the pulse energy increases (except for the two first points). By visual inspection of the color of centers created at different energies (Fig. 2), the density of centers created at the higher energies is at least the same as the density originated at the lower energies, indicating that the behavior exhibited in Fig. 4b does not follow the created centers density. We propose that this occurs due to the non-homogeneous black damaged regions that appear at the higher irradiation energies, which scatter and absorb both the exciting laser and the centers emission, decreasing the net detected light. These damaged regions are probably formed as a consequence of the bad optical quality of the PMMA samples (microbubbles and impurities) that initiate absorptions, which evolve to damages. Further study on samples with better optical quality is needed in order to characterize the centers and its creation threshold intensity.

4. Conclusions

Color centers were created in commercial grade transparent PMMA samples by ultrashort, high-intensity, laser pulses. Although photons at 800 nm are not an ionizing radiation, the multiphotonic absorption that occurs at the intensities originated at the short time scale of the pulses initiates a color center formation process around the laser focal point. Using this localization of the laser, spatial structures of color centers can be created inside polymers.

The damages (black regions) created inside the samples prevented us from creating a dose-like curve, indicating that better quality samples are needed in order to study the centers' creation process as a function of the energy. Nevertheless, the centers created can be used to explore the polymer interaction with radiations, ionizing or not.

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