Production of stabilized color centers in $YLiF_4$ crystals by high-intensity ultrashort laser pulses

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In this work we show that is possible to produce stable color centers in $YLiF_4$ crystals, with dimensional control, by focusing high-intensity ultrashort laser pulses in the bulk. In particular, with the spectroscopic characterization of ultrashort laser-irradiated YLF samples, it was possible to discuss the basic formation mechanisms of these centers.

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1. INTRODUCTION

The $YLiF_4$ (YLF) host crystal allows the growing of various laser media for generation at numerous wavelengths, from UV to near infrared.[1] The combination of weak thermal lensing, large fluorescence linewidth, and naturally polarized emission makes Nd:YLF an excellent material for cw and *Q*-switching operation.[2]

When the YLF crystal is exposed to high intensities of pumping radiation in the UV–visible spectral regions or ionizing radiation, degradation of the application-related characteristics and performance are implied. The study of induced defects as color centers is therefore a useful approach to understanding the relevance of laser-degradation processes in YLF crystals and their microscopic mechanisms.

Color centers are lattice vacancy defects that trap electrons or holes. They are easily created in single crystals at room temperature by ionizing radiation.[3] Color-center lasers have some important optical characteristics and if produced with spatial control can modulate the material refraction index to create waveguides or photonics devices.[4]

Femtosecond laser pulses can create color centers in fluoride crystals, as in LiF[5] and Na_2F (Ref. 6). In LLF ($LuLiF_4$) and YLF, up to now, these characteristics have been studied only for ionizing radiation.[7–9] We report here for the first time the creation of stable color centers in YLF by ultrashort laser pulses.

2. MATERIALS AND METHODS

In this paper we study pure YLF crystals grown by the zone refine (zf) method, and oxygen-doped YLF grown by the Czochralski technique under a controlled atmosphere. The samples were oriented, cut, and polished to 2 mm thickness.

The absorption spectra of the samples, at room temperature, were measured in the range from 200 to 800 nm using a Varian Spectrophotometer Cary 17 D and in the IR region using a Fourier transformer from Perkin–Elmer (Fig. 1).

To irradiate the samples, a Ti:sapphire chirped-pulse amplification system (coherent Mira Seed master oscillator seeding a Quantronix Odin amplifier) was used, producing a 1 kHz train of pulses, centered at 830 nm, with 640 μJ of energy and 60 fs of pulse duration (FWHM), in a $M^2=1.6$ beam. The beam was focused by a 200 mm lens, producing a converging beam with a waist of 25 μm. The samples were placed before the beam waist in such a way that the color-center creation threshold was achieved inside the crystals. The sample was then moved transversely to the beam for 3 mm to produce a plane of color centers. Three planes were created in each sample in order to enhance the optical density for the absorption measurements. A scheme of this irradiation can be seen in Fig. 2(a). In a second experiment represented in Fig. 2(b), the sample was kept motionless, with the beam impinging on it for 1 min, creating a track inside the sample. After the laser irradiation, the samples were stored at liquid-nitrogen temperature to preserve the introduced changes until the absorption spectra could be measured, since it is known that color centers can be destroyed or modified when exposed to room temperature[10] by charge recombination or vacancy mobility. After the absorption spectra were measured, the samples were stored at room temperature (RT) for three days, and their absorption spectra were then measured again.

To determine the color-center creation-intensity threshold, a YLF sample was placed in the focused laser beam before the waist, in a position where no color centers were formed, and was moved toward the waist until color centers were observed by the naked eye to be formed by the

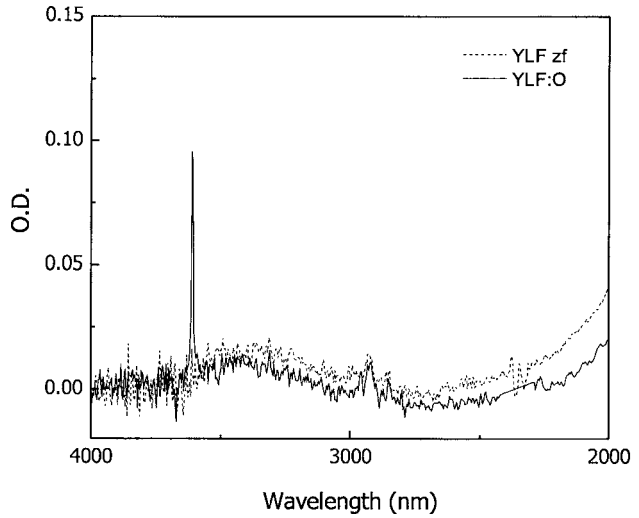

Fig. 1. Infrared absorption spectra of YLF zf and YLF:O crystals. The thin peak observed in the YLF:O spectra around 3600 nm corresponds to OH stretching.

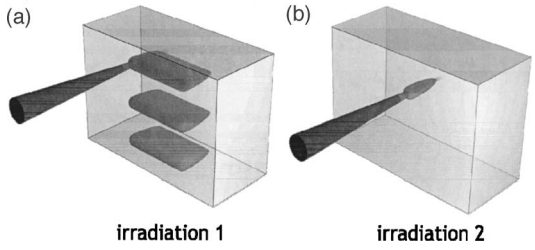

Fig. 2. Production of color centers with an ultrashort laser pulse. Irradiation 1 samples (a) were dislocated 3 mm over 3 min radiation, and three traces were produced. Each trace was separated by 1 mm. Irradiation 2 samples (b) were irradiated for 1 min along the crystals.

laser pulses. The sample position relative to the lens was measured, and the pulse intensity was calculated at the sample position.

The samples were also irradiated with an electron beam at room temperature (18 s, 2.8 kGy/s, 0.7 mA, 1.5 MeV), in regions that did not overlap the color centers region produced by the ultrashort laser pulses.

3. RESULTS

To determine the effects of the ultrashort-pulse irradiation in the YLF crystals, the absorption spectra of the samples kept in liquid nitrogen was measured. The results of the measurement described in Section 2 are shown in Fig. 3. In this figure we can see that the optical densities of each sample grows after being kept at RT for three days. This growing in the absorption of the visible bands results from a decrease of the vacuum–UV bands.[11,12] The increase in mobility that the vacancies undergo when brought from 77 K to RT allow some of the produced F centers to be transformed into more-complex centers, like F_2 and F_2^+, that absorb in the visible range.[10]

Figure 4 shows the absorption spectra of the electron-beam and ultrashort-pulse irradiated YLF and YLF:O samples after three days of storage at RT. Comparing these spectra, we see that the YLF:O samples have more defects than the YLF ones in both kinds of irradiation. We observe an F_2^+ center[7] absorption band, at approximately 650 nm, in YLF:O electron-irradiated and YLF and YLF:O laser-irradiated samples. This absorption band is responsible for the blue–green color observed in the samples. In YLF:O, the secondary oxygen defects produced with irradiation (O_2^- and O^-), play an important role in stabilization of color centers as F_2^+ (Ref. 10). In Fig. 4 it is also possible to see that the centers created by ultrashort-pulse irradiation in pure YLF crystals are more stable than the ones produced in pure YLF irradiated by electron beam. Since there is no oxygen in these samples, another kind of stabilization process must be taking place.

The color-center intensity threshold was calculated using the method described in Section 2 and the laser spot size w, given by the laser beam propagation law[13]:

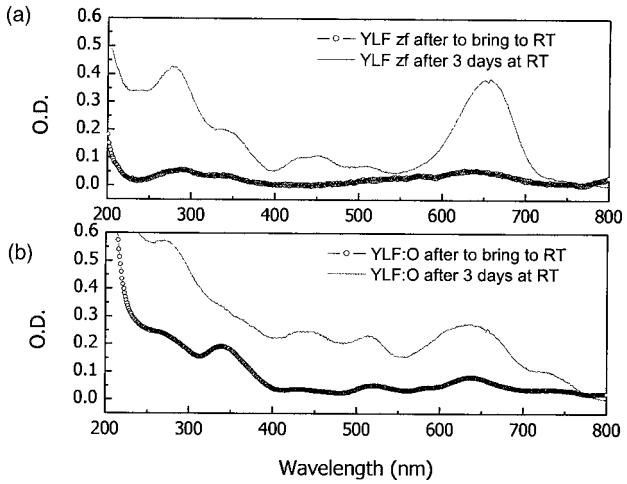

Fig. 3. Absorption spectra of color centers created in YLF crystals by 640 μJ, 60 fs laser pulses. In both graphics, the curves with circles are the spectra of the samples kept in liquid nitrogen, and the continuous curves are the spectra after three days at room temperature. (a) Results for the pure YLF sample; (b) results for the YLF:O doped sample.

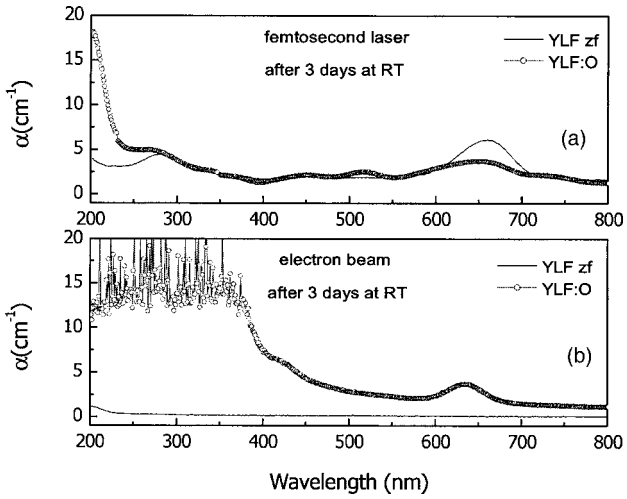

Fig. 4. Absorption spectra of YLF and YLF:O samples (a) after ultrashort laser pulses irradiation and (b) after electron irradiation.

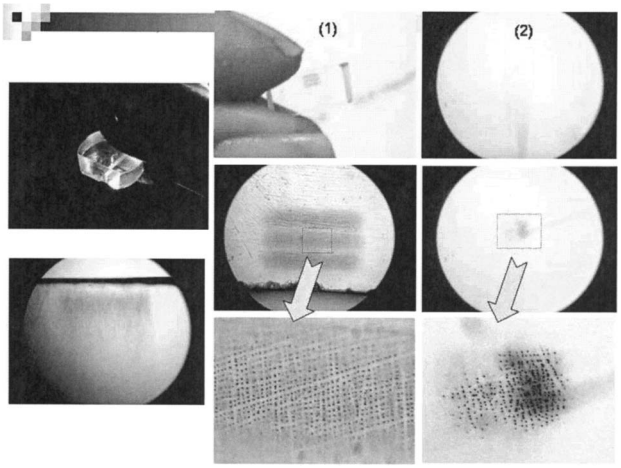

Fig. 5. Photographs of the YLF:O crystals irradiated with ultrashort laser pulses. It is possible to see a very thin trace in crystals, indicated by the arrows, corresponding to the laser interaction area. The colors of these traces are the same color of the electron irradiated crystals. (1) Traces produced by irradiation 1 and (2) track in frontal and lateral views in irradiation 2; the filaments have diameters on the order of 20 μm.

$$w = w_0\left\{1 + \left[\frac{M^2\lambda(z - z_0)}{\pi w_0^2}\right]^2\right\}^{1/2}, \qquad (1)$$

where $\lambda = 830$ nm is the laser wavelength, $z_0 = 19.8$ cm is the beam-waist position relative to the lens, $w_0 = 25$ μm is the beamwaist, $M^2 = 1.6$ is the beam-quality factor, and $z = 17.5$ cm is the sample position where color centers were observed to be formed by the laser pulses, resulting in $w = 390$ μm. In this measure the pulse energy was 547 μJ and the pulsewidth was 60 fs, resulting in a color-center creation threshold of 1.9 TW/cm^2.

To explain the color centers production by the ultrashort pulses, we propose a mechanism based in the electron avalanche that develops owing to a strong initial nonlinear multiphoton absorption.[14,15] This avalanche promotes many electrons to the conduction band, where they acquire kinetic energy from the laser field and create vacancies through an impact with the fluorine ions. When this anion vacancy traps an electron (neutralizing the vacancy charge), a F center is created. The second step in the production of defects involves the migration of primary defects and the formation of complex defects. These secondary processes are temperature and intensity rate dependent. We suggest that creation and destruction processes occur simultaneously during the ultrashort-pulse irradiation, since the fundamental and the harmonics[16] of the pumping laser can be absorbed by the defects.[5]

The production of stable color centers in pure YLF samples was obtained for the first time, according to our knowledge, as a consequence of the interaction of an ultrashort laser pulse with the material. In Fig. 5, we observe the produced traces under a microscope and can see tracks with diameters on the order of 20 μm, regularly spaced. These tracks probably correspond to clusters created by the laser beam that trap the color centers and consequently stabilize them. The microscopic photographs show that the produced tracks have cylindrical symmetry but are not homogeneous, presenting many filaments with periodic structure. Looking across the trace formed inside the crystals, it is possible to see a filamentary structure. The same structure is seen in the planes produced when the sample were moved laterally. In YLF:O a periodic structure is observed in a homogeneous color region (blue–green color). We think that a controllable refractive index change can be achieved by adjusting femtosecond laser irradiation parameters and subsequent annealing conditions. In this way, one can induce refractive index change for the crystals to fabricate internal diffraction gratings or optical waveguides, etc., for three-dimensional integrated-optics devices.

4. CONCLUSIONS

We created, for the first time to our knowledge, color centers in YLF crystals with high-intensity ultrashort laser pulses and measured their absorption spectra. We propose that the mechanism responsible for the center's creation is a multiphotonic process, depending on the crystal energy gap. Microscopic observation of the produced tracks show filamentation of the color centers, and we propose that these filaments (regions where cluster formations occur) are responsible for the color-center stabilization. Also, when produced in a controlled manner, these color-center tracks could be used to manufacture photonic devices.

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