Study of color centers created by high-intensity ultra short pulse laser interaction in solids

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Abstract

In this work we show that is possible to produce color centers inside fluoride crystals, YLF and LiF with dimensional control. A Ti:Sapphire CPA laser system operating at 830 nm was used, producing a train of 60 fs pulses at 1 kHz, in a beam with a peak power of 12.5 GW. The beam was focused by an 83 mm lens in the low power limit (no self-focusing). The samples were placed in such way that the beam waist was inside the materials. A comparison between the optical properties of color centers produced by ultra short laser irradiation, of both crystals was done and, it was possible to determine the center creation intensity threshold and therefore to discuss the basic formation mechanisms of these centers. Optical absorption and emission of produced color centers were measured.

Introduction

Color centers are lattice vacancies defects trapping electrons or holes. They are usually created in single crystals at room temperature, by irradiation with ionizing radiation [1].

Recently, it was shown that is possible to create color centers with interaction of ultra short pulse laser in crystals [2] and glasses [3]. In this case, the defects may be produced with dimensional control [4], by focusing a high-intensity ultra-short pulse laser in the material. Due to their absorption, a modulation of the material refraction index occurs, creating waveguides or photonics devices [5].

In this work we show that is possible to produce stable color centers in $YLiF_4$ (YLF) and in LiF fluoride crystals using a Ti:Sapphire laser. The optical properties of the color centers produced by irradiation with ultra short laser were performed, allowing the determination of the center creation intensity threshold and therefore the discussion of the basic formation mechanisms of these centers.

Experimental Setup

The pure LiF and YLF crystals were grown by the Czochralski technique under Argon atmosphere.

A Ti:Sapphire Chirped Pulse Amplified (CPA) laser system operating at 830 nm was used, producing a train of 640 μJ, 60 fs pulses at 1 kHz, in a beam with a M^2=1.6 and a peak power of 12.5 GW. The beam was focused by an 83 mm lens to a radius of 12 μm inside the samples. The irradiations were done at room temperature.

The absorption spectra of all samples were measured, at room temperature in the 200 nm-900 nm range, using a Varian Spectrometer Cary 17 D. The emission spectra were obtained by exciting the samples with a 150 Watts xenon lamp. The emissions of the samples were analyzed with a 0.5 m monochromator (Spex) and a PMT detector. The signal was amplified with an EG&G 7220 lock-in and processed by a computer.

Results and Discussions

Color center production by femtosecond pulse laser irradiation in fluoride crystals

The LiF crystal has a wide optical gap (~11.8 eV), therefore being a very good media to study the formation of color centers. The simplest color center is the F center formed by an electron trapped in an anion vacancy. When two, three and four F centers are aggregated, F_2, F_3 and F_4 centers are formed, respectively. When ionized or an electron is additionally trapped by these centers, positively or negatively charged color centers are formed (F_2^+ or F_2^- centers in the case of F_2 center), respectively. Table I resumes the known spectral characteristics of such color centers in LiF crystals.

Color center	absorption wavelength (nm)	emission wavelength (nm)
F	248	-
F_3	316, 374	-
F_2	444	678
F_3^+	448	541
F_2^+	645	910
F_2^-	960	1120

Table 1. Spectral characteristics of color centers in LiF.

In the figure 1a it is shown the absorption spectra obtained for the LiF and YLF crystals irradiated by the ultrashort pulse laser. For LiF crystals, F center is responsible for absorption around 250 nm, F_3^+ and F_2 centers are responsibly for the blue absorption band, called M band, due to the 448 nm (F_3^+) and 444 nm (F_2) absorption peaks. Besides the main M absorption band, the red absorption band peaking at the 632 nm band is due to F_2^+ center (ionized F_2 center).

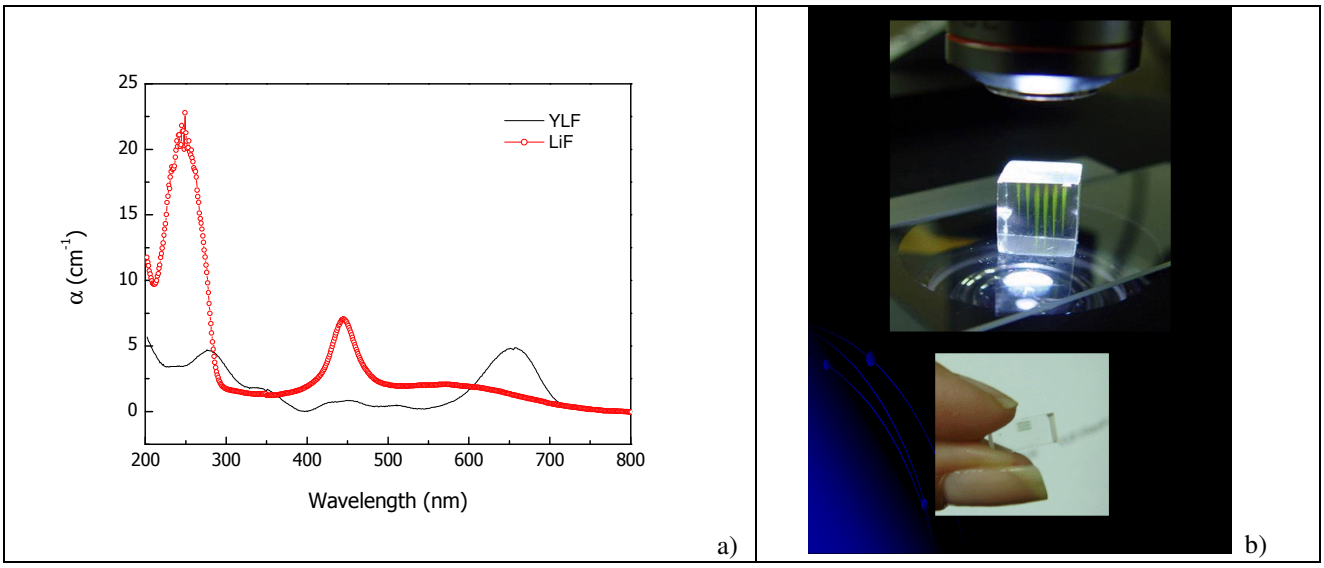

Figure 21. a)Absorption spectra of the tracks created in LiF and YLF crystals by 640μJ, 60fs laser pulses. b) Green emission of F_3^+ centers in LiF and color centers in YLF.

Correspondent absorption bands can be estimate by the Mollwo-Ivey [6] relations for absorption bands in YLF. They can be observed in the spectrum of figure 1a: F=296 nm, F_2= 473 nm, F_3=343 nm and F_2^+=650 nm, all shifted to the infrared. In the figure 1b it is possible to see the green luminescence of the F_3^+ color centers in LiF crystals illuminated with a white light and three tracks of color centers produced in an YLF crystal.

The emission spectra obtained exciting the samples around 650 nm (the main absorption band for YLF crystal) are showed in the figure 3 for the both crystals. We can observe two peaks in both samples, around 710 nm and ~900 nm (cut in the spectra is due to limitations of the emission system). Fixing emission at 710 nm we obtained excitation spectra. Two bands were observed at blue (around 430 nm) and red (around 600 nm), probably due to F_2 and F_2^+ absorptions, respectively. LiF and YLF crystals have the similar emission and excitation bands but with differences on the signal intensities and shifts in the maximum wavelength.

The pursuit for the stable F_2^+ centers in crystals it was an important issue in the past for building resonators. If both thermal and photo stability are present, this center can have high energy output and good efficiency [7]. Also, the spectral is shown to be very wide. We believe the stable centers produced in YLF can be useful for the construction of ultra fast color center lasers.

For YLF crystals, the calculated emission cross section for 710 nm emission band was approximately $2x10^{-17}cm^2$ (lifetime of 90ns).

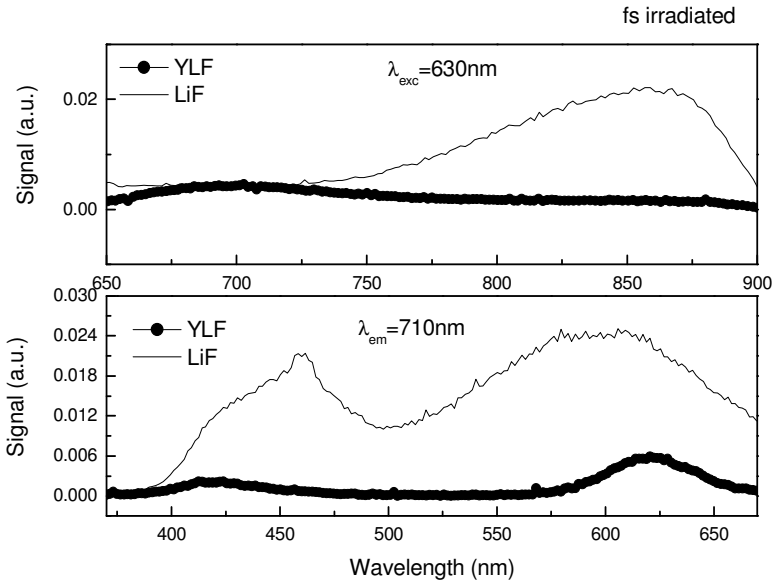

Figure 3. Emission spectra obtained in YLF and LiF crystals with excitation at 630 nm (upper graphic) and excitation spectra obtained fixing the emission at 710 nm (lower graphic).

Intensity Threshold

In order to determine the color center creation intensity threshold, the samples were placed in the focused laser beam before the waist, in a position were no color centers were formed, and were moved towards the waist until color centers were observed, by naked eye, to be formed by the laser pulses. The sample position relative to the lens was measured, and the pulses intensity was calculated at the sample position. Considering the laser spot size w, given by the laser beam propagation law [8]:

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

where λ=830nm is the laser wavelength, z_0=19.8cm is the beam waist position relative to the lens, w_0=25 μm is the beam waist, M^2=1.6 is the beam quality factor and z=17.5cm 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 pulse width 60 fs. By applying a method recently developed [9] it was obtained the color center creation threshold of 1.9 TW/cm^2 for YLF and 2.04TW/cm^2 for LiF crystals.

To explain the color centers production by the ultrashort pulses, we propose a mechanism based in the electron avalanche that develops due to a strong initial non-linear multiphoton absorption [10, 11]. This avalanche promotes many electrons to the conduction band, where they acquire kinetic energy from the laser field and create vacancies by impact with the fluorine ions. When this anion vacancy traps an electron (neutralizing the vacancy charge), an 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. Using a focused laser beam the density of primary defects formed is so much higher than the usual methods and therefore the probability of aggregation is very much increased. This can be seen by the ratio of the F to the M bands in YLF (fig. 1a). This ratio is much higher when the centers are produced by regular ionizing radiation [12]. We believe that there is equilibrium between the creation and destruction processes that occur simultaneously, during the ultrashort pulses irradiation, since the fundamental and the harmonics [13] of pumping laser can be absorbed by the defects as well as the white light generation. These centers are generally unstable with the combination of temperature and intense light [14.]

Conclusions

This paper describes a way to perform controlled ablation in undoped LiF and YLF crystals. Stable color centers in the YLF crystals were produced and characterized for the first time to our knowledge. We propose that the mechanism responsible for the centers creation is a multiphoton process depending

on the crystal energy gap. Also, when produced in a controlled way, these color center tracks could be used to manufacture photonic devices.

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