Color center production by femtosecond pulse laser irradiation in LiF crystals

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Abstract: We report the production of color centers in LiF single crystals by ultrashort high intensity laser pulses (60fs, 10 GW). An intensity threshold for color centers creation of 2 TW/cm^2 was determined, which is slightly smaller than the continuum generation threshold. We could identify a large amount of F centers that gave rise to aggregates such as F_2, F_2^+ and F_3^+. The proposed mechanism of formation is based on multiphoton excitation that also produce short lived F_2^+ centers. It is also shown that it is possible to write tracks in the LiF crystals with dimensional control.

OCIS codes: (320.2250) Femtosecond phenomena; (140.3380) Laser materials; (230.7370) Waveguides; (140.3330) Laser damage

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#3554 - $15.00 US Received 17 December 2003; revised 9 January 2004; accepted 12 January 2004

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1. Introduction

Color centers are lattice defects trapping electrons or holes, and are easily created in LiF crystals at room temperature by irradiation with ionizing radiation [1]. Color centers in ionic crystals present very interesting optical properties, such as optical transitions sensitive to the particular lattice, broad absorption and emission bands in the near UV, visible and near IR regions of the spectrum. Some of them present a four level optical cycle and are stable at room temperature [2,3]. Recently, color centers in glasses were produced with specific small design in order to create waveguides [4-6].

Up to now color centers were created mainly by ionizing radiation beams. High contrast photoluminescence patterns in LiF crystals were produced by soft x-rays from laser-plasma sources [7]. In this work we show that is possible to produce color centers in the bulk of LiF crystals with dimensional control, by focusing high-intensity ultra-short laser pulses inside the material. In particular, it is possible to determine the color centers creation intensity threshold and therefore to study the basic formation mechanisms of these centers. Due to the intensity dependence of this creation mechanism, it is possible to control the geometry of the affected volume in the crystal.

2. Experimental setup

Samples of ultra pure LiF single crystals were grown in our crystal growth facility by the Czochralski technique under Argon atmosphere.

A Ti:Sapphire CPA laser system operating at 830 nm was used, producing a train of 750 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, in the low power limit (no self-focusing). The samples were placed in such way that the beamwaist was inside the crystals. A scheme of the experimental setup is shown in Figure 1. The irradiation was done at room temperature. After the irradiation the samples were stored at liquid nitrogen temperature.

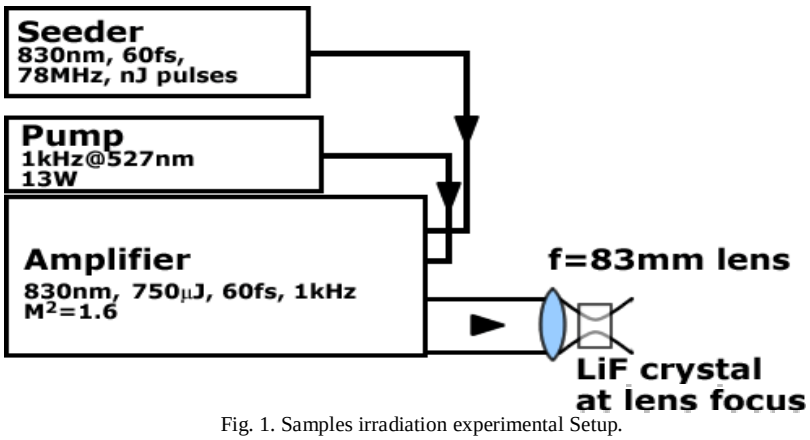

Fig. 1. Samples irradiation experimental Setup.

3. Results

Figure 2(a) shows a photograph of the effect of the focused laser beam impinging into a bulky LiF crystal with the beamwaist located inside it. A green emission and white light (continuum

#3554 - $15.00 US Received 17 December 2003; revised 9 January 2004; accepted 12 January 2004

[8-10]) generation along the beam path can be seen. Figure 2(b) shows a scheme of the shapes seen at the photograph, where the green light appears first and then the continuum, evidencing that the green emission begins at a lower intensity than the continuum. After the laser irradiation, the green emission geometry was preserved inside the crystal, forming a green track when viewed under white light.

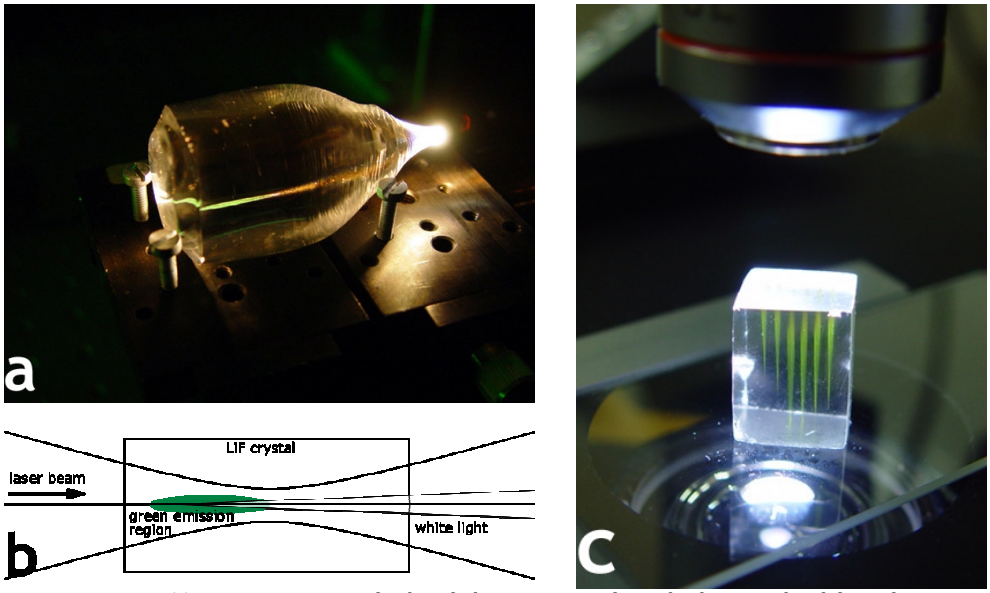

Fig. 2. (a) green emission and white light generation along the beam path while under irradiation by the femtosecond pulses (the pulses came from the left); (b) schematic representation of the light shapes of the preceding photograph: the color centers are created before the beamwaist (focal point) and before the white light. There are no color centers after the beamwaist because at the waist position crystal breakdown occurs, scattering the laser beam; (c) Emission of F_3^+ centers when excited by white light (the laser entered the sample from the top surface); note that these tracks start near the entrance surface of the sample, grow larger in radius and then get smaller near the beam focus position.

In order to investigate the green emission in a systematic way, a polished sample with 11.2×8.6×7.4 mm^3 was positioned along the laser beam, with its surface 73 mm away from the lens (83 mm focal distance), in such a way that the beamwaist was inside it at about 15 mm from the surface, in the low power regime (no self focusing). The sample was irradiated for 2 minutes (120,000 pulses), then it was moved 1 mm away from the lens and 1 mm aside, then another irradiation was made for 2 minutes. This procedure (displacement and irradiation) was repeated six times, engraving six tracks inside the sample. These tracks are shown in Fig. 2(c) with the crystal under exposure by white light. Considering the effect of self-focusing in LiF at the intensities used, the focus moves by ~5 mm to the entrance surface, therefore being located at ~10mm from this surface. As can be seen in Fig. 2(c), the green tracks start near the surface, many millimeters away from the presumed focus at high intensity (the tracks in Fig. 2(c) are 1mm apart, providing a scale). The absorption spectra of the tracks were measured (Fig. 3) following the irradiation and again after 10 days of storage at room temperature. The spectra covered the range 200 nm-1000 nm, using a dual beam Spectrophotometer (Varian Cary 17D).

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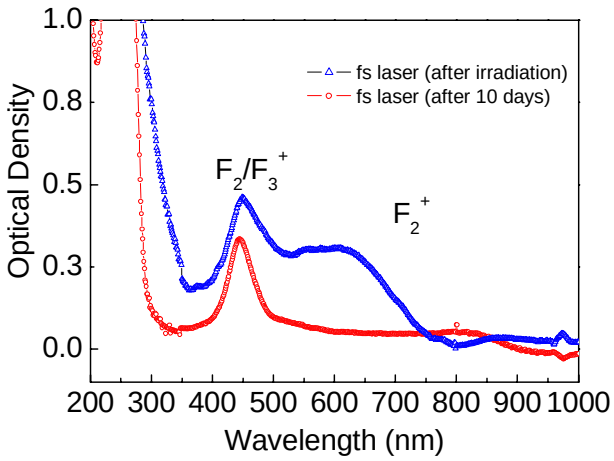

Fig. 3. Absorption spectra of the tracks created in LiF crystals by 750μJ, 60fs laser pulses (following irradiation and after ten days).

Comparing the data shown in Table 1 [11] with the absorption spectra of the tracks, the presence of color centers is clearly seen, with predominance of the 450 nm M absorption band (combination of F_2 and F_3^+). The laser irradiated LiF crystal absorption spectrum also shows the F_2^+ color center absorption band (645nm) immediately after laser irradiation. Therefore, color centers are created due to intense ultrashort pulses laser irradiation.

Table 1. Spectral characteristics of color centers in LiF. λ_a is the absorption central wavelength, E_a is the absorption peak , Δ is the half-width of the absorption band and λ_e is the emission central wavelength.

Color center	λ_a (nm)	E_a (eV)	Δ (cm^{-1})	λ_e (nm)
F	248	5.00		
F_3	316, 374	3.92, 3.31		
F_2	444	2.79	1450	678
F_3^+	448	2.77	2500	541
F_2^+	645	1.92	3500	910
F_2^-	960	1.29	1694	1120

At first one might think that the color centers are created by X-rays generated in the continuum. According to Brodeur and S. L. Chin [12], in LiF the continuum generated by 830 nm pumping extends to ~300 nm, therefore there are no X-rays involved in the color centers creation process. We propose that multiphoton ionization is the starting mechanism for color center formation under femtosecond pulses irradiation. In the LiF crystal the fluorine is a negative ion, and due to the femtosecond pulse multiphoton ionization [13], it becomes neutral. (In order to match the LiF 11.8 eV band gap energy, an eight 830 nm photon process is necessary.) Once it has no charge, the fluorine atom is not held in place by the crystalline field, and can be "kicked off" its position by the quivering motion of the accelerated electrons, leaving a vacancy behind. After the pulse, an electron can be captured by this vacancy, forming an F center. The other types of color centers are formed by the aggregation of F centers [14].

There are several interesting characteristics on the formation of these color centers. First, the formation of F aggregates *during* the irradiation. This can be confirmed by the green emission (broad band peaking at 541 nm) seen during the laser irradiation (Fig. 2(a)) that is characteristic of the F_3^+ color centers. They are excited by two 830 nm photons (laser light) being absorbed by the broad absorption band peaking at 448 nm. Second, the strong M band is also due to the F_2 color centers. The presence of these aggregates indicates that a high density

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of F centers is formed [14] by ultrashort pulses. Finally, it is well known that F_2 centers excited by strong blue light suffer a two photon photochemical reaction leading to F_2^+ color center production [15,16]. This process, that involves four 830 nm photons, is very likely because an 8 photon process is already onset. These centers are not stable, and along the time, they capture electrons and became F_2 centers again [14]. The recombined F_2 centers absorption spectrum, after 10 days, can be seen in Fig. 3, where there is a decrease in the F_2^+ band together with a increase in the F_2 one (due to their different oscillator strengths, the increase in one center band is different from the decrease in the other).

The color center tracks, shown in Fig. 2(c), start at the color center creation intensity threshold. This intensity threshold is determined by knowing the incident power and the maximum radius of the color center track, r_{max}, is given by [17]:

$$I_t = \frac{P_0}{e^1 \pi r_{\max}^2} \tag{1}$$

where P_0 is the pulse power and $e^1 = 2.7182\ldots$ is the base of natural logarithms. The maximum radius of the track, r_{max}, can be measured from an optical microscope image, as seen in Fig. 4. This intensity is related to the electrical field by:

$$E(V/m) = \sqrt{\frac{2}{\varepsilon_0 cn} I} = 27.43\sqrt{\frac{I(W/m^2)}{n}} \tag{2}$$

where ε_0 is the vacuum permissivity, c the speed of light and n the medium refractive index.

The maximum radius, averaged from measuring the six tracks, is r_{max}**=268 μm**, resulting in a color center creation threshold intensity, $\boldsymbol{I_t}$**=2038 GW/cm^2**, and consequently a threshold electric field of $\boldsymbol{E_0}$**=3.3·10^{7}V/cm**.

The mean kinetic (ponderomotive) energy of an electron quivering in the laser field is [18]:

$$U_p = \frac{e^2 E_0^2}{4m\omega_0^2} \tag{3}$$

where ω_0 is the laser frequency, and e and m are the electron charge and rest mass, respectively. Using the determined threshold electric field amplitude, the electron ponderomotive energy is $U_p = 0.09$ eV, and the maximum electron kinetic energy is 0.28 eV (3.17 U_p). This energy, although insufficient to generate X-rays, is enough to displace a neutral fluorine atom to an interstitial position, giving raise to the fundamental color center defect, the F center, as stated before.

Finally, one can see in Figs. 2(a) and 2(b) that the color center formation region begins at a lower intensity than the white light generation. This is assured by the threshold intensity for self focusing and white light generation in LiF that is 2.4 TW/cm^2, as calculated from the data by Brodeur and Chin [12], 20% above the intensity threshold for color center creation found in this work.

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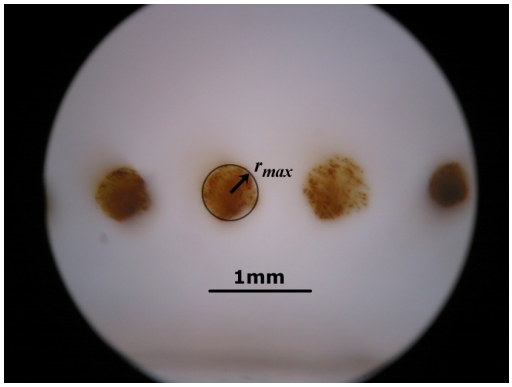

Fig. 4. Photography of the color center tracks, as seen longitudinally along the beam propagation axis, by an optical microscope. The centers creation intensity threshold could be determined by the laser power and the radius of the profile, seen in the picture.

4. Conclusions

Color centers were produced in the bulk of LiF single crystals by ultrashort pulse laser irradiation. The absorption and emission spectroscopic properties of these materials were measured showing that during the irradiation F, F_2, F_2^+ and F_3^+ color centers were created in the crystals.

The localized creation of color centers, due to the laser beam confinement, allowed us to determine the color center creation intensity threshold by a geometric method. Preliminary results indicate a color center formation threshold in LiF around $2\,TW/cm^2$. The threshold electric field could be calculated from this intensity threshold and therefore a maximum kinetic energy of the electron after ionization is ~0.3 eV. This and the minimum wavelength of 300 nm generated by LiF crystals under femtosecond pumping, assured that there is not enough kinetic energy to generate X-rays that could create color centers by ionizing radiation. We propose that the main mechanism for color center formation is the multiphoton ionization that neutralizes fluorine ions and their displacement by the quivering motion of electrons in the laser field.

As can be seen in expression 1, it is possible to control the maximum defect radius by controlling the incident power P_0. It is then possible to write a track with desired dimension, as it is needed for waveguiding, since there is a modulation in the refraction index due to the color center absorption bands.

Acknowledgments

We acknowledge the support of "Fundação de Amparo à Pesquisa do Estado de São Paulo," under the grant 00/15135-9.

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