

Confocal and Atomic Force Microscopies of Color Centers Produced by Ultrashort Laser Irradiation in LiF Crystals

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Abstract. We report properties of the spatial and spectral distribution of color centers produced in LiF single crystals by ultrashort high intensity laser pulses (60 fs, 10 GW) using confocal spectral microscopy and atomic force microscopy. We could identify a large amount of F centers that gave rise to aggregates such as F₂, F₄, F₂⁺ and F₃⁺ distributed in cracked shape brownish areas. We have taken a 3D image using confocal microscopy of the sample (luminescent image) and no difference is observed in the different planes. The atomic force microscopy image clearly shows the presence of defects on the modified surface. The formation of micrometer or sub-micrometer voids, filaments and void strings was observed and related to filamentation process.

Keywords: Color Centers, Ultrafast Phenomena, Waveguides, LiF

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INTRODUCTION

Color centers in ionic crystals present very interesting optical properties such as optical transitions sensitive to the surrounding lattice, broad absorption and emission bands in the near UV, visible and near IR regions of the spectrum[1]. Some of them present a four level optical cycle suitable for laser action, and are stable at room temperature[2-4].

LiF occupies a special place among the alkali halide crystals because it is not hygroscopic, possesses good physical and optical qualities, and stably hosts different species of color centers at room temperature[5]. The formation of optically active color centers in LiF by ionizing radiation (electrons and ions, gamma and X-rays) is a well-known phenomenon.

It was reported that color center formation in LiF increases the refractive index[6], and active channel waveguides were successfully fabricated by electron-beam lithography. Recently, it was shown that is possible to create color centers in LiF using ultrashort laser pulses[7]. This method allows the production of defects with dimensional control[8] by focusing the high-intensity ultrashort laser pulses inside the material, and optical waveguides and microgratings were fabricated deep inside LiF crystals[9, 10].

In this work, we study the distribution of color centers produced in LiF crystals by ultrashort laser pulses using confocal and atomic force microscopies.

EXPERIMENTAL SETUP

The samples of ultra pure LiF single crystals used in this work 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 converging lens to a radius of 12 μm , in the low power limit (no self-focusing). The samples were placed in such way that the beam waist was inside the crystals, and the irradiation was done at room temperature. The irradiation details are given in our previous work[7]. After the irradiation the samples were stored at liquid nitrogen temperature until measurements were performed. The color centers created were observed by absorption spectroscopy and also by atomic force and confocal microscopy.

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 laser irradiated LiF crystal with color centers was cleaved in a way that the color centers were at the crystal surface. The surfaces of the samples were then scanned in air with a Nanoscope IIIa Multimode (Digital Instruments) in contact mode, at a scan of about 0.500 Hz and $2 \times 2 \mu\text{m}^2$ of area, using Si_3N_4 cantilevers with spring constant of about 0.15 N/m and tip radius of 15 nm. Atomic force microscopy scan controls were appropriately adjusted (sufficient contact force and high gains) to avoid tip artifacts during samples scanning. The height images obtained were processed with Nanoscope software (version 5.12 r3).

The emission spectra were collected at different points within the sample by means of a confocal microscope Olympus Fluoview 1000 with spectral detection capability with 2nm resolution. Two different lasers with wavelengths 488nm and 543nm were used as excitation source in order to explore different possible color centers. A low magnification 10x objective was used in order to explore deeper inside the sample.

RESULTS

In our earlier work[7] we observed that various color centers and color centers aggregates were formed along the beam path and we could estimate the color center formation threshold ($\sim 2 \text{ TW}/\text{cm}^2$). The centers created are stable at room temperature, and we proposed that their creation was initiated by multiphoton excitation, followed by vacancy creation by pushing neutral atoms away from its equilibrium position in the lattice by the electrons quivering motion in the laser electric field.

Figure 1 presents a scheme of the color centers observation under the confocal microscope, where the brownish spots represent the color centers formed along the ultrashort pulses propagation path (z direction). The color centers emit light when illuminated, and the confocal microscope used has the ability of taking a spectrum at any marked region, and can pump the sample with two colors, generating fluorescence images, generating 3D images that show no significant differences between the centers formed along the pulses path. Figure 2 and Figure 3 show the confocal images (z section) and spectra measured from representative regions of the sample when excited by 488 nm and 543 nm light. The colored rectangles are the regions where the spectra were taken (averages over the entire rectangle). Within the range of resolution (several microns wide, ten microns or more high) no difference is seen in the spectra measured from the different spots, but the luminescence spectra are modified when the pump wavelength is changed. This indicates that different color centers, all in the same region, are being pumped. The 488 nm light excites mainly F_2 and F_3^+ centers that emit around 650 nm and 540 nm, respectively[11] (Figure 2). Under excitation at 543 nm two emission bands around 620 nm and 650 nm are observed (Figure 3). The emission band at 620 nm is tentatively ascribed to the emission of F_4 centers.

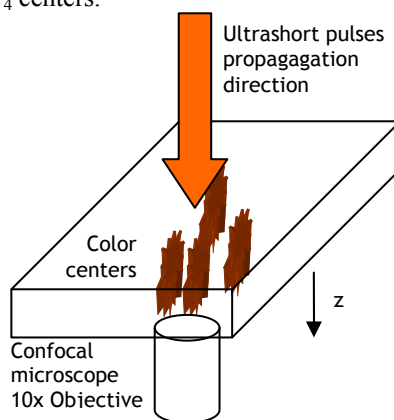


FIGURE 1. Experimental setup for the confocal microscopy measurements.

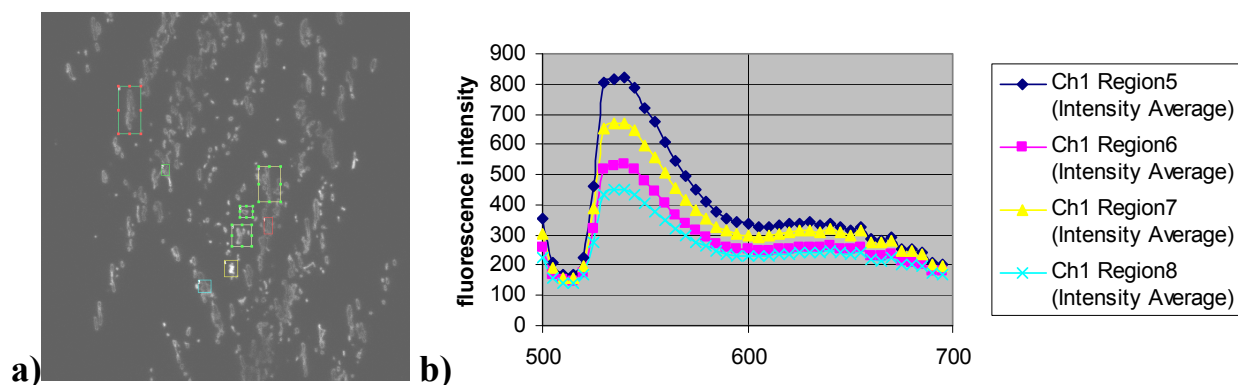


FIGURE 2. a) Confocal microscope image showing the regions where the spectra were taken (rectangles) under 488 nm pump. b) Fluorescence spectra for each region.

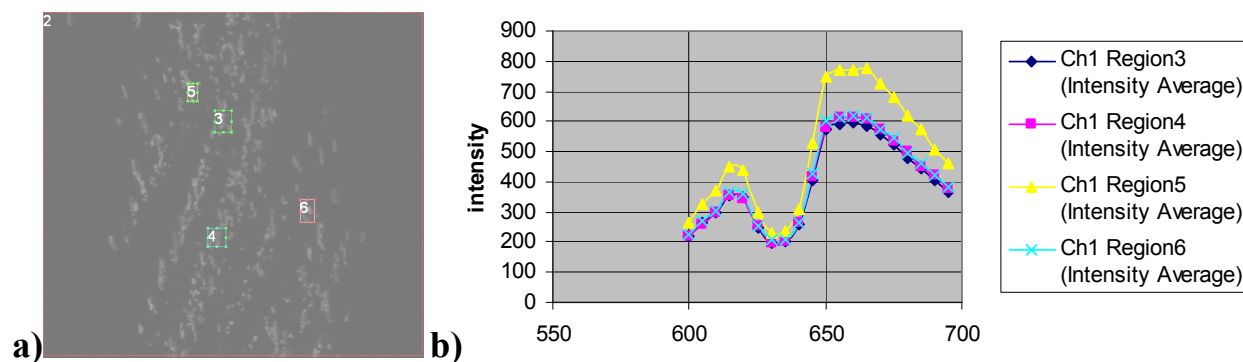


FIGURE 3. a) Confocal microscope image showing the regions where the spectra were taken (rectangles) under 543 nm pump. b) Fluorescence spectra for each region.

Atomic force microscopy (AFM) pictures of irradiated samples are shown in Figure 4. In AFM measurements, a probe consisting of a sharp tip (nominal tip radius is on the order of 10 nm) located near the end of a cantilever beam, is raster scanned across the sample surface using piezoelectric scanners. Changes in the tip-sample interaction are monitored using an optical lever detection system, in which a laser beam is reflected off of the cantilever and onto a position sensitive photodiode. During scanning, a particular operating parameter is maintained at a constant level, and images are generated through a feedback loop between the optical detection system and the piezoelectric scanners. The obtained results shown regions with and without tracks, correspondent to regions with and without color centers, and a 3D structure with dimensions between 100 nm and 1 μm can be observed. The formation of micrometer or sub-micrometer voids, filaments and void strings is discussed with the multiphoton ionization process, the avalanche ionization process and the nonlinear laser pulse self-action effect when femtosecond laser pulses propagate in wide-bandgap materials[12]. We propose that this structure pattern observed in ultrashort pulse laser irradiated LiF crystals is due to filamentation of laser pulse in the crystal. When a laser pulse interacts with LiF crystal the laser beam maintains a near constant beam waist over many Rayleigh lengths due to a temporal balance between self-focusing[13] and plasma defocusing. The defocusing effect of the plasma will balance the self-focusing and thus, limits the peak intensity of the laser pulse during the propagation. After the laser pulse is gone, a long plasma channel is left behind. This plasma channel is normally referred to as a “filament”. At the same time, through self phase modulation and self-steepening, the laser pulse self-transforms to a “white light laser pulse” featuring a supercontinuum in the material. In the case of LiF crystals we can see in Figure 5 the white light (supercontinuum) generation under ultrashort laser pulses incidence and also the by green emission of color centers. Multiple filamentation originates from local random inhomogeneities in the medium or irregularities of the beam profile and is usually unavoidable [14, 15].

The ability to localize optical energy in bulk media and filamentation control[14, 16] opens possibilities in areas like micromachining, like three-dimensional material modification and fabrication within bulk materials without

surface damage; the feasibility of “optically fabricating” photonic devices like resonators, beam-shapers, interferometers and amplifiers.

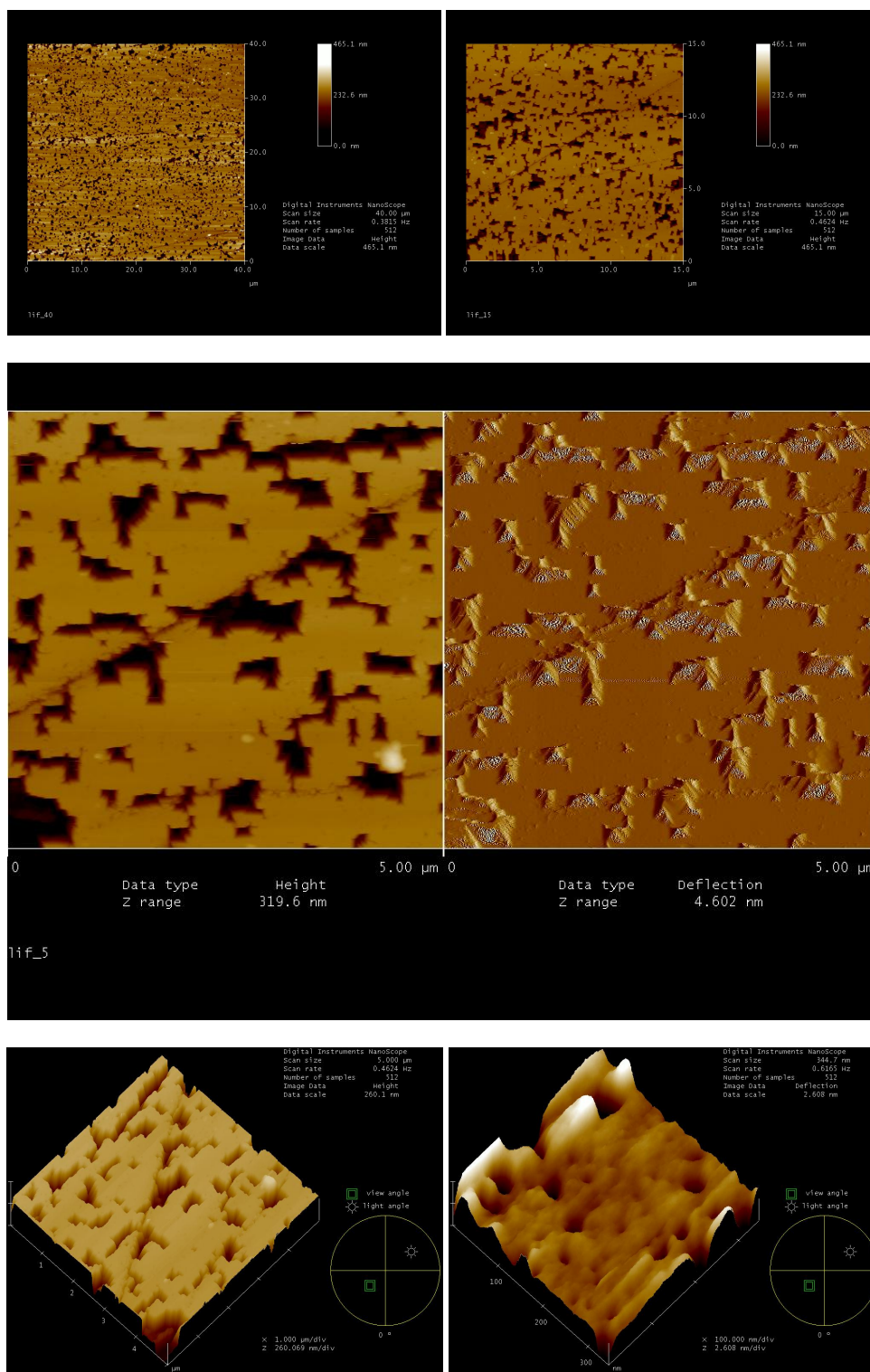


FIGURE 4. AFM 3D magnified image of color centers created in the LiF crystal bulk, observed on the cleaved face.

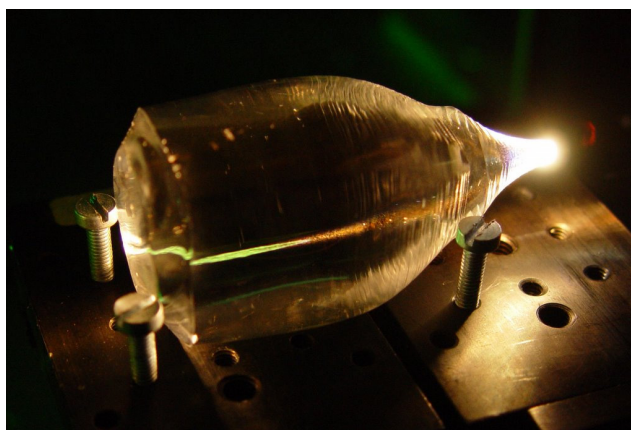


FIGURE 5. Green emission and white light generation along the beam path while under irradiation by the femtosecond pulses (the pulses came from the left).

CONCLUSIONS

Color centers were produced in the bulk of LiF single crystals by ultrashort laser pulses 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.

Within the range of resolution for the confocal microscope no difference was observed in the spectra measured from the different spots, but the luminescence spectra are modified when the pump wavelength is changed. The 488 nm light excites mainly F_2 and F_3^+ centers. Under excitation at 543 nm two emission bands around 620 nm and 650 nm are observed. The emission band at 620 nm is tentatively ascribed to emission of F_4 centers.

The AFM image clearly shows the presence of defects on the modified exposed bulk. The formation of micrometer or sub-micrometer voids, filaments and void strings was observed and related to filamentation process. Controlling the filamentation is then possible to write a track with desired dimension, as it is needed for wave guiding. Therefore, the present technique will be useful in the fabrication of three-dimensional colored industrial art object, optical memory, and micro-optical devices.

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