

# Determination of a dose-like curve for active colour centres produced in LiF single crystals by ultrashort high intensity laser pulses and a preliminary investigation of their spectral and spatial properties by confocal and atomic microscopies

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## Abstract

In this paper, the spatial and spectral properties of colour centres produced in LiF single crystals by ultrashort high intensity laser pulses are reported. The emission spectra of the centres were measured conventionally and also by confocal microscopy. A large amount of F centres that gave rise to aggregates such as  $F_2$ ,  $F_4$ ,  $F_2^+$  and  $F_3^+$  could be identified, showing a microscopic homogeneous distribution. The coloured surfaces were also spatially characterized by atomic force microscopy, and the images show the presence of defects on the modified surface. The formation of micrometric and sub-micrometric structures was observed and related to filamentation processes.

**Keywords:** colour centres, ultrafast phenomena, waveguides, LiF

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

LiF occupies a special place among the alkali halide crystals. LiF is not hygroscopic, possesses good optical and physical properties, and can host different species of colour centres at room temperature [1]. Colour centres in LiF present broad absorption and emission bands in the near UV, visible and near IR regions of the spectrum [2]. Some of these bands present a four level optical cycle suitable for laser action, and are stable at room temperature [3–5].

The formation of optically active colour centres in LiF by ionizing radiation (electrons and ions, gamma-rays and x-

rays) is a well-known phenomenon. It was reported that colour centre formation in LiF increases the refractive index [6], and active channel waveguides were successfully fabricated by electron-beam lithography. Recently, it was shown that it is possible to create colour centres in LiF using ultrashort laser pulses [7]. This method allows the production of defects with geometrical control [8] by focusing the high intensity ultrashort laser pulses inside the material, and optical waveguides and microgratings were fabricated deep inside LiF crystals [8, 9].

In this work, we determine a dose-like curve for the colour centre formation in LiF crystals as a function of the ultrashort pulse energy using fluorescence spectroscopy, and study the

microscopic distribution of the colour centres using confocal and atomic force microscopies.

## 2. Experimental set-up

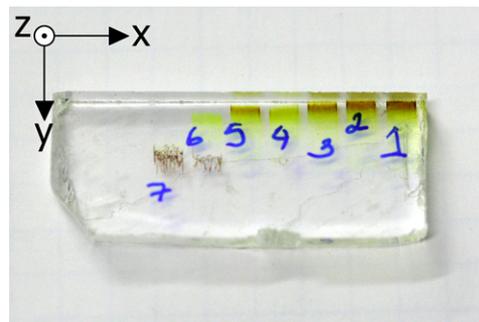
The ultrapure LiF single crystals used in this work were grown in our crystal growth facility by the Czochralski technique under argon atmosphere [10]. All the samples used in this work were prepared cleaving the crystals (all sample surfaces are cleaved). Colour centres were produced inside the LiF samples by ultrashort laser pulses. The emission spectra of the created centres were measured by a spectrometer, and also by a confocal microscope. The centres' absorption spectra were measured by a dual beam spectrometer (Cary 17D). The coloured surfaces were also probed by atomic force microscopy.

For creating the colour centres, a Ti:sapphire CPA laser system operating at 830 nm, producing a train of 60 fs pulses at 1 kHz, in a beam with a  $M^2 = 1.6$ , was used. The beam was focused inside the samples by an 83 mm converging lens to a radius of 12  $\mu\text{m}$ , in such a way that there was no ablation at the sample surface. All the irradiations were done at room temperature.

For the absorption and emission spectra measurements, a  $40 \times 15 \times 5 \text{ mm}^3$  sample was irradiated with the laser impinging on one of the  $40 \times 5 \text{ mm}^2$  faces ( $xz$  surface in figure 1), and propagating inside the sample in the  $y$  direction. The sample was placed in a computer controlled translation table, and was independently moved along the  $x$  and  $z$  axes in sinusoidal oscillations with different frequencies for 5 min, in order that a volumetric region with colour centres was formed. The amplitudes of the movements in the  $x$  and  $z$  directions were 3 mm and 0.5 mm, respectively. The sample was irradiated, at different positions, with 80, 96, 152, 126, 194, 232, and 275  $\mu\text{J}$  pulses, for 5 min for each irradiation, forming regions with different colour centre densities, as can be seen in figure 1. The absorption spectra of these regions were measured two days after irradiation, through the  $z$  direction (spectrometer beam impinging on the  $xy$  face, figure 1), in the range 200–800 nm by a dual beam Spectrophotometer (Varian Cary 17D). To obtain a colour centre formation dose-like curve, each colour centre region emission spectra was measured under 440 nm excitation (second harmonic from a Femtolasers Rainbow oscillator), and its emission was measured with a fibre spectrometer (Newport OSM-400 VIS-IR). The excitation laser propagated inside the sample in the  $y$  direction, and the emission was collected through the  $xy$  face (figure 1).

Two other LiF samples were cleaved and irradiated for the confocal and atomic force microscopies studies. Colour centres were created by 750  $\mu\text{J}$  pulses, without moving the sample (the irradiation details are given in our previous work [7]). After the irradiation, the samples were left at room temperature until the colour centres stabilized, and then were cleaved again in a plane transversal to the laser propagation direction, in a way that the colour centres were at the crystal surface. Each microscopy measurement was performed in a different sample.

The confocal microscopy measurements were performed with an Olympus Fluoview 1000 confocal microscope with



**Figure 1.** Regions of colour centres produced by ultrashort pulses; the regions marked as 1, 2, 3, 4, 5, 6, and 7 correspond to colour centres produced by pulses with energies 275, 232, 194, 126, 152, 96, and 80  $\mu\text{J}$ , respectively.

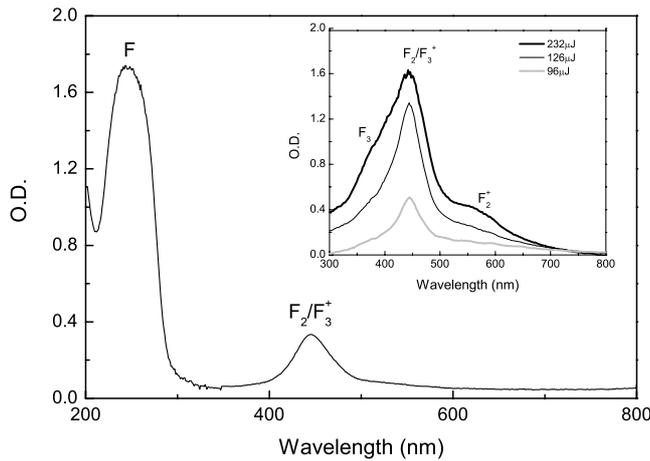
spectral detection capability, and the emission spectra of the colour centres were measured at different positions. For these emission spectra measurements, the colour centres were excited under 488 and 543 nm in order to explore different possible colour centres. A low magnification objective (10 $\times$ ) was used in order to explore deeper inside the sample.

The atomic force measurements were done, in air, with a Nanoscope IIIa Multimode (Digital Instruments) in contact mode, at a scan of about 0.500 Hz and over  $2 \times 2 \mu\text{m}^2$  of area, using  $\text{Si}_3\text{N}_4$  cantilevers with spring constant of about 0.15  $\text{N m}^{-1}$  and tip radius of 15 nm. The atomic force microscopy scan controls were appropriately adjusted (sufficient contact force and high gains) to avoid tip artefacts while scanning the samples. The height images obtained were processed with Nanoscope software (version 5.12 r3).

## 3. Results

After ultrashort pulse laser irradiation various colour centres and colour centre aggregates are formed in LiF crystals along the beam path, and the estimated colour centre formation threshold is 2  $\text{TW cm}^{-2}$  [7]. The centres 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 the equilibrium position in the lattice by the electrons' quivering motion in the laser electric field. The presence of  $\text{F}_2$  and  $\text{F}_3^+$  centres indicates that the primary F centres are created in high concentrations, since the secondary centres are originated from the coalescence of migrating F centres; also the creation of ionized centres is enhanced [7] when comparing to traditional ionizing radiation processes.

In figure 2 the absorption spectrum of a LiF crystal irradiated with ultrashort pulses is shown. The most important absorption band in LiF crystals occurs around 250 nm, corresponding to the primary F centre. Due to the samples' thicknesses and irradiation conditions, very intense F centre bands, difficult to be adequately resolved, were originated. The  $\text{F}_3^+$  and  $\text{F}_2$  centres are responsible for the almost overlapping absorption band, generally called the M band, due to their absorptions at 444 nm ( $\text{F}_2$ ) and 448 nm ( $\text{F}_3^+$ ). Besides the main M absorption band, other aggregate defects have been detected: absorption bands in the region between 315 and 375 nm are



**Figure 2.** Absorption spectra of the colour centres produced in LiF by ultrashort pulse irradiation. The absorption band around 250 nm corresponds to F centre absorption and could not be adequately resolved in the samples. The inset graph shows details of absorption curves following irradiation by 232, 126 and 96  $\mu\text{J}$  pulses.

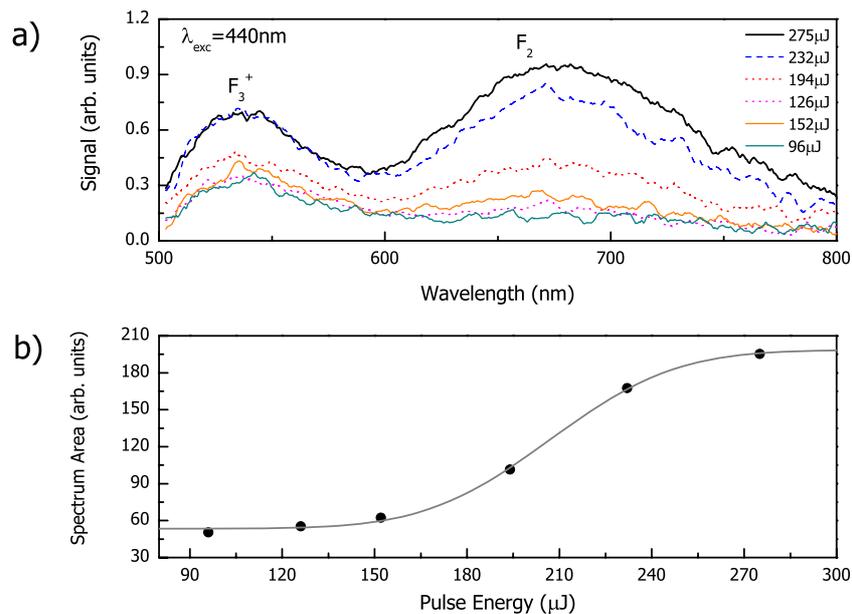
due to the  $R_1$  and  $R_2$  transition of three associated F centres ( $F_3$  centre); and 520 and 545 nm bands, attributed to  $N_1$  and  $N_2$  transitions of four associated F centres (N centre). The band due to the  $F_2^+$  centre (ionized  $F_2$  centre) at 632 nm is not observed [11]. The presence of these aggregates indicates that a high density of F centres is formed [11] by ultrashort pulses during the irradiation. From the absorption spectra it is possible to estimate the  $F_2$  and  $F_3^+$  centre concentrations in each sample using the Smakula formula [12]. Table 1 presents the centres' estimated concentrations calculated from the colour centres' spectra. For these calculations, the refractive index value used was 1.39, the width of the absorption bands at half-maximum, at room temperature, was taken from the literature [13] (0.16 eV for  $F_2$  and 0.29 eV for  $F_3^+$  centres),

**Table 1.** Estimated concentrations of  $F_2$  and  $F_3^+$  colour centres produced with different ultrashort pulse energies: 232, 126, and 96  $\mu\text{J}$ .

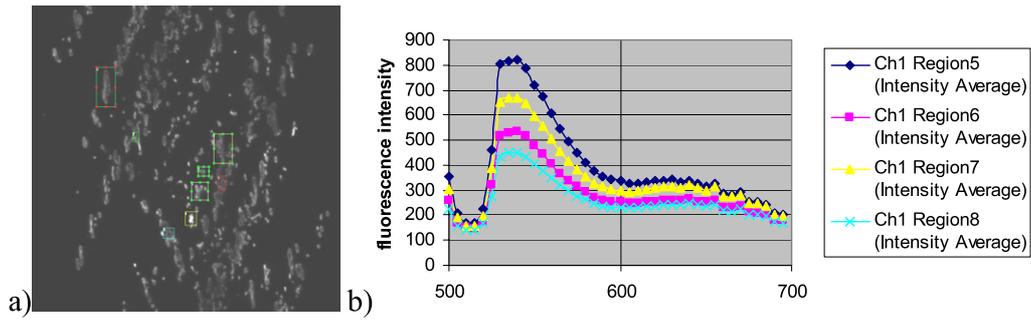
Pulse energy ( $\mu\text{J}$ )	Colour centre density ( $10^{16} \text{ cm}^{-3}$ )	
	$F_2$	$F_3^+$
232	(O.D. = 0.97) 23.0	(O.D. = 0.53) 22.8
126	(O.D. = 0.70) 16.6	(O.D. = 0.49) 21.1
96	(O.D. = 0.19) 4.5	(O.D. = 0.24) 10.3

and each band optical density was obtained by a Gaussian decomposition of the sample spectrum. An oscillator strength of 0.5 was assumed, and the colour centres' region thickness was considered to be 0.5 mm, since the samples were moved by this amount during the irradiation, as described in section 2.

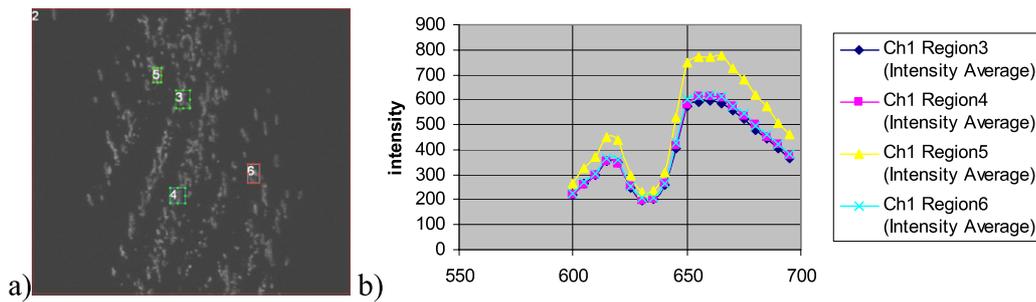
The emission spectra for  $F_3^+$  and  $F_2$  centres produced by different ultrashort pulse energies, obtained under excitation at 440 nm, are shown in figure 3(a). In these spectra we observe the typical broad emission bands related to transitions of the  $F_3^+$  and  $F_2$  centres centred at 535 nm and 670 nm, respectively. It was not possible to detect emission from the colour centres formed at the lower irradiation energy (80  $\mu\text{J}$ , region 7 in figure 1), so this point is not plotted in the graphic. A growth of the emission spectra area between 500 and 800 nm is clearly observed with the increase in the pulse energy, evidencing that a greater density of centres is created at higher intensities, corroborating the results obtained using the Smakula formula (table 1). A plot of the spectrum area as a function of the pulse energy exhibits a dose-like behaviour with a saturation, as shown in figure 3(b). The creation of colour centres must be investigated at higher pulse energies, but this saturation indicates that it is not possible to create an arbitrarily high concentration of colour centres in LiF by ultrashort laser pulses.



**Figure 3.** (a) Emission spectra obtained under excitation at 440 nm for centres produced by different ultrashort pulse energies, indicated inside the graphic. (b) Colour centre formation dose-like curve obtained as a function of the ultrashort pulse energy.



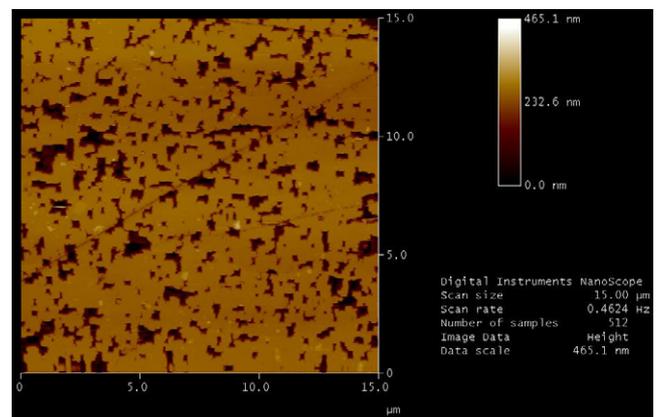
**Figure 4.** (a) Confocal microscope image showing the regions where the spectra were taken (rectangles) under 488 nm pump. (b) Fluorescence spectra for each region.



**Figure 5.** (a) Confocal microscope image showing the regions where the spectra were taken (rectangles) under 543 nm pump. (b) Fluorescence spectra for each region.

The confocal microscope used has the capability of measuring emission spectra at any chosen region, defined by the objective utilized, and can pump the sample with two wavelengths, generating 3D images. Figures 4 and 5 show the confocal images taken in planes transversal to the laser propagation direction, and emission spectra measured from representative regions of the same sample when excited by 488 and 543 nm light, presenting no significant differences between the centres formed along the pulses' propagation path. The coloured 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 depth) no difference is seen in the spectra measured from the different spots (apart from the spectra amplitude, since they were not normalized by the volume from the region where each one was measured), evidencing that the colour centres are created with a homogeneous distribution (in this scale). When the pump wavelength is changed, the luminescence spectra are modified, indicating that different colour centres, all created by the ultrashort pulses in the same region, are being pumped. The 488 nm light excites mainly  $F_2$  and  $F_3^+$  centres that emit around 670 nm and 540 nm, respectively [11] (figure 4). Under excitation at 543 nm two emission bands around 620 and 670 nm are observed (figure 5). The emission band at 620 nm is tentatively ascribed to the emission of  $F_4$  centres.

In atomic force microscopy (AFM) measurements, a probe consisting of a sharp tip (the nominal tip radius is of 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



**Figure 6.** AFM 3D magnified image of colour centres created in the LiF crystal bulk, observed on the cleaved face transversal to the laser propagation direction.

using an optical lever detection system, in which a laser beam is reflected off 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. Figure 6 presents an AFM image of the cleaved face of the irradiated sample, in the region where colour centres were created. In this image it is possible to observe structures with dimensions between 100 and 1 μm (black regions). We propose that these structures correspond to clusters of defects [14] such

as colour centres and charged particles. These defects are a consequence from the avalanche process resulting from the multiphotonic ionization, and from the nonlinear self-action effects when femtosecond laser pulses propagate in wide-bandgap materials [15]. We also propose that these clusters are due to the filamentation of the laser pulses 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 [16] and plasma defocusing (self-trapping). The defocusing effect of the plasma will balance the self-focusing, thus limiting the peak intensity of the laser pulses during the propagation. After the laser pulse ends, a long plasma channel (filament) is left behind. Simultaneously, 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, the white light (supercontinuum) generation under ultrashort laser pulse incidence is observed during the centre creation (see figure 2(a) of our previous work [7]). Multiple filamentation originates from local random inhomogeneities in the medium or irregularities of the beam profile and is usually unavoidable [17, 18].

The ability to localize optical energy in bulk media and filamentation control [17, 19] opens possibilities in areas such as micromachining, three-dimensional material modification, and fabrication within bulk materials without surface damage, and the feasibility of 'optically fabricating' photonic devices such as resonators, beam-shapers, interferometers and amplifiers.

#### 4. Conclusions

Colour centres were produced in the bulk of LiF single crystals by ultrashort laser pulse irradiation, and by measuring the absorption and emission spectra, they were determined to be  $F$ ,  $F_2$ ,  $F_3^+$  and  $F_4$  centres. There is a high density of secondary centres (aggregates) formed during the irradiation, and a colour centre production dose-like curve was obtained, indicating that the density of the centres created by ultrashort pulses reaches an intensity saturation in the conditions used. Within the range of resolution for the confocal microscope no difference was observed in the spectra measured from the different spots, evidencing that the centres are homogeneously distributed in the few micrometres scale. The 488 nm light excites mainly  $F_2$  and  $F_3^+$  centres. Under excitation at 543 nm two emission bands around 620 and 670 nm are observed.

The AFM image clearly shows the presence of defects on the modified exposed bulk. The formation of micrometric and sub-micrometric structures was observed and related to filamentation processes. By controlling the filamentation it is then possible to write a track with desired dimension, as is needed for waveguiding. Therefore, the present technique will be useful in the fabrication of three-dimensional coloured industrial art objects, optical memories, and micro-optical devices.

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