Fluorescence Properties of Colour Centres Produced by Ultrashort Laser Irradiation in LiF Crystals

R E Samad 1, L C Courrol 2, L Gomes 1, I M Ranieri 1, S L Baldochi 1, A Z de Freitas 1 and N D Vieira Jr 1

1 Centro de Lasers e Aplicações, IPEN–CNEN/SP, São Paulo, SP - Brazil, 05508-000
2 Departamento de Ciências Exatas e da Terra, UNIFESP, Diadema, SP - Brazil, 09972-270

Corresponding author e-mail: resamad@gmail.com

Abstract. LiF is a nonhygroscopic alkali halide crystal which possesses good optical and physical properties, and can host different species of colour centres at room temperature. Colour centres in LiF present broad absorption and emission bands in the near UV, visible and near IR regions of the spectrum. In this paper we study spectroscopic properties of colour centres produced in LiF by ultrashort laser pulses. The absorption and emission properties of these materials were measured showing that during the irradiation F, F₂, F₃⁺, F₂⁻ and F⁻ colour centres were created in the crystals. A colour centres formation dose-like curve as a function of the ultrashort pulse energy was determined using fluorescence spectroscopy.

1. Introduction
Colour centres 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, 3].

LiF occupies a special place among the alkali halide crystals because it is nonhygroscopic, possesses good physical and optical qualities, and hosts different species of colour centres at room temperature[4]. The formation of optically active colour centres in LiF by ionizing radiation such as charged particles (electrons and ions) as well as by gamma and X-rays is well-known.

It was reported that colour centre formation in LiF increases its refractive index, and active channel waveguides were successfully fabricated by electron-beam lithography [5-13]. Recently, it was shown that is possible to create colour centres in LiF using ultrashort laser pulses [14-17]. This method allows the production of defects with dimensional control by focusing the high-intensity ultrashort laser pulses inside the material, and optical waveguides and microgratings were produced deep inside LiF crystal.

In this work, we study the fluorescence optical properties of colour centres produced in LiF crystals by ultrashort laser pulses and determine the F₂, F₃⁺, and F⁻ formation dose-like curve in LiF crystals as a function of the ultrashort pulse energy.
2. 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[18]. All samples used in the reported experiments were cleaved.

For creating the colour centres, 60 fs pulses from a Ti:Sapphire CPA laser system (Quantronix Odin) operating at 830 nm, at 1 kHz repetition rate, in a beam with a M²=1.6, were used. The pulses maximum energy was 275 µJ, and the beam was focused inside the samples by an 83 mm converging lens to a radius of 12 µm, in such a way that there was no ablation at the sample surface. All irradiations were done at room temperature.

For the absorption and emission spectra measurements, a 40 × 15 × 5 mm³ sample was irradiated with the laser impinging on one of the 40 × 5 mm² face (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 in the x and z axes in sinusoidal oscillations with different frequencies during 5 minutes, 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, 126, 152, 194, 232 and 275 µJ pulses, during 5 minutes for each irradiation, forming regions with different colour centres densities, as can be seen in Figure 1. Two days after irradiation, the absorption spectra were measured, through the z direction, in the range 200 nm-800 nm by a dual beam Spectrophotometer (Varian Cary 17D). For obtaining a colour centre formation dose curve, each colour centre region was excited by 440 nm laser light from the second harmonic from a Femtolasers Rainbow oscillator, and its emission spectrum was measured by a Newport OSM-400 VIS-IR fibre spectrometer.

3. Results
Figure 2a shows the absorption spectra of the colour centres created in the LiF crystal under three different ultrashort pulses energies. A strong absorption band around 250 nm, corresponding to F centres, could not be resolved due to the thickness of the centres region, and for this reason is not shown. The shoulder observed in the region between 315 nm and 375 nm is due to F₂ centres (three associated F centres) absorption. F₁ and F₂ centres are responsibly by the almost overlapping absorption band at 444 nm (F₂ or two associated F centres) and 448 nm (F₁⁺ or ionized F₁ centres); the 520 nm and 545 nm bands are attributed to F₄ centres (four associated F centres). The band due to the
F$_2^+$ centre (ionized F$_2$ centre) at 632 nm is not observed. The presence of these aggregates indicates that a high density of F centres is formed by ultrashort pulses during the irradiation.

From the absorption spectra shown in figure 2a it is possible to estimate the F$_2$ and F$_3^+$ centres concentrations in each sample using the Smakula formula [19] explicitly written in terms of the sample optical density (OD) and length ($l$):

\[
N_f = 1.29 \times 10^{17} \left( \frac{n}{n^2 + 2} \right)^2 \frac{2.303 \times OD}{l} W
\]  

(1)

For these calculations, whose results are shown in Table 1, the refractive index value used was 1.39, the width of the absorption bands at half-maximum, $W$, at room temperature, was taken from the literature [20] (0.16 eV for F$_2$ and 0.29 eV for F$_3^+$ centres); the optical density for each band was obtained by a Gaussian decomposition of the sample spectrum, show in Figure 2b only for the most intense spectrum for clarity. An oscillator strength of $f = 0.5$ was assumed, and the colour centres’ region thickness was considered to be $l = 0.5$ mm since the samples were moved by this amount during the irradiation.

**Table 1.** Concentrations of F$_2$ and F$_3^+$ colour centres produced with different ultrashort pulse energies 232, 126 and 96 µJ.

| Pulse Energy (µJ) | Centres Concentration (10$^{17}$ cm$^{-3}$) |
|-------------------|---------------------------------------------|
|                   | F$_2$                                      | F$_3^+$                                    |
| 232               | (OD = 1.00) 2.376                          | (OD = 0.37) 1.593                         |
| 126               | (OD = 0.60) 1.426                          | (OD = 0.18) 0.775                         |
| 96                | (OD = 0.31) 0.737                          | (OD = 0.11) 0.474                         |

Figure 2. a) Absorption spectra of the colour centres produced in LiF by ultrashort pulses irradiation for three different energies: 232, 126 and 96 µJ. b) Gaussian decomposition of the spectrum correspondent to the 232 µJ irradiation along with the experimental data (circles); the gray lines are the individual Gaussians and the black line is its sum.

Figure 3 shows the emission spectrum of colour centres produced by the 232 µJ ultrashort pulses, exciting the sample with 440 nm laser light propagating in the $y$ direction and detected by a fibre spectrometer looking at the $z$ direction. A 3-Gaussians fit was done to the experimental data to determine the curves for the F$_3^+$, F$_2$ and F$_2^-$ centres emissions. The emission of the F$_2^+$ centre is centred
on 1.4 eV (900 nm) and could not be fitted due to the 2nd order of the laser scattering that peaks at 880 nm. In this spectrum we observe the typical broad emission bands related to transitions of the \( \text{F}_3^+ \) and \( \text{F}_2 \) centres at 2.35 eV and 1.85 eV (528 nm and 670 nm), respectively, shown in table 2, and also an intense emission band at 1.17 eV (1060 nm) due to the \( \text{F}_2^- \) emission.

**Table 2.** Optical characteristics of colour centres produced in LiF crystals.

| Centre | Absorption Energy (eV) | Absorption Wavelength (nm) | Emission Energy (eV) | Emission Wavelength (nm) |
|--------|------------------------|----------------------------|----------------------|--------------------------|
| F      | 5.00                   | 248                        | -                    | -                        |
| \( \text{F}_3 \) | 3.92, 3.32          | 316, 374                   | -                    | -                        |
| \( \text{F}_2 \) | 2.79                | 444                        | 1.85                 | 670                      |
| \( \text{F}_3^+ \) | 2.77                | 448                        | 2.35                 | 528                      |
| \( \text{F}_2^- \) | 1.29                | 960                        | 1.17                 | 1060                     |

The peak intensities and band areas of \( \text{F}_3^+ \), \( \text{F}_2 \), and \( \text{F}_2^- \) colour centres emissions, obtained from the 3-Gaussians fit, were plotted as a function of the pulses energies to obtain the dose-like curves shown in figures 4a and 4b. The growth of the emission intensities and areas is clearly observed with the increase in the pulse energy, evidencing that a greater density of centres is created at higher intensities, corroborating the concentration growth calculated using Smakula formula, shown in table 1. It can be seen that, under the irradiation condition used in this work, the density of the centres created by ultrashort pulses seems to approach saturation, but this behaviour has to be investigated at higher pulse energies to be confirmed.

![Figure 3](image-url)  
*Figure 3.* Emission spectra obtained under excitation at 440 nm for centres produced by 232 µJ ultrashort laser pulse energies, showing a 3-Gaussians fit to the centres emission peaks. The laser scattering peak is the grating second order of the 440 nm emission.
Figure 4. Colour centres dose-like curves obtained as a function of the ultrashort pulse energy, calculated from the 3-Gaussians fit: a) emission peak intensity b) emission band area.

4. Conclusions
After ultrashort pulse laser irradiation, various stable colour centres and colour centres aggregates were formed in LiF crystals along the beam path. The centres created are stable at room temperature. We proposed that the colour centres 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. By measuring absorption and emission spectra, the colour centre were determined to be F, F$_2$, F$_3^+$, and F$_2^-$ centres. There is a high density of secondary centres (aggregates) formed during the irradiation, and a colour centre production dose-like curve was obtained. This dose curve suggests that the density of the centres created by ultrashort pulses reaches an intensity saturation, but this behaviour has to be investigated at higher pulse energies.

5. References
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