Colour-centre concentrations in broad-band light-emitting strip waveguides in Lithium Fluoride

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Abstract. The concentrations of primary F centres and F2 and F3+ aggregate defects were evaluated as a function of the irradiation dose in broad-band light-emitting single-mode strip waveguides directly written with 12 keV electrons at the surface of a LiF crystal. From a careful best-fit procedure of the optical transmission spectra, measured on microstructures only few tens of micrometers wide, the spectral contributions of several types of colour centres were identified and quantified. This characterization provided useful information for the optimization of these confining microstructures and for the development of waveguide colour centre lasers.

1. Introduction
Lithium Fluoride (LiF) crystals and films have shown high potential for the realization of optoelectronic devices thanks to the very interesting optical properties of colour centres (CCs), which can be generated by low energy electrons [1,2] or by exposure to energetic photons, such as soft [3] and hard [4] X-rays or intense ultra-short laser pulses in the infrared [5,6]. In particular, the laser-active F3 and F3+ aggregate CCs (two electrons bound to two and three anion vacancies, respectively) show broad and intense photoluminescence in their emission bands peaked at 670 and 535 nm, under simultaneous optical excitation in their almost overlapping absorption bands at about 450 nm, even at room temperature (RT). Nowadays, one of the most promising fields of application of CCs in LiF is in the development of active optical micro-devices, among them broad-band visible-emitting colour-centre waveguide lasers [6,7], based on the peculiar spectroscopic features of active electronic defects in this promising material.

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Despite of the advantages the waveguide configuration provides for laser action and the successful results assessed in the case of low energy electrons [7,8] and ion-beam irradiation [9,10], the full spectral characterization, hence the optimization, of LiF-based single-mode active waveguides still remains a very difficult task.

The stable formation of high concentrations of primary and aggregate defects within a thin surface layer of the crystal locally induces a spectral-dependent modification in the refractive index of the irradiated volume with respect to the surrounding materials. In the case of single-mode strip waveguides induced in LiF crystals by 12 keV electron irradiation, an increase of the order of $10^{-3}$ in the real part of the index of refraction in the green-red wavelength interval [11] is sufficient to confine the laser-active $F_2$ and $F_3^+$ photoluminescence under optical pumping in the blue spectral range [7,8].

In this paper CC volume concentrations are evaluated as a function of the irradiation dose for three active micro-strips produced by 12 keV electrons on the same LiF crystal. The obtained results are discussed in connection with the modifications of the complex refractive index in the irradiated volume and the waveguide amplifying properties.

2. Experimental

Low-energy electron beams of energy 12 keV were used to produce three optically-active coloured strips, 3 mm long and about 150 $\mu$m wide, at the surface of a polished LiF single crystal of size (20x15x2.5) mm$^3$. Irradiations were performed at RT in a scanning electron microscope, at a fixed current of 10 nA, for increasing exposure times of 12, 24 and 48 minutes. These active strip waveguides were successfully characterized with confocal fluorescence microscopy [12] and optical transmittance measurements were taken in a highly versatile spectrophotometer [13], which can measure microstructures few tens of micrometer wide in the spectral range from 220 to 800 nm.

3. Results and discussions

The light-emitting strip waveguides have comparable width of ~145 $\mu$m, as deduced from the fluorescence image reported in figure 1 under blue illumination. The bright areas correspond to the irradiated channels, which emit green and red photoluminescence due to the stable formation of $F_3^+$ and $F_2$ aggregate defects, respectively. The fluorescence emission is clearly visible even by naked eyes under Argon laser excitation at the wavelength of 458 nm, as shown in figure 2.

![Figure 1](image1.png)  
**Figure 1.** Fluorescence image of a coloured strip induced on a LiF crystal by irradiation with 12 keV electrons under blue illumination.

![Figure 2](image2.png)  
**Figure 2.** Photograph of coloured strips induced on a LiF crystal by irradiation with 12 keV electrons under Argon laser illumination.
The strips appear uniformly coloured, with quite well defined boundaries and constant width. In figure 2 the optical transmittance spectra measured outside (blank crystal) and inside the three coloured strips induced with 12 keV electrons at increasing doses are reported. The minima of the transmittance spectra at \( \approx 245 \text{ nm} \) and at \( \approx 445 \text{ nm} \) are clearly observed. They are ascribed to the primary F centre (an anion vacancy occupied by an electron) absorption band, and to the M one, due to the overlapping of \( F_2 \) and \( F_3^+ \) absorption bands [14]. The transmittance minima values at the peak wavelength of the M absorption bands decrease monotonically with the increase of irradiation dose.

![Figure 3](image)

**Figure 3.** Optical transmittance spectra of three coloured strips induced on a LiF crystal by irradiation with 12 keV electrons at increasing doses. The measured spectrum of the blank crystal is also reported for comparison.

A crucial problem concerning heavily irradiated LiF crystals is the coexistence of several kinds of aggregate defects with often overlapping absorption bands, which makes it difficult to clearly evaluate the single contributions due to individual centres. Other spectroscopic features, ascribed to several kinds of larger aggregate defects, can be recognized [15]: e.g., the absorption features located at 315 and 380 nm are attributed to the \( R_1 \) and \( R_2 \) transitions of the \( F_3 \) defect, consisting of three adjacent F centres. The 515 and 545 nm absorption bands are attributed to the \( N_1 \) and \( N_2 \) transitions of the \( F_4 \) defects (four associated F centers). The M-band spectral range, where the \( F_2 \) and \( F_3^+ \) absorption bands overlap, is further complicated by the presence of another broad absorption band, which appears as a shoulder of the M band on the short wavelength side and it is associated to the presence of Li colloids [15,10]. A semi-classical dipole-electromagnetic field interaction model, which consider CCs in LiF as elementary two-level quantum systems interacting with the electromagnetic field by means of a dipole-type Hamiltonian, later generalized to include the contribution of inhomogeneous Gaussian absorption bands [16], was successfully applied to evaluate how CCs modify the complex refractive index [17]. The complex permittivity of the irradiated surface layer can be modeled as the sum of distinct absorption-band contributions, each one due to different types of CCs; it is dependent on the photon energy, on the amplitudes of the dielectric susceptibilities at the resonance absorption energies of CCs for Lorentzian and Gaussian bands, and on their half widths at half maximum (HWHMs). The dielectric susceptibilities, \( \chi \), are also dependent on the penetration depth of low-energy electrons, due to the proportionality of these quantities to the concentration of CCs along the depth [12], i.e. the dipole densities of harmonic oscillators, which were assumed as flat along the depth, fixed equal to 1.3 \( \mu \text{m} \) according to Monte Carlo simulations [2,12]. The fit parameters during data reduction of the experimental spectra were the resonance energies, the HWHMs, and the dielectric-susceptibility...
amplitudes of the bands associated with each type of CC, from which the contributions to the absorption coefficient were derived. The obtained best-fit results are summarized in table 1 for the strip irradiated with 12 keV electrons at the highest dose of 7.8x10^{-3} C/cm².

**Table 1.** Band parameters resulting from the best fit of the transmittance spectrum for the strip irradiated with 12 keV electrons at the highest dose of 7.8x10^{-3} C/cm². The confidence intervals were evaluated with a Monte Carlo algorithm (40 statistical counts).

| Centre type | Band type | E (eV)     | HWHM (eV) | \( \langle \text{max} | \text{Im}(\chi) \rangle \) |
|-------------|-----------|------------|-----------|-----------------------------|
| F           | G         | 5.038 ± 0.003 | 0.363 ± 0.005 | 0.0369 ± 0.003 |
| F₃(R₁)      | L         | 3.99 ± 0.05  | 0.14 ± 0.11  | 0.0017 ± 0.008 |
| F₃(R₂)      | L         | 3.31 ± 0.12  | 0.39 ± 0.14  | 0.0068 ± 0.0009 |
| Li colloids | G         | 2.98 ± 0.02  | 0.14 ± 0.042 | 0.0072 ± 0.0023 |
| F₂         | L         | 2.79⁺⁺⁺      | 0.103        | 0.0162 ± 0.0044 |
| F₃⁺        | L         | 2.77⁺⁺⁺      | 0.139        | 0.0213 ± 0.0034 |
| F₃(N₁)      | L         | 2.42 ± 0.03  | 0.09 ± 0.19  | 0.0014 ± 0.0040 |
| F₃(N₂)      | L         | 2.49 ± 0.13  | 0.17 ± 0.09  | 0.0036 ± 0.0033 |

* Gaussian (G) or Lorentzian (L).
** Kept fixed in the best fit.

The introduction of Gaussian bands, especially for the F one, improved significantly the best-fit of the measured transmittance spectra. All the contributions of larger aggregate defects listed in table 1 were necessary, as one could expect because of the high doses involved. The band located at 416 nm was also provisionally fitted with a Mie-based model, but the Gaussian band shape improved the best fit results, suggesting that other spectral contributions from not yet well identified defects could be present. By using Smakula’s formula, the volume concentrations in the irradiated strips were derived for the primary F and aggregate F₂ and F₃⁺ CCs and are reported in figure 4 as functions of the irradiation dose.

**Figure 4.** Volume concentrations of the primary F and aggregate F₂ and F₃⁺ CCs in three coloured strips induced on a LiF crystal by irradiation with 12 keV electrons at increasing doses.
In the most coloured strip, a maximum F-centre concentration of 3.3x10^{19} cm^{-3} was estimated by assuming the oscillator strength \( f \) equal to 0.56 [18]. The F-centre density increases with the irradiation dose in the investigated range, even if the values seem to be close to saturation. As far as the M band is concerned, a preferential production of \( F_3^+ \) defects with respect to the \( F_2^+ \) ones was obtained, which could be ascribed to the nature of the bombarding charged particles, electrons, even for irradiation performed at RT. For the \( F_2^+ \) centres a value of \( f \) equal to 0.28 [18] was utilized, while for \( F_3^+ \) centres an absorption cross section \( \sigma_{F_3^+} = (7.1 \pm 0.1) \times 10^{-17} \) cm^2 was adopted [19]. In the present case, the maximum of \( F_2^+ \) and \( F_3^+ \) densities were estimated as 7x10^{18} and 3x10^{19} cm^{-3}, respectively. The \( F_3^+ \) concentration progressively increases with the irradiation dose, while the \( F_2^+ \) appears to remain constant. It should be noticed that the relative errors of the calculated concentrations are similar for these two kinds of CCs.

In conclusions, spectral contributions of several types of CCs were identified and quantified vs. the irradiation dose in broad-band light-emitting single-mode strip waveguides directly written with 12 keV electrons at the surface of a LiF crystal. At highest doses, the increase in the primary F-centre concentration improve the confining properties of the \( F_2^+ \) and \( F_3^+ \) CCs photoluminescence [17]; a preferential formation of charged \( F_3^+ \) defects, which are laser-active in the green wavelength interval, was identified. However, the presence of larger aggregate defects, like \( F_2^+ \) centres, which absorb light in the same spectral range where the \( F_3^+ \) photoemission is located, increases the absorption losses and prevents amplification in the green [7]. In the case of red-emitting \( F_2^+ \) laser-active defects, the improved optical confinement properties makes possible to achieve positive net gain coefficients [7], which increase with irradiation doses.

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