F and F-aggregates colour centres in lithium fluoride for high spatial resolution x-ray imaging

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Abstract. Stable formation of primary F and aggregate F$_2$ and F$_3$$^+$ colour centres in LiF crystals irradiated with a X-ray table-top source was investigated by optical absorption and photoluminescence measurements as a function of the irradiation dose. The F absorption band intensity follows a power law behaviour as a function of dose with a single exponent equal to 0.77, a value in excellent agreement with the predictions of a unified model for colour centres formation. The aggregate defects photoluminescence response appears suitable for applications in high dynamic range imaging plate X-ray detectors based on photoluminescence of coloured LiF. The choice of polycrystalline LiF thin films grown on different substrates allows one to obtain high resolved images even when more penetrating X-rays are used, as the colour centres formation is limited in depth by the film total thickness.

1. Introduction
A novel soft X-ray imaging detector based on the photoluminescence (PL) of active colour centres in Lithium Fluoride, LiF, thin layers was lately proposed [1,2] and is currently under further development [3] for investigation of biological specimens, characterization of materials and devices, as well as transfer and test of light-emitting micro and nano-patterns. A relevant advantage of this type of LiF-based detector is that it can be used both in the form of crystals and of films deposited onto different substrates, like silicon or glass [4]. Large area homogeneous thin films can be obtained by simple and well assessed physical deposition methods.

Recently, this X-ray imaging detector based on optical reading of colour centres PL was proposed and successfully tested also in the hard X-ray region [5] using a table-top X-ray micro-source. The high spatial resolution on a large field of view, a wide dynamic range, versatility and simplicity of use of the LiF-based imaging detector allow to obtain absorption radiographies of geometrical microstructures and biological objects, placed in close contact with its surface during X-ray irradiation. A spatial resolution of about 250 nm was demonstrated in the optical images obtained through confocal laser scanning fluorescence microscopy [5]; these micro-radiographies were read by simultaneously collecting the PL of F$_2$ and F$_3$$^+$ aggregate electronic point defects (two electrons

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bounded to two and three anion vacancies, respectively). Their broad visible PL bands, peaked at ~ 678 and ~ 541 nm, respectively, are both simultaneously excited with the 458 nm line of an Argon laser, located in the M band spectral region [6], where their almost overlapping absorption bands are present [7].

In this work a careful spectroscopic investigation of LiF crystals irradiated in air by a laboratory X-ray tube with a Cu anode was carried out through systematic optical absorption and PL measurements performed at room temperature (RT) as a function of the irradiation dose. An example of X-ray micro-radiography of a biological object on a LiF imaging detector consisting of a LiF film grown on silicon is reported.

2. Experimental
Commercially available LiF crystals of diameter 25 mm and thickness 2 mm, polished on both sides, were irradiated in air with an X-ray micro-source (NOVA 600, Oxford Instruments) of nominal source size 15 µm at a 20 W power. This laboratory X-ray tube was equipped with a Cu anode emitting quasi-monochromatic radiation, strongly peaked at about 8 keV (Kα1 and Kα2 lines) with a minor contribution at 8.9 keV (Kβ1 line). The emitted radiation is transmitted through a 245 µm thick Be window. The distance between the sample and the Cu target was 3.5 cm and several areas of typical dimensions (5x5) mm² were exposed for irradiation times from 1 to 90 minutes (fluencies in the range 68-6100 mJ/cm²) by moving the LiF crystals behind an open aperture in a thick Pb sheet. Optical transmittance spectra were measured at RT by using a Lambda 19 Perkin-Elmer spectrophotometer in the near ultraviolet and visible spectral range, extending from 200 to 800 nm at a wavelength resolution of 2 nm. Visible PL spectral measurements of the irradiated LiF samples were performed under quasi-continuous optical excitation with an Argon laser line at 458 nm. The filtered PL signal was focused in a 40 cm focal length monochromator equipped with a photomultiplier detector connected to a lock-in amplifier.

3. Results and discussions
In figure 1 the RT optical absorption spectra of coloured LiF crystals irradiated for several times, corresponding to different doses, were reported. The main spectral features were the F and M absorption bands, located at ~ 245 nm [8] and at ~ 450 nm [6], respectively.

![Figure 1. RT optical absorption spectra of X-ray coloured LiF crystals irradiated at several doses. The blank crystal contribution has been subtracted.](image-url)
Their intensities grew with the increasing of dose. At the highest dose, the F band reached the instrumental saturation value. These optical absorption spectra were used in the quantitative evaluation of the amount of electronic defects inside the samples. In fact, the absorption band area is directly connected to the colour centres concentration $N$ via the following Smakula formula [9], applied for bands of known shape,

$$N(\text{cm}^{-3}) = A \frac{n}{(n^2 + 2)^2} \frac{W(\text{eV})}{f} \alpha_{\text{max}} (\text{cm}^{-1})$$

where the band full-width at half-maximum, $W$, and the maximum value of the absorption coefficient, $\alpha_{\text{max}}$, appear; $n$ is the refractive index of the crystal at the wavelength corresponding to the absorption band peak and $f$ is the oscillator strength of the transition responsible for that absorption. $A$ is a calculated constant of value $0.87 \times 10^{17}$ for Gaussian bands.

Figure 2 reported the peak intensities of the F absorption bands, in O.D., for LiF crystals irradiated at different X-ray doses (J/cm$^2$). They were derived from the X-ray source technical characteristics, taking into account the attenuation of the Be window and of the propagation in air. The X-ray doses were also reported in the top axis of figure 2 in keV/cm$^3$. These values were calculated taking into account the limited penetration of this kind of radiation in LiF, which was assumed equal to the attenuation length of X-rays at the energy of the Cu-K$\alpha$ transition, which corresponds to $\sim 330$ µm. Obviously the same value was utilised to derive $\alpha_{\text{max}}$. According to the Smakula formula, assuming $f$ equal to 0.56 [10] and $n = 1.4203$ [11], the F centre densities for different X-ray doses were calculated and reported on the right axis of figure 2. The primary F defects concentration reached values higher than $10^{19}$ cm$^{-3}$.

![Figure 2](image)

**Figure 2.** Optical density at 245 nm of LiF crystals irradiated at different X-ray doses (left axis). The F colour centre concentrations are also reported (right axis). The solid curve is a best fit of the experimental data (see text for details).

The best fit of the experimental points in figure 2, based on least squares minimisation, indicated that the F absorption band intensity follows a power law behaviour as a function of dose with a single exponent equal to 0.77. This result is in excellent agreement with the predictions of a unified model [12], suitable for the description of the general behaviour of colour centres formation in several alkali halide crystals under irradiation, which provided a value of 0.75 for LiF. The same value was found in stage III of the coloration curve for LiF crystals irradiated at RT by 3 keV electrons [13].
The energy needed to produce an F centre, from which the coloration efficiency can be estimated, is calculated between 0.24 and 0.61 keV, which appears quite low and it corresponds to more than 13 F centres/photon. Since approximately 50% of the absorbed X-ray radiation above the fluorine edge in LiF is re-emitted as X-ray fluorescence [14] this efficiency corresponds roughly to 0.5 – 1 keV per F centres. So again, several F defects were created for each X-ray photon absorbed.

The same procedure was applied to the M absorption band, which was decomposed as the sum of two Gaussian bands, according with the F$_2$ and F$_3^+$ bands' parameters reported in [7]. These aggregate defects reached maximum concentrations of the order of 7x10$^{16}$ cm$^{-3}$, but it was not possible to describe their evolution as a function of dose with a similar power law. As a matter of fact, the ratio between the intensities of F to M band in the absorption spectra of figure 1 is quite high, of the order of 10 at the highest doses. This behaviour seems to indicate that the primary F centres concentration initial increases [14] and successively it is followed by the aggregation of larger complex defects at highest doses, in the used conditions with a dose-rate of 1.13 mW/cm$^2$.

In order to better investigate the F$_2$ and F$_3^+$ aggregate colour centre behaviour as a function of irradiation dose, laser induced visible PL spectra under laser excitation at 458 nm were also measured at RT in the same experimental conditions for all the samples. As example, in figure 3, the PL spectrum of a LiF crystal irradiated at a high dose is reported, together with the best fit obtained as the sum of two Gaussian bands, whose main parameters, i.e. peak energies and width, are consistent with the values reported in [7] for F$_2$ and F$_3^+$ red and green PL bands, respectively.

![Figure 3. RT photoluminescence spectrum (solid) of a X-ray coloured LiF crystals irradiated at a dose of 4068 mJ/cm$^2$. The best fit (dotted) is obtained as the sum of two Gaussian bands, attributed to F$_2$ (dashed) and F$_3^+$ (dash-dotted) centres.](image)

In figure 4 the PL intensities of the F$_2$ and F$_3^+$ PL bands in X-ray irradiated LiF crystals as a function of irradiation time are reported. Their emission signals cover two decades in the investigated dose range, a behavior which looks like suitable for practical use in X-ray imaging detectors based on the PL of these active defects.
Figure 4. RT photoluminescence intensities of $F_2$ and $F_3^-$ aggregate colour centre in LiF crystals irradiated at different X-ray doses under laser excitation at 458 nm.

This imaging-plate X-ray LiF-based detector possesses intrinsic high spatial resolution on a large field of view, has a wide dynamic range and is easy to use, as it is insensitive to visible light and it does not need any development after irradiation. In order to fully exploit its capabilities, the use of LiF polycrystalline thin films thermally evaporated on glass or silicon substrates appears more suitable. Typical thicknesses between 0.5 and 2 $\mu$m for these films can be selected [4]; as a consequence they are entirely colored by high penetrating hard X-rays. However a large fraction of energy is deposited in the substrate and the effective PL signal is lowered with respect to thick crystals. Further investigations are in progress to test and optimize their response, in order to reduce the irradiation times. The wide dynamic range of the LiF film detector, already exploited for soft X-rays [3], has been confirmed by microradiographs of biological objects. As example, a human hair bulb X-ray radiography obtained on a LiF film, reported in figure 5, was obtained in the same experimental set-up with an irradiation time of 10 minutes.

Figure 5. Confocal fluorescence image of a man-hair bulb X-ray microradiograph stored on a 1.4 $\mu$m thick LiF film grown on a silicon substrate, under optical excitation at 458 nm. The reference line is 50 $\mu$m.
The brightest areas correspond to the more irradiated ones, i.e. the less absorbing features within the sample. The internal structures are clearly distinguished. Several bright spots are visible in the figure; they are attributed to light scattered from dust particles and/or from film mechanical damage in the optical reading process. A better control of the handling procedures in all the experimental phases can drastically reduce such artifacts.

In conclusions, stable formation of primary F and aggregate $F_2$ and $F_3^+$ colour centres in LiF crystals irradiated with an X-ray table-top source equipped with a Cu anode was investigated as a function of irradiation dose. The formation efficiency for F defects was derived from careful optical absorption measurements and it follows a power law behaviour as function of the dose. The PL spectra intensities look suitable for the development of high dynamic response X-ray imaging detectors based on LiF thin films. Further experiments are in progress to better investigate the absorption and photoluminescence properties of F-aggregate colour centres in LiF crystals and thin films.

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