Primary and aggregate color centers in proton irradiated LiF crystals and thin films for luminescent solid state detectors

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Abstract. Proton beams of 3 MeV energy, produced by the injector of a linear accelerator for proton therapy, were used to irradiate at room temperature lithium fluoride crystals and polycrystalline thin films grown by thermal evaporation. The irradiation fluence range was $10^{11}$-$10^{15}$ protons/cm$^2$. The proton irradiation induced the stable formation of primary and aggregate color centers. Their formation was investigated by optical absorption and photoluminescence spectroscopy. The $F_2$ and $F_3^+$ photoluminescence intensities, carefully measured in LiF crystals and thin films, show linear behaviours up to different maximum values of the irradiation fluence, after which a quenching is observed, depending on the nature of the samples (crystals and films). The Principal Component Analysis, applied to the absorption spectra of colored crystals, allowed to clearly identify the formation of more complex aggregate defects in samples irradiated at highest fluences.

1. Introduction
Color centers (CCs) in lithium fluoride (LiF) crystals and thin films found application in optically pumped solid-state lasers [1] and miniaturised light-emitting devices [2], due to the high efficiency of their photoluminescence (PL) process. Recently, LiF crystals and thin films have been also proposed as novel solid-state soft x-ray and neutron imaging detectors [3,4], based on the optical reading of the visible PL of the radiation-induced $F_2$ and $F_3^+$ (two electrons bound to two and three close anion vacancies, respectively) CCs. These laser-active defects possess almost overlapping absorption bands peaked around 450 nm, called M band [5], and, under light excitation in this spectral range, they emit broad PL bands peaked at 678 nm and 541 nm for $F_2$ and $F_3^+$ CCs, respectively.

On the other hand, ion beams of different energies are widely investigated for applications ranging from material modifications [6,7] to radiobiology and radiotherapy. With the aim to use PL of point defects in LiF for proton beam monitoring and dosimetry, we recently started the investigation of the optical properties of stable CCs induced by proton beams in LiF crystals and thin films [8].

Proton beams of 3 MeV energy, produced by a linear accelerator (LINAC) used as the injector of a proton therapy LINAC, under development at ENEA Frascati [9], were used to irradiate at room temperature (RT) LiF crystals and polycrystalline thin films grown by thermal evaporation [2]. The irradiation fluence range was $10^{11}$-$10^{15}$ protons/cm$^2$. Proton irradiation induced the stable formation of primary (F) and aggregate (mainly $F_2$ and $F_3^+$) CCs. Their formation was investigated by optical absorption and photoluminescence spectroscopy and the Principal Component Analysis (PCA) was applied to the absorption spectra of colored crystals.
2. Materials and Methods
Exposed samples were 10x10x1 mm³ LiF crystals polished on both faces, commercially available (MacroOptica Ltd.), and polycrystalline LiF thin films, about 1 µm thick, grown by thermal evaporation on glass substrates [10] kept at a constant temperature of 300 °C during the deposition process, performed in a vacuum chamber at a pressure below 1 mPa, at the Solid State Lasers Laboratory in ENEA Frascati. The starting material consists of LiF microcrystalline powder (Merck Suprapur, 99.99% pure), heated at about 800 °C in a water-cooled tantalum crucible. The evaporation rate, monitored in situ by an INFICON quartz oscillator, was automatically controlled at a fixed value of 1 nm/s during the growth.

Proton beams of 3 MeV energy were produced by the PL7 model LINAC by ACCSYS-HITACHI. At the output of the machine beamline a 50 µm thick kapton window was placed, which reduced the impinging protons energy to 2.23 MeV. LiF samples were irradiated in air at RT.

During proton irradiation, LiF crystals and films were fixed on an aluminium mask with a 3 mm pin-hole, in order to irradiate them on circular spots with the highest and most uniform transversal intensity distribution of the proton beam. The average beam current was 1 µA in 60 µs-long pulses at a repetition frequency of 50 Hz. The irradiation fluence covered the range of $10^{11}$-$10^{15}$ protons/cm² by varying the total number of pulses delivered to different LiF samples.

Optical absorption spectra were acquired at RT on the irradiated areas of LiF crystals by a Perkin-Elmer Lambda 950 spectrophotometer with 1 nm resolution. The PL spectra of LiF crystals and films were measured at RT by pumping in a continuous wave regime with the 457.9 nm line of an Argon laser, which allows to simultaneously excite the green and red emissions of $F_3^+$ and $F_2$ CCs [11]. The PL signal was spectrally filtered by a monochromator and acquired by means of a photomultiplier with lock-in technique. The PL spectra were corrected for the instrumental calibration.

3. Results and Discussion
Figure 1 shows the PL spectra of LiF crystals irradiated by 3 MeV protons at seven fluence values in the interval from $1.5\times10^{12}$ to $6.4\times10^{14}$ protons/cm². They consist of two broad emission bands peaked around 540 nm and 670 nm, ascribed to $F_3^+$ and $F_2$ centers, respectively [11]. The emission band intensities are proportional to the fluence up to values of the order of $10^{14}$ protons/cm², after which a quenching starts to be observed. The PL spectra of LiF films irradiated in the same experimental conditions (not shown) exhibit the same spectral features of LiF crystals.

![Figure 1. Photoluminescence spectra of LiF crystals irradiated by a 3 MeV proton beam at seven fluence values, measured at room temperature under laser pumping at 457.9 nm.](image-url)
associated with the contribution to the total PL of the F$_2$ and F$_3^+$ CCs, were obtained for every spectrum and plotted against the proton irradiation fluence. The results are shown in figure 2.

According to figure 2, the PL intensity of both F$_2$ and F$_3^+$ CCs in crystals is more than one order of magnitude higher than in LiF films. In LiF crystals, radiation induced defects are produced inside a volume whose depth is comparable with protons implantation depth (45 µm at 2.23 MeV, according to simulations performed by SRIM [12]), within which they lose all their energy [13]. On the contrary, in LiF films the collected PL is emitted by CCs located in a LiF layer of thickness 1 µm, where only a small fraction of the total proton energy is lost, the rest being released in the glass substrate.

The PL intensity behaviour with fluence of F$_2$ CCs shows a linear increase up to 2.0x10$^{13}$ protons/cm$^2$, while at higher fluences saturation effects start taking place, resulting into a PL sub-linear behaviour. Also in LiF films the PL signal is proportional to the fluence values, but the linear optical response reaches the fluence value of 8.0x10$^{13}$ protons/cm$^2$, then turning into sub-linear.

Concerning the PL intensity behaviour of F$_3^+$ CCs with fluence, it shows a linear increase up to 10$^{13}$ protons/cm$^2$ in both LiF crystals and films. The PL intensity difference between F$_2$ and F$_3^+$ CCs in both crystals and films is almost constant up to a fluence of 10$^{13}$ protons/cm$^2$, but with further increasing fluence, such a difference starts increasing. In particular, in the fluence interval from 10$^{13}$ to 10$^{14}$ protons/cm$^2$ the PL intensity of F$_3^+$ CCs increases sub-linearly with fluence, but starts decreasing from fluence values of 10$^{14}$ protons/cm$^2$ in LiF crystals and 2.0x10$^{14}$ protons/cm$^2$ in LiF films.

The F$_2$ and F$_3^+$ PL quenching effects observed at higher fluence values could be explained by thoroughly examining the absorption spectra of irradiated LiF crystals.

Figure 3 shows the optical absorption spectra of LiF crystals irradiated by a 3 MeV proton beam at seven fluence values, measured at room temperature.
superposition of the $F_3^+$ and $F_2$ centers absorption bands (M band), respectively [5,11]. For crystals irradiated with fluences higher than $10^{14}$ protons/cm$^2$, other bands could be observed. They were peaked around 320, 380 and 550 nm and are ascribed to $F_3(R_1)$, $F_3(R_2)$ and $F_4(N_2)$ more complex aggregate centers, respectively [7,14]. The last one could contribute to the observed $F_3^+$ PL quenching effect, causing re-absorption.

The application of PCA [15] to the second derivative of the absorption spectra in the 300-600 nm spectral range allowed us to extract more detailed information. PCA allows one to reduce the dimensionality of a data set while retaining as much as possible of its variation, hence showing data in a simplified manner.

Figure 4. Principal Component Analysis score plot showing the variances associated with the first two principal components (Score 2 vs Score 1). The ellipse shows the cluster formed by dots representing the spectra of samples irradiated up to a fluence of 2.0x10$^{13}$ protons/cm$^2$.

In figure 4 is reported the score plot showing the variances associated with the first two principal components, which contain most of the variation present in all spectra. Up to a fluence of 2.0x10$^{13}$ protons/cm$^2$, the spectra (represented by dots) belong to the same cluster (circled), as they are very similar. When the fluence value gets higher, the spectra are not clustered, as they start to be different from each other. This result shows a clear relationship between the absorption spectra and the PL sub-linear behaviour, which started from the fluence value of 2.0x10$^{13}$ protons/cm$^2$, as shown in figure 2.

The main peaks of the first two principal components (not shown) have confirmed the presence of absorption bands at 320, 380 and 550 nm, but three more bands have been found at 520, 430 and 465 nm. The first one can be ascribed to $F_4(N_1)$ CCs [14], while the other ones cause M band broadening, whose main components could be related to the presence of nanometric lithium colloids [7,16]. Their formation is due to complex phenomena related to the high proton energy release, especially at the end of the penetration path (Bragg peak) [6].

4. Conclusions
The PL intensity of 3 MeV proton-induced $F_2$ and $F_3^+$ color centers was measured in LiF crystals and thin films in a wide interval of irradiation fluence. At the lowest fluences a linear optical response of their PL signal was obtained for both kinds of samples. At the highest fluences, the $F_2$ and $F_3^+$ PL signal reaches saturation, but in LiF crystals it is achieved at lower values than in LiF films. The PCA was applied to all the optical absorption spectra of proton irradiated LiF crystals, to highlight the formation of more complex aggregate defects, among them $F_3$, $F_4$ and nanometric lithium colloids, whose complex spectral features often are superimposed to the broad absorption bands of $F_2$ and $F_3^+$ defects. PCA showed to be a very powerful tool to extract the spectral information from optical absorption spectra, where overlapping bands often coexist. It can support systematic studies of the PL response of proton beam detectors based on CCs PL in LiF crystals and thin films.

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