Optical spectroscopy and imaging of colour centres in lithium fluoride crystals and thin films irradiated by 3 MeV proton beams


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Lithium fluoride is a well-known dosimeter material and it is currently under investigation also for high-resolution radiation imaging detectors based on colour centre photoluminescence. In order to extend their applications, proton beams of 3 MeV energy, produced by a linear accelerator, were used to irradiate LiF crystals and thin films in the fluence range of $10^{10}-10^{15}$ protons/cm$^2$. The irradiation induces the formation of colour centres, mainly the primary F centre and the aggregate F$_2$ and F$_3$ defects, which are stable at room temperature. By optical pumping in the blue spectral region, the F$_2$ and F$_3$ centres emit broad photoluminescence bands in the visible spectral range. By conventional fluorescence microscopy, the integrated photoluminescence intensity was carefully measured in LiF crystals and thin films as a function of the irradiation fluence: a linear optical response was obtained in a large range of fluence, which is dependent on the used LiF samples. Colour centres concentrations were estimated in LiF crystals by optical absorption spectroscopy. It was possible to record the transversal proton beam intensity profile by acquiring the photoluminescence image of the irradiated spots on LiF films.

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1. Introduction

Among insulating materials, lithium fluoride (LiF) is a radiation-sensitive dielectric well known in dosimetry and used in optoelectronic light-emitting devices [2–5]. Various kinds of ionising radiation generate stable primary and aggregate defects, better known as colour centres (CCs), in LiF crystals [6] and thin films [7]. The simplest defect that can be generated is the so-called F centre, which is formed when a negatively charged ion is dislocated in the crystal lattice, leaving an electron trapped in a positively charged vacancy. Aggregates of F centres have characteristic absorption bands located in the visible spectral region and several of them exhibit intense Stokes-shifted photoluminescence (PL) at room temperature (RT) by optical pumping in the same spectral interval [8]. Recently, LiF crystals and thin films have been successfully tested as solid-state X-ray [9,10] and neutron [11] imaging detectors, based on the optical reading of the PL of radiation-induced visible-emitting CCs. In particular, the use of thin films of thickness lower than the radiation penetration allows higher versatility by tailoring their emission properties. On the other hand, ion beams of different energies are widely investigated for applications ranging from material modifications to radiobiology and radiotherapy. The use of low penetrating elementary particles is particularly interesting in LiF because it makes possible to prepare thin coloured layers to depths of a few micrometres with high concentration of defects located close to the surface of the crystal-line material [3,7,15]. Moreover, it allows to monitor the formation of CCs in the irradiated thin layer up to the saturation defect concentrations through optical absorption measurements. A major advantage of using ion beams [14,15] is that one can deposit energy at a higher rate than for conventional X-ray irradiation into a limited volume. The energy is delivered via a mixture of processes, which are generally separated out as those involving electronic excitation and, at low energies, nuclear stopping regime [16].

In this paper we present experimental results about the stable CCs formation in LiF crystals and thin films, grown by thermal evaporation, irradiated by 3 MeV protons in a large interval of beam fluences. By conventional optical fluorescence microscopy, the integrated F$_2$ and F$_3$ PL intensity was carefully measured in LiF crystals as well as in thin films as a function of the irradiation fluence. The formation of the primary F centres and of the aggregate F$_2$ and F$_3$ electronic defects (two electrons bound to two and three close anion vacancies, respectively) was investigated also by optical absorption and emission spectroscopy [17]. It was also possible to record the transversal proton beam intensity profile by acquiring the PL image in proton-irradiated LiF films.
2. Materials and methods

Exposed LiF samples were \((10 \times 10 \times 1) \text{ mm}^3\) crystals polished on both faces and polycrystalline thin films, 1 \text{ mm} thick, grown by thermal evaporation on glass substrates \cite{7} kept at 300 °C during the deposition process, performed in a vacuum chamber at a pressure below 1 mPa. 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 mm/s during the growth.

Proton beams of 3 MeV energy were produced by a linear accelerator (PL7 model by ACSYS-HITACHI) working as the injector of the prototype of a protontherapy linac under development at ENEA C.R. Frascati \cite{18}. A 50 \text{ mm} thick kapton window was placed at the output of the machine beamline. The LiF samples were irradiated in air at a distance of 10 mm from this exit window. Simulations performed by SRIM software \cite{19} determined the energy of protons impinging upon LiF target to be 2.23 MeV, with an estimated implantation depth, \(R_p\), of about 45 \text{ μm}.

During proton irradiation at RT, LiF samples 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 \text{ μA} in 60 μs-long pulses at a repetition frequency of 50 Hz. The fluence covered the range of \(10^{10}–10^{13} \text{ protons/cm}^2\) by varying the total number of pulses delivered to different LiF samples.

Optical absorption measurements at normal incidence of coloured circular spots produced by proton beam irradiation of LiF crystals were performed at RT by a Perkin-Elmer Lambda 950 spectrophotometer in the 190–1400 nm spectral range. PL spectra in the wavelength range between 490 nm and 800 nm. 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.

The integrated intensity of the \(F_2\) and \(F_3\) CCs PL signal was measured by a fluorescence microscope Nikon Eclipse 80-1 C1, equipped with a Hg lamp and a 4 × objective (N.A. = 0.13). The blue emission of the Hg lamp, peaking at 434 nm, was selected in order to simultaneously excite the PL of the \(F_2\) and \(F_3\) CCs, respectively, whose broad absorption bands are almost overlapped at around 450 nm, called M band \cite{8}. 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.

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3. Results and discussion

Fig. 1 shows the integrated CCs PL signal as a function of the proton fluence in LiF crystals and films. In LiF crystals, it increases with fluence and shows a linear behaviour in the range of \(3 \times 10^{11}–2 \times 10^{13} \text{ protons/cm}^2\), while at higher fluences more complex saturation effects take place, and it will be discussed below. Also in LiF films the PL signal is proportional to the fluence values, but the linear optical response is shifted towards higher fluences, covering the range of \(3 \times 10^{12}–2 \times 10^{14} \text{ protons/cm}^2\), after which, a plateau appears. It should be noted that the PL signal is always higher in LiF crystals than in thin films. In LiF crystals electronic defects are produced inside a volume whose depth is comparable with that of the total volume traversed by impinging protons, about 45 μm, within which they lose all their energy. On the contrary, in LiF films the collected PL is emitted by CCs located in a LiF layer only 1 μm thick, where only a small fraction of the total proton energy is lost, the rest being deposited in the glass substrate. By comparison, bare glass substrates, irradiated in similar conditions, showed no PL under 458 nm excitation, although some darkening was observed in white light. In the fluence interval where crystals and films show a linear optical response, the integrated PL intensity of aggregate CCs in crystals is more than one order of magnitude higher than in LiF films. At lowest fluences, below the linearity intervals, the camera background noise becomes comparable to the collected PL signal and mainly affects the observed behaviour. In LiF films this effect starts to be significant at higher minimum fluences than in LiF crystals, because the PL signal intensity is one order of magnitude lower.

The spectral contributions of \(F_2\) and \(F_3\) defects to the integrated visible PL intensity in LiF crystals and films was investigated by PL spectra in the wavelength range between 490 nm and 800 nm. Fig. 2 reports the PL spectra of both the LiF crystal and film irradiated with a fluence of \(5.6 \times 10^{13} \text{ protons/cm}^2\) and measured in the same experimental conditions. They consist of two broad emission bands peaked at 540 nm and 680 nm, ascribed to \(F_2\) and \(F_3\) centres, respectively \cite{8,20}. The PL signal of the coloured LiF film is multiplied by a factor 10 for a better comparison and the increase of the PL signal below 510 nm is due to the weak tail of the emission band of the diode used for exciting CCs emission. It is possible to ascertain again a difference of more than one order of magnitude between the PL intensities of these light-emitting CCs in LiF film and crystal; the peak intensity ratio of the \(F_2\) emission band with respect to the \(F_2\) one is similar for both irradiated samples at this fluence.

The defects formation was investigated also by optical absorption spectroscopy to estimate the average CC densities in coloured LiF crystals. Fig. 3 shows the absorption spectra of five samples irradiated in the fluence range of \(2.1 \times 10^{12}–9 \times 10^{14} \text{ protons/cm}^2\),
defects [22]. They may cause PL luminescence emission and may cause PL absorption bands, the situ-
trans-
centres, respectively [12] and the broad absorption aggregate defects, the maximum average volume
densities start to change in the irradiated volume, assuming a colouration depth equal to
fluences. The average F, F2 and F3 defect concentrations in the fluence interval 2.7 × 10^{12}–9 × 10^{14} protons/cm² is shown in the inset (see text for details).

Fig. 3. RT absorption spectra of five LiF crystals proton irradiated at several fluences. The average F, F2 and F3 defect concentrations in the fluence interval 2.7 × 10^{12}–9 × 10^{14} protons/cm² is shown in the inset (see text for details).

cm², where the two main absorption bands, peaking at 248 nm and at around 450 nm, grow with increasing fluence. They are the F band, attributed to the primary F electronic defects, and the M band due to F2 and F3 CCs, respectively. Unless the limited proton colouration depth, the more intense F absorption band appears truncated because of the typical transmission detection limit of standard spectrophotometers. The spectral features of the F band are well known from the literature and a best fit with a Gaussian band can be successfully applied to estimate the O.D. values. Due to the full overlapping of the F2 and F3 absorption bands, the situa-
tion is more complex for these two kinds of point defects. The peak and full width at half maximum of the M band is dependent on the ratio between the F2 and F3 volume concentrations [20], but this effect is negligible in the investigated samples, even at the highest fluences. Their deconvolution by an appropriate best fit procedure with two Gaussian bands, whose main parameters are compatible with the values reported in literature [20], allows to derive the O.D. values for both kind of defects with the exception of the samples irradiated at the lowest fluences. The Smakula formula [6, 7] was used to estimate the average defect concentrations in the irradiated volume, assuming a colouration depth equal to 45 μm. The behaviour is reported for all the fluences in the inset of Fig. 3. Although it is well-known [12] that these volume densities are unrepresentative of the peak concentration along the depth, they reach very high values, close to the saturation ones. It should be pointed out that the growth for the F centre is very similar to those reported in [15] for LiF crystals irradiated with protons of similar energy (2.8 MeV) up to fluences of 10^{14} H⁺/cm². For the F2 and F3 aggregate defects, the maximum average volume densities are compatible with PL concentration quenching phenomena [21], which could be responsible of the PL saturation behaviour observed in Fig. 1. As a matter of fact, at the highest fluences also the ratio between F2 to F3 densities start to change (see inset of Fig. 3). It should be noted that in the absorption spectra of the sample irradiated with the highest fluences in Fig. 1, other minor spectral contributions can also be distinguished, clearly ascribed in the literature to more complex aggregate defects: those at 316 and 374 nm are caused by the R1 and R2 transitions of F3 centres, respectively [12] and the broad absorption features at around 530 nm is due to the F4 defects [22]. They strongly overlap the F3 luminescence emission and may cause PL re-absorption phenomena which can also affect the optical response of LiF crystals at the highest fluences in Fig. 1. On the contrary, very few data are available in the literature about sys-
tematic investigation of PL of ion-induced F2 and F3 centres in LiF films [23]. Their specific structural, morphological and optical properties can strongly affect the CCs aggregation and stabilization processes [24].

By optical fluorescence microscopy, it was possible to record the transversal proton beam intensity profile by acquiring the PL image of LiF films irradiated on a large area. Fig. 4 shows the PL image of the proton beam stored by CCs in a LiF film irradiated at a fluence of 5.6 × 10^{13} protons/cm² without the pin-hole mask during the irradiation. As the camera field of view could not cover the full width of the proton beam, the image was obtained by assembling four frames. Although the CCs PL signal in LiF films is one order of magnitude lower than in crystals, films are able to store information about the proton beam intensity with high spatial resolution and revealing even subtle intensity differences. The 8-bit camera used to acquire the image did not result adequate to show with an optimal greyscale accuracy all the information stored in LiF.

Fig. 4. PL image of the proton beam transversal section stored by CCs in a 1 μm thick LiF film at a fluence of 5.6 × 10^{13} protons/cm². As the camera field of view could not cover the full width of the proton beam, the image was obtained by assembling four frames.
4. Conclusions

In conclusion, the integrated and spectral PL intensity of proton-induced F\textsubscript{2} and F\textsuperscript{+}\textsubscript{3} centres was carefully measured in LiF crystals and thin films in a wide interval of irradiation fluence. A linear optical response was obtained, which is dependent on the used LiF samples. Primary and aggregate average defect concentrations were estimated in irradiated LiF crystals by optical absorption spectroscopy. The obtained results were discussed and compared with the existing literature. The concentration quenching and re-absorption phenomena of the integrated PL signal are more effective in LiF crystals with respect to film only 1\,\mu m thick. However, the sensitivity of the optical reading technique and the high emission efficiency of the F\textsubscript{2} and F\textsuperscript{+}\textsubscript{3} centres, combined with the good optical quality of the thermally evaporated LiF films, allow to record the transversal proton beam intensity profile by acquiring the PL image of the irradiated spots on LiF films. The presented results are encouraging for the use of LiF films as high-resolution solid state proton detectors. By using a cooled camera with a higher sensitivity and lower noise, it is expected to extend the linearity regime of LiF film based proton detectors towards lower fluences of at least two orders of magnitude. Systematic studies are under way for a careful comparison of the PL spectra of LiF crystals and thin films to get a better insight about their behaviour.

References