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Photoluminescence of radiation-induced color centers in lithium fluoride thin films for advanced diagnostics of proton beams

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Systematic irradiation of thermally evaporated 0.8 μm thick polycrystalline lithium fluoride films on glass was performed by proton beams of 3 and 7 MeV energies, produced by a linear accelerator, in a fluence range from 10^{11} to 10^{15} protons/cm². The visible photoluminescence spectra of radiation-induced F_2 and F_3^+ laser active color centers, which possess almost overlapping absorption bands at about 450 nm, were measured under laser pumping at 458 nm. On the basis of simulations of the linear energy transfer with proton penetration depth in LiF, it was possible to obtain the behavior of the measured integrated photoluminescence intensity of proton irradiated LiF films as a function of the deposited dose. The photoluminescence signal is linearly dependent on the deposited dose in the interval from 10^3 to about 10^6 Gy, independently from the used proton energies. This behavior is very encouraging for the development of advanced solid state radiation detectors based on optically transparent LiF thin films for proton beam diagnostics and two-dimensional dose mapping. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4923403>]

Various kinds of ionizing radiations generate stable primary and aggregate defects, also known as color centers (CCs), in lithium fluoride (LiF) crystals¹ and thin films.² CCs in LiF are well known for applications in light-emitting miniaturized devices^{3–6} and tunable solid-state lasers,⁷ but they were proposed also for the development of novel high-spatial resolution solid-state soft X-ray imaging detectors.^{8,9} Such applications exploit the broad photoluminescence (PL) bands of CCs in LiF, stable at room temperature (RT), which efficiently emit in the visible and near-infrared spectral ranges. Among them, the laser-active F_3^+ and F_2 CCs (two electrons bound to three and two anion vacancies, respectively) possess almost overlapped absorption bands, at about 450 nm (M band),¹⁰ so that, under light excitation in this spectral range, they simultaneously emit green (F_3^+) and red (F_2) luminescence, peaking at 541 and 678 nm, respectively.^{10,11} In the last years, their optical emission properties under light excitation were investigated in pure and doped LiF materials in different forms^{12–16} for application in radiation dosimetry.

Very recently, we have started the investigation of the optical absorption and emission properties of CCs induced in LiF crystals and thin films by low-energy protons.^{17,18} In this letter, we present experimental results about the PL response of F_3^+ and F_2 point defects in optically transparent thermally evaporated LiF thin films, irradiated by 3 and 7 MeV protons in a large interval of irradiation dose.

The exposed samples were polycrystalline LiF films,¹⁹ nominally about 1 μm thick, grown by thermal evaporation on 1 mm thick glass substrates 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 Laser Laboratory in ENEA C.R. Frascati. The starting material consisted 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. Several substrates were mounted on a rotating sample holder, in order to achieve a better thickness uniformity.²⁰

With the aim of determining the optical properties of the deposited LiF thin films, one of them, grown on a silica substrate, was carefully analyzed to estimate its thickness and the spectral dispersion of the optical constants of it within a suitable wavelength range ($190 \text{ nm} \leq \lambda \leq 1200 \text{ nm}$). The thickness of the film was first evaluated by measuring with a mechanical profilometer Tencor P-10 the step height due to the coating border at 9 evenly distributed positions and then averaging the data. The resulting mean thickness was $(0.80 \pm 0.04) \mu\text{m}$. As far as the optical constants of the LiF layer are concerned, they were estimated by best fitting the parameters of a thin-film theoretical model²¹ to the measured absolute specular reflectance and direct transmittance spectra, which were taken with a Perkin-Elmer Lambda 900 spectrophotometer. In this case, a one-term Sellmeier and a Gaussian function in the photon-energy domain were used to represent the refractive index and extinction coefficient of the film, respectively. The best-fitting dispersion of the refractive index is shown in Figure 1, where it is also compared to tabulated data for bulk LiF²² modified, by using Maxwell Garnett's equation, for a suitable packing density of 90.5% (i.e., 9.5% of voids in the film). The main film parameters resulting from the analysis were film thickness of

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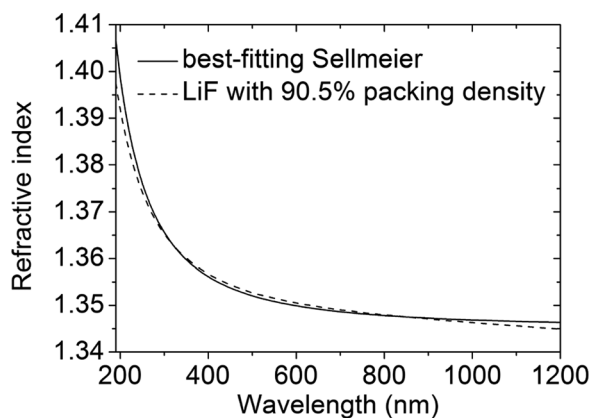


FIG. 1. Dispersion curve (Sellmeier model) of the thermally evaporated LiF film refractive index as resulting from the best fit of reflectance and transmittance experimental spectra. The corresponding dispersion of LiF, obtained by applying to bulk refractive index data a correction for a packing density of 90.5%, is also shown.

(854 ± 1) nm, linear inhomogeneity along the film growth axis²¹ of (-0.5 ± 0.3)%, deviation from parallelism of the film faces²¹ amounting to (2.0 ± 0.1)%, and surface r.m.s. roughness of (18.3 ± 0.2) nm. The extinction coefficient was estimated to be less than 10^{-3} in the visible range, a value which still ensures a very good degree of transparency for a film which is less than $1 \mu\text{m}$ thick.

Proton beams of 3 and 7 MeV energy were produced by a linear accelerator (PL7 model by ACCSYS-HITACHI) working as the injector of the prototype of a protontherapy linac under development at ENEA C.R. Frascati.²³ A $50 \mu\text{m}$ thick kapton window was placed at the output of the machine beamline. The LiF samples were irradiated at RT in air at a distance of 10 mm from this exit window and were attached on an aluminum mask with a 3 mm pin-hole, in order to irradiate them on circular spots with the most uniform transversal intensity distribution of the proton beam. The beam current was $1 \mu\text{A}$ in $60 \mu\text{s}$ -long pulses at a repetition rate of 50 Hz. The irradiation fluence covered the range from 10^{11} to 10^{15} protons/cm² by varying the total number of pulses delivered to different LiF films.

The PL spectra were measured at RT in the wavelength range between 480 nm and 800 nm 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 in the irradiated LiF films.² 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 laser power was 25 mW with a power density on the sample of 8.9×10^{-2} W/cm², which caused no detectable photobleaching effects during the acquisition of spectra. All the PL measurements were performed 24 h after irradiation, which assured aggregate CCs stabilization.²⁴ Samples were kept in darkness, while measurements repeated within some months after irradiation showed no significant change in the PL response, confirming the CCs stability. By comparison, bare glass substrates, irradiated in similar conditions, showed no detectable PL under 457.9 nm laser excitation, although some darkening was observed in white light. Measurements

of as grown unirradiated LiF films were also performed, but they showed no detectable PL.

PL spectra of two samples irradiated with 3 and 7 MeV protons at the same fluence of 1.5×10^{12} protons/cm² are shown in Figure 2. They consist of two broad emission bands peaked at about 540 nm and 680 nm, ascribed to F_3^+ and F_2 centers, respectively.^{11,12} The PL spectral features (peak positions and half-widths) remained unchanged in the investigated fluence range (not shown). Figure 3 shows the PL signal integrated in the whole examined spectral range as a function of the fluence of 3 and 7 MeV protons. It increases with fluence and shows a linear behavior up to 8×10^{13} protons/cm², while at higher fluences saturation effects take place and a plateau appears. At all the investigated fluence values, the integrated PL intensity is always higher in the LiF films irradiated at 3 MeV than at 7 MeV.

Such a behavior can be explained by simulations performed using SRIM software.²⁵ The inset of Figure 3 reports the linear energy transfer (LET) calculated by SRIM as a function of the proton implantation depth in the whole LiF film-based detector for 3 and 7 MeV proton beams in the experimental conditions described above. LET is continuously increasing with depth, reaching the maximum value (Bragg peak) almost at the end of the implantation path. In LiF films, due to their limited thickness ($0.8 \mu\text{m}$), LET can be considered as constant and only a very small fraction of the total proton energy is lost in them, the rest being deposited in the glass substrate. As shown in the inset of Figure 3, the LET is lower for 7 MeV protons ($12 \text{ keV}/\mu\text{m}$) than for 3 MeV protons ($28.4 \text{ keV}/\mu\text{m}$), which is consistent with the lower PL intensity of 7 MeV proton irradiated LiF films in Figures 2 and 3.

The LET calculated by SRIM software allows one estimating the total dose (D) deposited in the LiF films by using the following formula:

$$D = \frac{L \cdot \Phi}{\rho},$$

where L is LET, Φ is the proton fluence, and ρ is the material density. The film density can be estimated in a simplified way by considering the film as an aggregate of material “grains” separated by air interstices. The fraction of the total

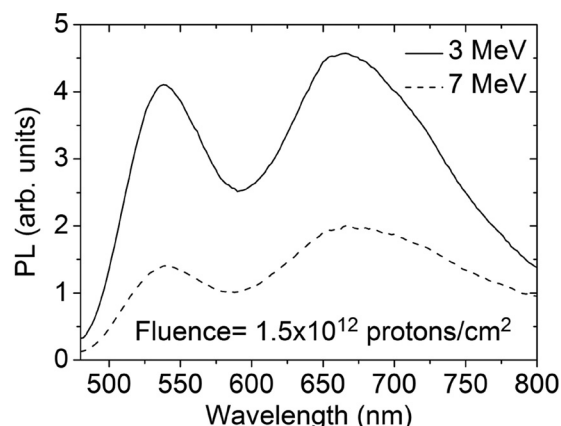


FIG. 2. Photoluminescence spectra of $0.8 \mu\text{m}$ thick LiF films irradiated by 3 and 7 MeV proton beams at a fluence of 1.5×10^{12} protons/cm², measured at RT under laser pumping at 457.9 nm.

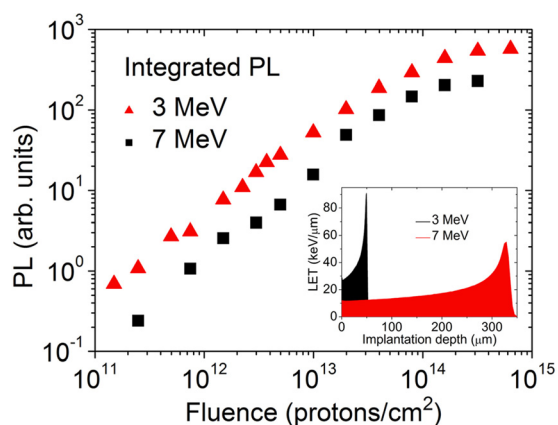


FIG. 3. Integrated visible photoluminescence signal as a function of the 3 and 7 MeV proton fluence in colored $0.8\ \mu\text{m}$ thick LiF films grown on a glass substrate. (Inset) SRIM simulation of the linear energy transfer as a function of the proton implantation depth in the LiF film-based detector.

volume occupied by the LiF material is assumed to be the packing density value derived from the refractive index spectrometric characterization (see Figure 2).

Figure 4 shows the PL signal integrated in the whole spectral emission range as a function of the estimated dose deposited by both 3 and 7 MeV proton beams in the used LiF films. It increases with dose and shows a linear behavior from the lowest dose value of $10^3\ \text{Gy}$ up to $4 \times 10^5\ \text{Gy}$. Moreover, the PL response of the LiF films is independent on the proton beam energies in the investigated dose interval.

An important characteristic of the solid state LiF film radiation imaging detectors based on PL by CCs is the possibility of storing information about the transverse proton beam intensity. The inset of Figure 4 shows the image of a 3 MeV proton beam stored in a LiF film detector, read by a conventional fluorescence microscope (Nikon Eclipse 80-i) equipped with a color CCD camera. By a careful calibration of the visible PL signal as a function of the irradiation dose (see Figure 4), one can obtain a transverse two-dimensional dose mapping of proton beams.

In conclusion, the integrated and spectral PL intensities of 3 and 7 MeV proton-induced F_2 and F_3^+ electronic defects were carefully measured in optically transparent $0.8\ \mu\text{m}$ thick

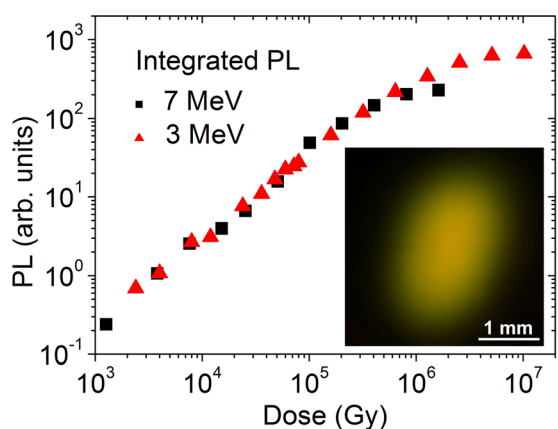


FIG. 4. Integrated visible photoluminescence signal as a function of the 3 and 7 MeV proton dose in colored $0.8\ \mu\text{m}$ thick LiF films grown on a glass substrate. (Inset) Photoluminescence image of a 3 MeV proton beam stored by color centers in the LiF film-based detector.

LiF films, thermally evaporated on glass substrates, in a wide interval of irradiation dose. A linear PL response was obtained and the PL intensity values are independent of the beam energy in a large dose range.

The high emission efficiency of the F_2 and F_3^+ centers and the good optical quality of the thermally evaporated LiF films allow to record the transversal proton beam intensity profile by directly acquiring the PL image of the irradiated spots on LiF films using a conventional fluorescence microscope as reading instrument.

The presented results are very encouraging for the use of LiF thin films as high spatial resolution solid state proton imaging detectors and dosimeters at high doses. Systematic experimental investigations will be essential to investigate the PL response dependence on both the dose-rate and at higher proton energies, as well as the effect of temperature on the PL measurements around RT. The possibility of reusing the LiF films after CCs bleaching, by thermal annealing at $400\ ^\circ\text{C}$ for 30 min, was recently reported for X-ray irradiated LiF films by a Japanese group²⁶ and experiments are planned also on proton irradiated LiF films grown in different conditions.

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