

Advanced spectroscopic investigation of color centers in LiF crystals exposed to 6 MV X-ray clinical beams

M. A. VINCENTI^(*)

*ENEA C.R. Frascati, Fusion and Technologies for Nuclear Safety and Security Dep.
Via E. Fermi 45, 00044 Frascati (RM), Italy*

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Summary. — Polished LiF crystals were irradiated by using 6 MV X-rays produced by a clinical linear accelerator. The irradiation doses (absorbed dose to water) covered the 1–100 Gy range. Optical absorption spectra show stable formation of primary F defects, while the M absorption band, located at around 450 nm and due to the aggregate F_2 and F_3^+ color centers, was not detectable. By using the Smakula formula, a concentration of 1.2×10^{16} and 1.9×10^{16} F/cm⁻³ was obtained for LiF crystals irradiated at 50 and 100 Gy, respectively. Under argon laser excitation at 457.9 nm, photoluminescence spectra of the irradiated LiF crystals exhibited the characteristic F_2 and F_3^+ broad emission bands. The integrated photoluminescence intensity of F_2 and F_3^+ defects as a function of the irradiation dose shows a linear behaviour in the investigated dose range. This result is confirmed by the measurements of the F_2 and F_3^+ integrated photoluminescence intensity performed by using a conventional fluorescence optical microscope under blue lamp illumination. These preliminary experimental results are encouraging for further investigation of nominally pure LiF crystals as clinical dosimeters based on optical reading of photoluminescence emitted by radiation-induced color centers.

1. – Introduction

Point defects in insulating crystals (impurity ions, color centers, etc.) represent one of the most investigated fields in solid-state physics connected with optical properties. Among them, color centers in alkali halides (AH) occupy a special place because they were studied carefully as a model case for more complex point defects [1]. Among AH crystals, lithium fluoride (LiF) stands apart because of its peculiar physical and optical properties, which make it an interesting material for photonic applications [2]. LiF crystals are hard and almost insoluble in water. Among AH, the cation-anion distance,

^(*) E-mail: aurora.vincenti@enea.it

0.201 nm, is the shortest and the Li^+ and F^- ions possess the smallest radius among the alkali and halide ions, 0.06 and 0.136 nm, respectively. LiF melting point is lower than the values for the series of alkali fluorides and its band gap, greater than 14 eV, is the largest with respect to dielectric materials. LiF is optically transparent from about 120 nm to $7\ \mu\text{m}$ and, for this reason, it is widely used as window material, especially in the ultraviolet (UV) spectral region [3]. LiF can host laser-active electronic defects, known as color centers (CCs), characterized by a wide tunability and a great stability at room temperature (RT), but, contrary to the other AH, the usual techniques of additive coloration are not effective in the formation of electronic defects in this material. LiF can be colored by ionising radiation, such as X-rays, γ -rays, electrons, protons, neutrons, α particles and heavier charged ions. Each radiation type gives rise to different kinds of damaging processes according to its nature, particle or photon, and its energy. The effective atomic number of a compound, Z_{eff} , used to characterize its radiation response, indicates if it approximates or deviates from soft tissue [4]. In order to determine the dose absorbed by human tissue under irradiation by ionising radiation, it is desirable to use tissue-equivalent dosimeter materials, *i.e.* materials whose Z_{eff} is equal to 7.4, which is the effective atomic number of water [4]. LiF is one of such materials: it is almost tissue equivalent because its Z_{eff} is equal to 8.14.

In LiF, primary and aggregate CCs produced by ionising radiations are stable at RT, another peculiar characteristic of this material, and give rise to optical absorption bands extending from the UV through the visible (Vis) up to the near infrared (NIR) regions of the electromagnetic spectrum. Many of them, if properly excited with electromagnetic radiation, emit broad photoluminescence (PL) bands in the Vis and NIR spectral regions [5]. This work is focused on CCs, which derive from anion vacancies and particularly on the primary F centers and the aggregate visible-emitting F_2 and F_3^+ electronic defects. The primary F color center consists of an anionic vacancy occupied by an electron. Its absorption band, called F band, is located at around 248 nm [6]. Up to now, the PL originating from the F electronic defects in LiF has not been detected unambiguously, but a weak emission is theoretically expected at around 900 nm [7]. The F centers play a crucial role as primary defects, which can aggregate to form complexes. The aggregate F_2 electronic defect consists of two nearest-neighbour F centers along a $\langle 100 \rangle$ direction of the cubic lattice, while F_3 color center consists of three F centers in nearest-neighbour sites in the (111) plane. F_2 and F_3^+ aggregate centers (two electrons bound to two and three anion vacancies, respectively) possess almost overlapping broad absorption bands located at a wavelength equal to 450 nm, which together form what is generally called M band [5]. Under optical pumping in this spectral region they emit Stokes-shifted broad PL bands peaked at 678 and 541 nm for F_2 and F_3^+ centers, respectively [5, 8]. Table I reports the values of peak position (E_a , E_e), full width at half maximum ($FWHM_a$, $FWHM_e$) of the absorption and emission bands of these color centers at RT [6, 8], together with their luminescence lifetime [9].

One of the crucial problems concerning irradiated LiF crystals and films is the co-existence of several kinds of aggregate defects with often overlapping absorption bands, which makes difficult to clearly identify and measure the partial contribution due to the individual electronic defects. An accurate determination of the spectroscopic parameters of absorption and emission bands of F_2 and F_3^+ defects was possible by absorption and photoluminescence measurements performed on suitably treated gamma-colored LiF crystals, which contain mainly one of these CCs [8].

In the last fifteen years, LiF crystals and thin films were proposed as solid-state luminescent imaging detectors with submicrometric spatial resolution for soft X-rays up

TABLE I. – *Spectroscopic parameters of color centers in LiF at RT. E_a and $FWHM_a$ are peak position and full width at half maximum of the absorption bands. E_e and $FWHM_e$ are peak position and full width at half maximum of the emission bands and τ is their luminescence decay time.*

Center	E_a (eV) λ_a (nm)	$FWHM_a$ (eV)	E_e (eV) λ_e (nm)	$FWHM_e$ (eV)	τ (ns)
F	5.00 ^[6] 248	0.76 ^[6]			
F ₂	2.79 ^[8] 444	0.16 ^[8]	1.83 ^[8] 678	0.36 ^[8]	17 ^[9]
F ₃ ⁺	2.77 ^[8] 448	0.29 ^[8]	2.29 ^[8] 541	0.31 ^[8]	11.5 ^[9]

to energies of 80 keV [10]. Recently, their use was extended to low-energy proton beam characterization and imaging [11, 12].

Due to its tissue equivalence, LiF is a well-known dosimeter material in pure [13] and doped form [14], which was used as clinical dosimeter based on thermoluminescence (TL) for over 60 years [4]. Recently, the TL properties of γ -irradiated LiF crystals have been extensively investigated in order to associate the observed TL glow peaks to different kinds of CCs [15], highlighting the paramount influence of impurities in TL measurements [16].

Recent investigations have been focused on the use of doped LiF as a dosimeter based on optically stimulated luminescence (OSL) [17] and photoluminescence (PL) [18]. These results have motivated novel research aimed to study nominally pure LiF crystals as dosimeters based on optical reading of the PL emitted by radiation-induced CCs. Their advantages could be fast evaluation time (seconds), stability of PL signal at RT (multiple evaluations without signal loss), reusability due to the possibility to erase the “information stored by irradiation” by thermal annealing processes performed at appropriate temperature. In this work the preliminary results of the spectral investigation of radiation-induced CCs in nominally pure LiF crystals irradiated by 6 MV X-ray in the clinical relevant dose range of 1–100 Gy are presented.

2. – Materials and methods

A set of nominally pure, commercially available, LiF crystals, dimensions $(5 \times 5 \times 0.5)$ mm³, polished on both sides, were irradiated under full electronic equilibrium conditions using 6 MV X-rays produced by a clinical linear accelerator at the Tom Baker Cancer Centre, Calgary, Canada. A (10×10) cm² field size was set for all the irradiations and the LiF crystals were positioned at the center of the square radiation field. The irradiations were set to 1, 10, 20, 50 and 100 Gy with a dose-rate of 4.66 Gy/minute. All the doses refer to dose to water. After the irradiation, the LiF crystals were kept in the dark, but they were not protected from environment room light exposure during the optical absorption and PL measurements performed at RT. The optical absorption measurements of the irradiated and an unirradiated LiF crystals were performed using a Perkin-Elmer Lambda 950 spectrophotometer (Waltham, MA, USA) at normal incidence.

The spectral range was set to 190–800 nm with a 1 nm resolution. The laser-induced PL measurements were performed at RT using a continuous wave mode Argon laser tuned at the wavelength of 457.9 nm, in order to simultaneously excite the visible PL of F_2 and F_3^+ CCs. The PL emission was spectrally analyzed in the 480–800 nm range by a monochromator (Horiba Jobin Yvon, Triax 320) equipped with a grating blazed at 500 nm, with a 2 nm resolution and detected by a photomultiplier (Hamamatsu H7422-50) using a lock-in technique. All the PL spectra were corrected for the instrumental spectral response. The integrated PL signal emitted by the irradiated LiF crystals was measured using a conventional wide-field optical microscope (Nikon Eclipse 80i-C1) in fluorescence mode. The excitation light source was a mercury lamp OSRAM HBO 103W/2 (power 100 W). The light of the excitation mercury lamp as well as the acquired PL signal from the colored LiF crystals were properly filtered. The excitation optical filter transmits light in the 450–490 nm spectral interval, while the acquisition filter allows the collection of light at wavelengths higher than 520 nm. The used two-dimensional detector for the PL signal acquisition was a sCMOS camera (Andor Neo), 2560×2160 pixels (pixel size $6.5 \mu\text{m}$), front illuminated and cooled at -30°C .

3. – Results and discussion

Figure 1 shows the optical absorption coefficient, expressed in cm^{-1} , of an unirradiated LiF crystal and of the LiF crystals irradiated at 10, 50 and 100 Gy by 6 MV X-rays, as a function of energy. The F absorption band, peaked at 5 eV (see table I), due to the stable formation of the primary F electronic defects, is clearly observed for the LiF crystals irradiated at the highest doses (50 and 100 Gy). The M absorption band, peaked at around 2.75 eV (about 450 nm), due to F_2 and F_3^+ CCs, is not clearly detected even for the highest irradiation doses used in this investigation. For the LiF crystals irradiated at 50 and 100 Gy, the concentration of F CCs was evaluated by using the Smakula formula [1]. For each spectrum, the absorption coefficient at the peak of the F absorption band and

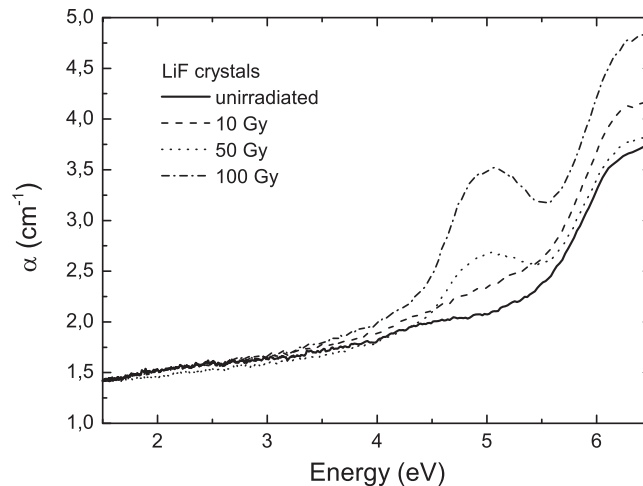


Fig. 1. – Optical absorption coefficient of LiF crystals irradiated at several doses (10, 50 and 100 Gy) by 6 MV X-rays, as a function of energy. The spectrum of an unirradiated LiF crystal is reported for comparison.

the FWHM were obtained by using a Gaussian best-fit procedure. The estimated concentration of F defects was 1.2×10^{16} and $1.9 \times 10^{16} \text{ cm}^{-3}$, respectively, assuming an oscillator strength of 0.56. Photoluminescence measurements are more sensitive than the absorption ones to reveal the presence of visible-emitting CCs in irradiated LiF crystals. Figure 2 reports the PL spectra of the LiF crystals irradiated at 1, 10, 20, 50 and 100 Gy by 6 MV X-rays, excited at 457.9 nm. Each Net PL spectrum shown in fig. 2 is obtained by subtracting the PL spectrum of an unirradiated LiF crystal from each measured PL spectrum of the irradiated samples. Each spectrum consists of the overlap of two broad emission bands arising from the aggregate F_2 and F_3^+ CCs, peaked at a wavelength of 678 and 541 nm, respectively (see table I). The separate contributions of the emission bands due to F_2 and F_3^+ defects to each Net PL spectrum were obtained by a best-fit procedure using two Gaussian curves (free best-fit parameters). An example of best-fit procedure is shown in fig. 3. The obtained peak position and the FWHM of the F_2 and F_3^+ emission bands are in agreement with well-assessed literature in LiF crystals [8]. The Net integrated PL signal associated with each Net PL spectrum, defined as the sum of the areas under the two Gaussian bands, *i.e.* the sum of the contributions due to F_2 and F_3^+ CCs, was plotted as a function of the irradiation dose in fig. 4. Figure 4 also shows the data best-fit (solid line) obtained using the power function $PL = A \times D^b$, where D is the irradiation dose in Gy and A and b are free fit parameters. As evidenced by the best-fit (exponent $b = 0.99$), the integrated PL as a function of the irradiation dose shows a linear behaviour in the investigated dose range [19]. The linearity of the PL response of LiF crystals irradiated using 6 MV X-rays in the clinically relevant dose range (1–100) Gy, which is a very desirable feature of any radiation detector, was obtained with a reproducibility within 5%. The reproducibility, which highlights the stability of the radiation-induced F_2 and F_3^+ CCs at RT, was derived performing PL measurements of the irradiated LiF crystals three times in a period of about six months. In each measurement session, the PL spectrum of each sample was obtained as average of at least three measurements.

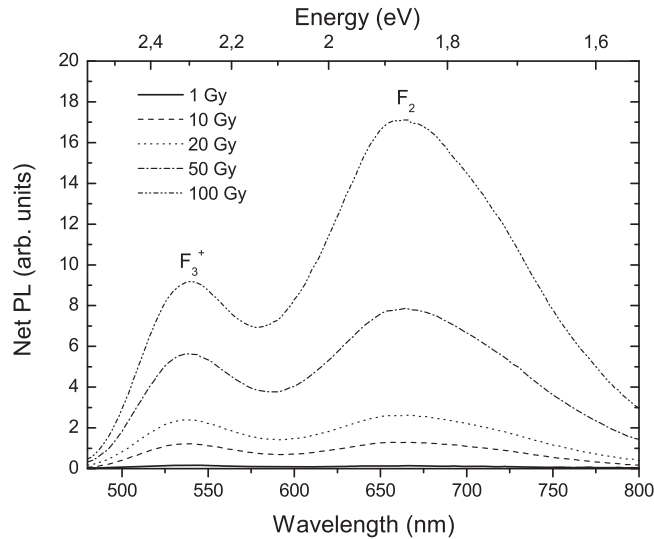


Fig. 2. – RT laser-induced PL spectra of LiF crystals irradiated at 1, 10, 20, 50 and 100 Gy by 6 MV X-rays.

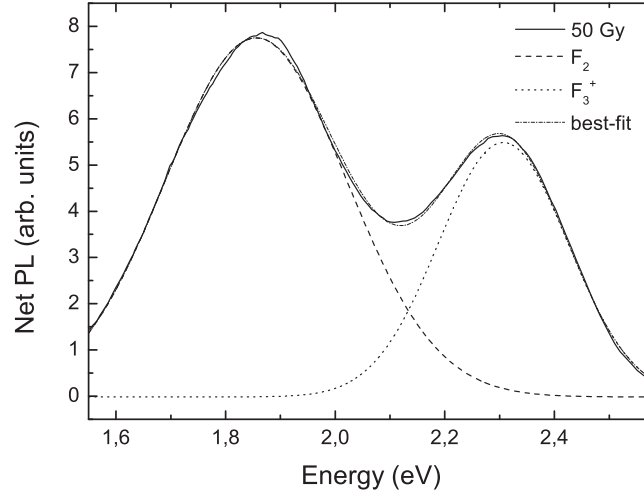


Fig. 3. – Net PL spectrum of the LiF crystal irradiated at 50 Gy by 6 MV X-rays best-fitted as the sum of two Gaussian bands, ascribed to F_2 and F_3^+ emission bands.

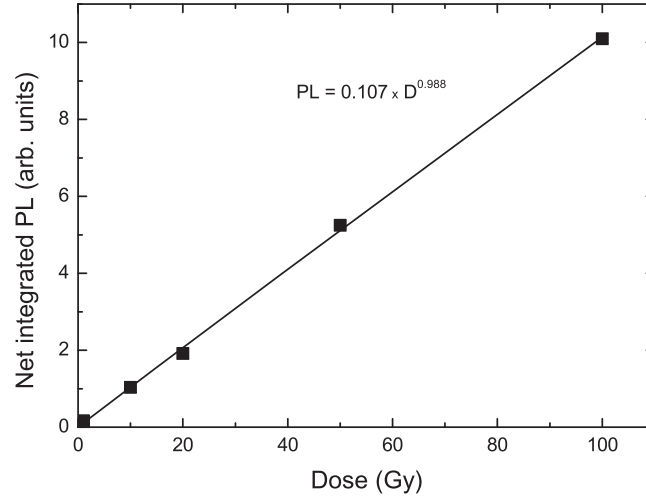


Fig. 4. – Net integrated PL signal as a function of the absorbed dose for the irradiated LiF crystals and best-fit (solid line).

F_2 and F_3^+ integrated PL intensity emitted by the irradiated LiF crystals was also measured using an optical microscope in fluorescence mode, under blue lamp illumination. In order to take into account potential variation of the lamp intensity and/or sCMOS sensitivity, for each measurement of the PL signal emitted by irradiated LiF crystals, an unirradiated LiF crystal was positioned side by side close to the irradiated sample, as shown in fig. 5. Optical fluorescence images of the irradiated LiF crystals were sequentially acquired in identical experimental conditions. For each image, the integrated PL signals from two identical square areas of $0.975 \times 0.975 \text{ mm}^2$, set at a distance of 1.62 mm from the contact border of the unirradiated and colored LiF crystals,



Fig. 5. – Fluorescence microscope images of an unirradiated LiF crystal (left) side by side close to an irradiated sample (right) for the LiF crystals irradiated at 1, 50, 100 Gy.

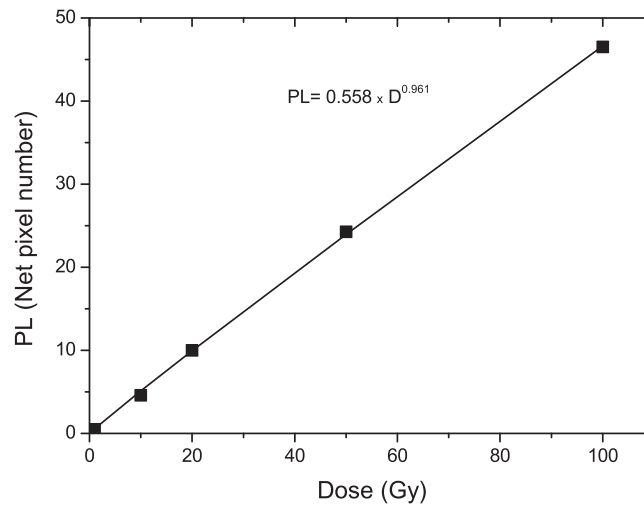


Fig. 6. – Fluorescence microscope net integrated PL signal as a function of the absorbed dose for the irradiated LiF crystals and best-fit (solid line).

see fig. 5, were acquired. Their subtraction, in terms of pixel number, determines the Net integrated PL of each irradiated LiF crystal. Figure 6 reports the Net integrated PL, derived from the acquired images, as a function of the irradiation dose [20]. In agreement with the results derived from the PL spectra of colored LiF crystals, the Net integrated PL obtained from optical microscope measurements again shows a linear behaviour in the investigated dose range, as evidenced by the best-fit procedure (exponent $b = 0.96$) reported in fig. 6.

4. – Conclusions

The use of nominally pure LiF crystals as dosimeters based on optical reading of the F_2 and F_3^+ PL has been investigated for 6 MV X-rays in the clinically relevant dose range from 1 to 100 Gy. The linearity of the integrated PL response due to the cumulative contribution of F_2 and F_3^+ electronic defects as a function of the irradiation dose was demonstrated, starting from the laser-induced visible PL spectra of the investigated samples. This result is confirmed by the optical response resulting from the images acquired by using an optical microscope operating in fluorescence mode. The linearity of

PL response, which is a very desirable feature of any radiation detector, was obtained with a reproducibility within 5%.

A comprehensive investigation of the response reproducibility requires additional investigation to assess LiF crystal-batch reproducibility, the potential role of dopant and the re-usability of LiF crystals after thermal annealing. Flat energy dependence dose response, dose-rate independence, good dose resolution (sensitivity), etc., which are fundamental features of an ideal dosimeter, need to be investigated.

Further work is also in progress to increase the PL reading sensitivity, *i.e.* to obtain a higher signal to noise ratio, in order to explore the possibility to evaluate the PL signal for LiF crystals irradiated at doses below 1 Gy.

This preliminary results provides experimental evidence of the potential application of nominally pure LiF crystals as clinical dosimeters based on optical reading of F_2 and F_3^+ photoluminescence.

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