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Visible photoluminescence of color centers in LiF crystals for absorbed dose evaluation in clinical dosimetry

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Abstract. Among insulating materials, lithium fluoride (LiF) has been successfully used as ionizing radiation dosemeter for more than 60 years. Thermoluminescence (TL) has been the most commonly used reading technique to evaluate the absorbed dose. Lately, optically stimulated luminescence (OSL) of visible emitting color centers (CCs) has also been explored in pure and doped LiF. This work focuses on the experimental behaviour of nominally pure LiF crystals dosemeters for 6 MV x rays at low doses based on photoluminescence (PL) of radiation induced CCs. Polished LiF crystals were irradiated using 6 MV x rays produced by a clinical linear accelerator. The doses (absorbed dose to water) covered the 1-100 Gy range. Optical absorption spectra show stable formation of primary F defects up to a maximum concentration of $2x10^{16}$ cm^{-3}, while no significant M absorption band at around 450 nm was detected. On the other hand, under Argon laser excitation at 458 nm, PL spectra of the irradiated LiF crystals clearly exhibited the characteristic F_2 and F_3^+ visible broad emission bands. Their sum intensity is linearly proportional to the absorbed dose in the investigated range. PL integrated intensity was also measured using a conventional fluorescence optical microscope under blue lamp illumination. The relationship between the absorbed dose and the integrated F_2 and F_3^+ PL intensities, represented by the net average pixel number in the optical fluorescence images, is also fairly linear. Even at the low point defect densities obtained at the investigated doses, these preliminary experimental results are encouraging for further investigation of CCs PL in LiF crystals for clinical dosimetry.

1. Introduction

Among insulating materials, lithium fluoride (LiF) in pure and doped form has been successfully used as clinical dosemeter based on thermoluminescence (TL) for over 60 years. In the last decade Al_2O_3:C, used as an optical stimulated luminescence (OSL) dosemeter, has been consolidated as a cost-effective clinical and personal dosimetry system [1]. OSL provides fast evaluation (ms), high sensitivity, wide dose range and dose image capabilities. These desirable dosimetric properties have encouraged research aimed to investigate the use of LiF as a photoluminescence (PL) based dosemeter [2]. Among aggregated color centers (CCs) produced by ionizing radiation in LiF, F_2 and F_3^+ defects, which consist of two electrons bound to two and three close anion vacancies, respectively, have almost overlapping absorption bands (M band) centered around 450 nm [3] and, therefore, can be simultaneously excited with a single pump wavelength in the blue spectral interval. On the other hand, they exhibit two different broad emission bands in the green (F_3^+) and red (F_2) spectral ranges [4]. In the last decades they were proposed for novel solid state luminescent detectors at high spatial resolution for soft x rays [5] based on LiF crystals and thin films [6]. Recently, their use was extended to proton beam characterization [7].

In this work the preliminary results of the optical investigation of radiation-induced CCs in 6 MV x ray irradiated pure LiF crystals in the clinically relevant dose range of 1-100 Gy are presented. Even at these low doses, optical absorption and PL spectra were measured at room temperature (RT) and a conventional optical microscopy based reading system has been successfully used for the integrated visible PL signal evaluation.

2. Materials and Methods

A set of nominally pure, commercially available, LiF crystals, of dimensions 5x5x0.5 mm^3, 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 10x10 cm^2 field size was set for all the irradiations. 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. All the doses refer to doses 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. The PL measurements were performed at RT and in a period of time after the irradiations that spanned from 6 weeks to 6 months.

The optical absorption measurements of the irradiated and blank (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 spectra measurements were performed at RT using a continuous wave mode Argon laser at a fixed power of 25 mW. The laser was tuned at the wavelength of 458 nm in order to simultaneously excite the F_2 and F_3^+ CCs emission. Their photoemission 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. A computer controlled acquisition system developed at ENEA Frascati was used for all the PL measurements. It is worth noting that 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 confocal optical microscope **(**Nikon Eclipse 80i-C1) working as a conventional wide-field optical microscope in fluorescence mode. The excitation light source was a mercury lamp OSRAM HBO 103W/2 (power 100W). The light of the mercury lamp (excitation) as well as the fluorescence (PL signal) of the LiF crystal were properly filtered. The excitation optical filter transmits light in the 450 – 490 nm spectral interval, while the output one (reading) 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**),** 2560x2160 pixels, pixel size 6.5 micron, front illuminated and cooled at -30°C. The PL integrated signal from all the irradiated crystals was obtained by directly extracting the average pixel number (gray level) of a circular area of approximately 0.75 mm^2. The freely available image processing software imageJ was used for all the image-PL analysis. All the images were converted to JPEG format and therefore the pixel numbers were limited to the 0-255 level, even if the used sCMOS resolution was 11 bit.

3. Results and Discussion

The absorption spectra, in optical density (O.D.), of a blank LiF crystal and of the LiF crystals irradiated at 10, 50 and 100 Gy by 6 MV x rays are shown in figure 1. Only these results are presented for the sake of clarity. The F absorption band, due to the primary F CCs, located around 250 nm, is clearly observed for the 50 and 100 Gy dose levels only. The M absorption band, due to F_2 and F_3^+ CCs, centred around 450 nm, is not detectable even for the highest doses used in this investigation [5]. The evaluation of the electronic defect concentrations inside the irradiated LiF crystals, was performed by using the Smakula formula [8]. For each spectrum, the O.D. of the blank LiF crystal was subtracted, in order to highlight the effects of coloration. The full width at half-maximum (FWHM) and the absorption coefficient at the band peak of the F absorption band were obtained by using a Gaussian best fit-procedure. The resulting concentrations of F CCs were 1.25×10^{16} and 1.95×10^{16} cm^{-3} for the LiF crystals irradiated at 50 and 100 Gy, respectively. For the M band, the absorption signal is comparable with the measurement noise. On the base of the Smakula formula, it was possible to obtain a rough estimation of the maximum concentration of F_2 CCs induced by the irradiation. In this case, the FWHM known from literature [8], and the absorption coefficient at 450 nm (around the band peak of the M absorption band) were used. The concentration of aggregate F_2 CCs was below 6×10^{14} cm^{-3}.

The PL spectra shown in figure 2 clearly present the two characteristic broad emission bands of the aggregate F_2 and F_3^+ defects. A background correction was applied: the net PL spectra were obtained by subtracting a blank spectrum (the spectrum of an unirradiated LiF crystal, used as "zero" dose reference) from every measured photoemission spectrum obtained for each irradiated LiF crystal. The F_2 and F_3^+ broad emission bands are centred around 678 and 541 nm, respectively. After converting the wavelengths from nm to eV, the rescaled PL spectra were fitted as the sum of two Gaussian bands (see figure 3), whose spectral parameters (peak position and FWHM) are in agreement with well-assessed literature in LiF crystals [9]. The areas under the Gaussian bands are associated with the contribution to the integrated PL of the F_2 and F_3^+ CCs. The integrated PL signal, defined as the sum of the PL signals from the two Gaussian bands, was obtained for every spectrum and plotted against the absorbed dose. These results are presented in figure 4. A power function (solid line in figure 4) was used for the fit. The exponent value of 0.99 confirms the linear behaviour of the PL response as a function of the absorbed dose.

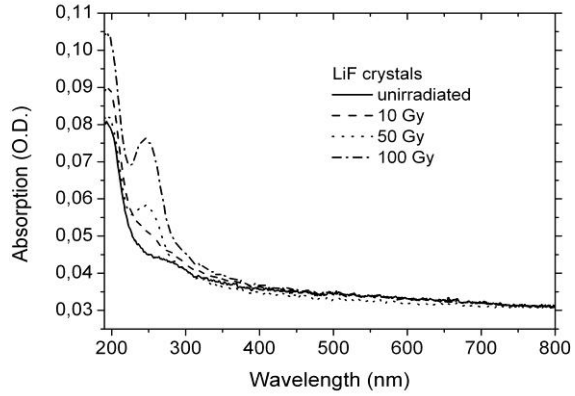

Figure 1. RT optical absorption spectra of 6 MV x rays irradiated LiF crystals at several doses. The spectrum of a blank crystal is reported for comparison.

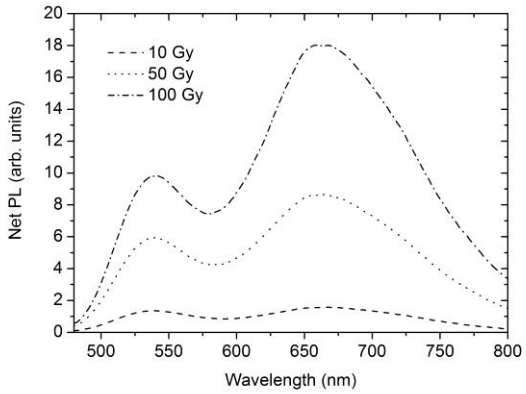

Figure 2. RT laser induced (458 nm) PL spectra of 6MV x-ray irradiated LiF crystals at 10, 50 and 100 Gy.

In the fluorescence microscope integrated PL signal measurements, in order to account for potential variations on the lamp intensity and/or sCMOS sensitivity, an unirradiated LiF crystal was always positioned side by side close to the irradiated LiF crystal, as illustrated in figure 5 for the 50 Gy x rays irradiated LiF crystal. Under this arrangement, the optical images of two identical circular areas set at a distance of 0.35 mm from the middle line (border line between the unirradiated and irradiated LiF crystal), were sequentially acquired in identical conditions. The difference between the mean pixel number of the irradiated crystal and the corresponding zero dose pixel number is defined as the net pixel number, which is associated with the PL signal of the irradiated crystal.

The integrated PL signal derived from the images of the irradiated crystals at all doses is presented in figure 6. Again it shows a linear behaviour in the investigated dose range (exponent 0.96), in agreement with the PL vs dose plot in figure 4, derived from the PL spectra. The error bars associated with the net pixel number estimates varied from 1.1 to 2.0 pixel number (standard deviation of the pixel number within the circular area). The percentage error is of the order of 4% at a dose of 100 Gy and rises at about 50% for 1 Gy irradiation and it is mainly due to the relatively high noise and low PL signals from the irradiated crystals. A significant increase in the sensitivity of the fluorescence microscope acquisition is required in order to effectively evaluate doses below 10 Gy level.

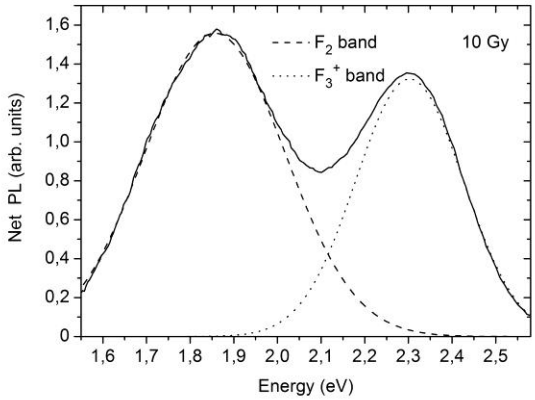

Figure 3. Net PL spectrum of the 6 MV x-ray irradiated LiF crystal at 10 Gy, best-fitted as the sum of two Gaussians bands, ascribed to the F_2 and F_3^+ CCs emission bands.

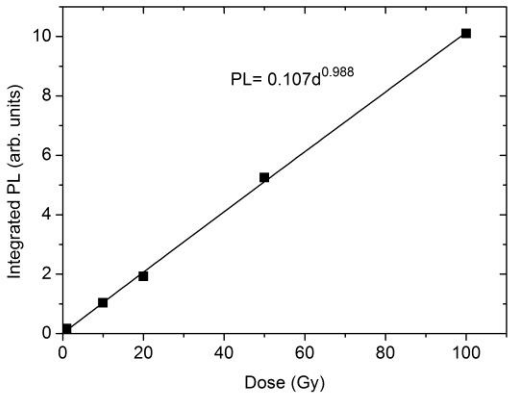

Figure 4. Integrated PL intensity as a function of the absorbed dose for all the 6 MV x rays LiF irradiated crystals and linear best fit (solid).

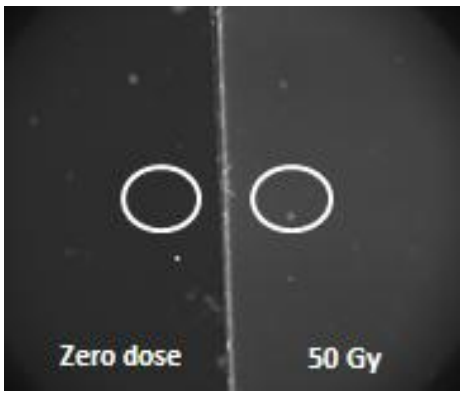

Figure 5. Fluorescence microscope image of a blank (zero dose) and the 50 Gy 6 MV x ray irradiated LiF crystals. The two white circles show the areas selected for the measurement of the integrated PL signal.

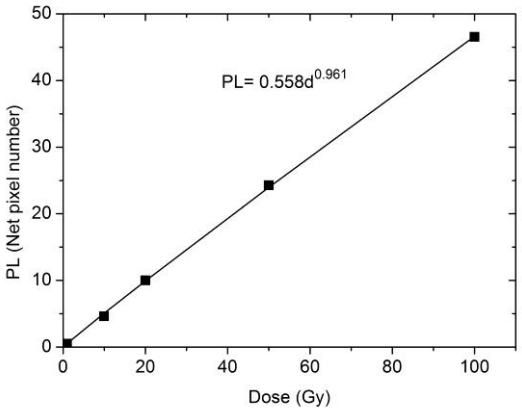

Figure 6. Fluorescence microscope integrated PL signal (Net pixel number) as a function of the absorbed dose for all the 6 MV x-ray irradiated LiF crystals.

4. Conclusions and further work

The use of pure LiF crystals as PL dosemeters in the clinically relevant 1 to 100 Gy dose range has been investigated for 6 MV x rays irradiation. The linearity of the integrated PL response of F_2 and F_3^+ electronic defects as a function of dose, derived from the laser induced visible PL spectra, is consistent with the optical response detected with a fluorescence microscope system. This linearity is a very desirable feature of any radiation detector. Even at the low electronic defect densities (F and F_2 concentrations below $2x10^{16}$ cm^{-3} and $6x10^{14}$ cm^{-3}, respectively) obtained at the investigated doses, these preliminary experimental results grant further investigation of CCs PL in LiF crystals for clinical dosimetry. A modified excitation light system as well as a more effective optical filtering of the excitation and emitted PL from the LiF irradiated crystals is under optimization, in order to address the low sensitivity of the fluorescence microscope reading system. Re-usability of the LiF crystals and laser induced PL reproducibility after thermal annealing requires additional investigation.

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