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

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Outline

Introduction

Lithium fluoride: material properties;

Primary and aggregate colour centres in LiF.

LiF crystals coloured by 6 MV x-rays

Optical absorption spectra and colour centres concentrations;

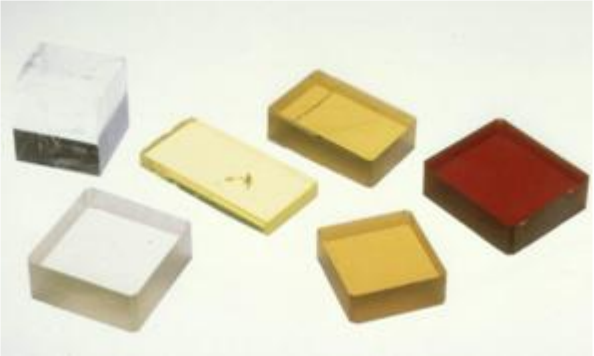
Laser-induced photoluminescence (PL) measurements;

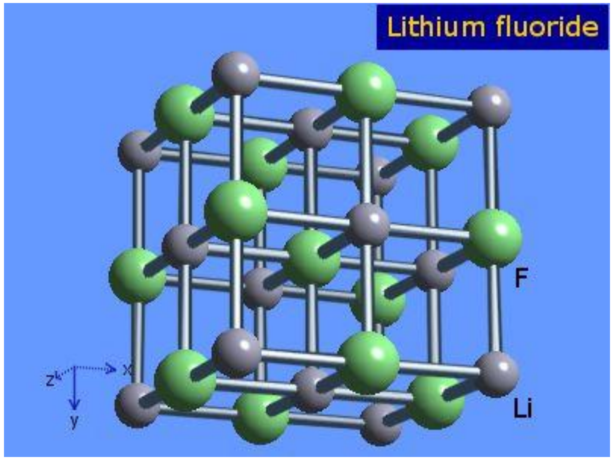
Fluorescence optical microscope measurements.

Conclusions

Lithium fluoride

LiF is an interesting material for several applications because of its peculiar chemical-physical and optical properties. It is used for the realization of light-emitting miniaturized devices and it is also a well-known dosimeter material in pure and doped form (LiF:Mg,Ti, LiF:Mg,Cu,P to enhance its sensitivity to ionising radiations and/or to obtain the near tissue-equivalence of the material).





Nearest neighbour distance (Å)	2.013
Melting point (° C)	848.2
Density (g/cm^3 a RT)	2.639
Molecular weight	25.93 9
Refractive index at 640 nm, RT	1.391 2
Solubility (g/100 g H_2O a RT)	0.134
Hardness (Knoop)	102

- fcc ionic crystal;
- hard;
- almost not-hygroscopic;
- optically transparent from 120 nm to 7μm (gap 14 eV);
- it can be colored only by ionizing radiations (X-rays, γ rays, UV light, elementary particles and ions). The irradiation of LiF gives rise to stable formation at room temperature (RT) of primary and aggregate colour centres (CCs) characterized by wide tunability and high emission quantum efficiency, even at RT;
- polycrystalline LiF films can be grown by thermal evaporation on different substrates.

Tissue equivalence:
effective atomic number Z_{eff} for a compound

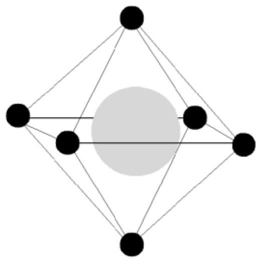
Effective atomic number, Z_{eff}, is used to characterize the radiation responce of a compound in many technical and medical applications. It indicates if a compound approximates or deviates from soft tissue (**tissue equivalence/water equivalence**).

$$Z_{eff} = \sqrt[m]{\sum_i a_i \cdot Z_i^m}$$

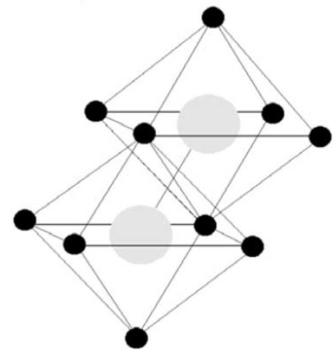
a_i is the fractional electron content of element i
Z_i is the atomic number of element i
m is a number between 3 and 4, typically set at 3.5 (photoelectric domain).

Material	Composition (%)	Z_{eff}
BeO	Be:36 O:64	7.2
Water	***H:11 O:88***	***7.5***
Air	N:76 O:23.18 Ar:1 C:0.01	7.8
LiF	***Li:27 F:73***	***8.3***
Al_2O_3	Al:47 O:53	11.3
SiO_2	Si:47 O:53	11.8
Compact bone	O:44 Ca:21 C:14 P:10 H:4	13.6

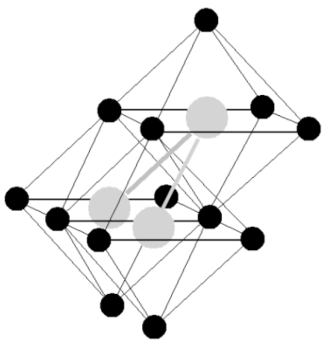
Color centers in LiF



F



F_2

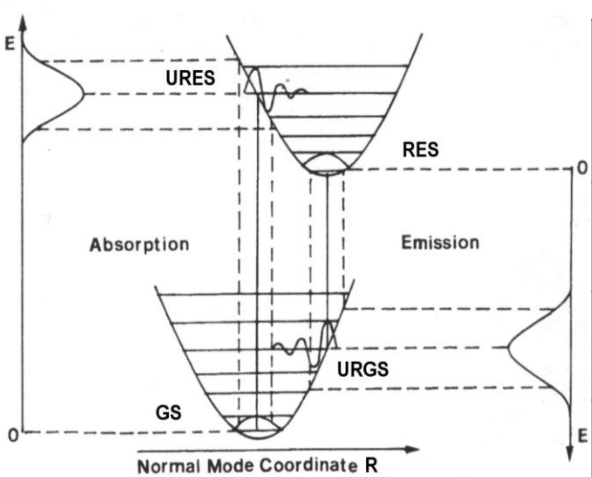


F_3

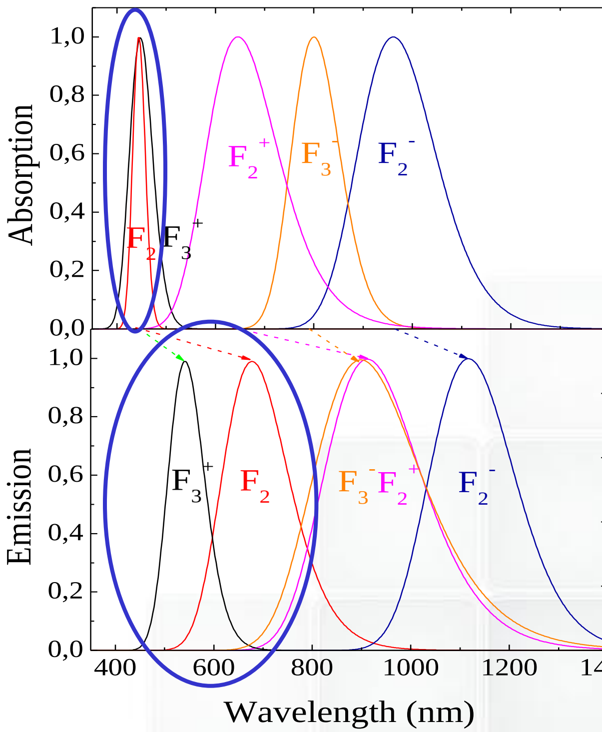
F center is an anion vacancy occupied by an electron.

F_2 electronic defect consists of two nearest-neighbour F centres along a <100> direction of the cubic lattice.

F_3 colour centre consists of three F centres in nearest-neighbour sites in the (111) plane.



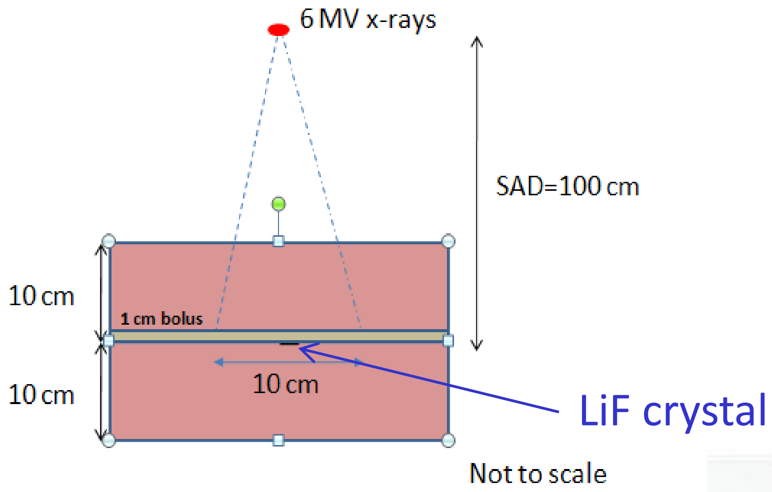
Center	E_a (eV, nm)	E_e (eV, nm)	Hw_a (eV)	Hw_e (eV)
F	5.00, 248	-	0.76	
F_2	2.79, 444	1.83, 678	0.16	0.36
F_3^+	2.77, 448	2.29, 541	0.29	0.31



6 MV X-ray irradiation of LiF crystals

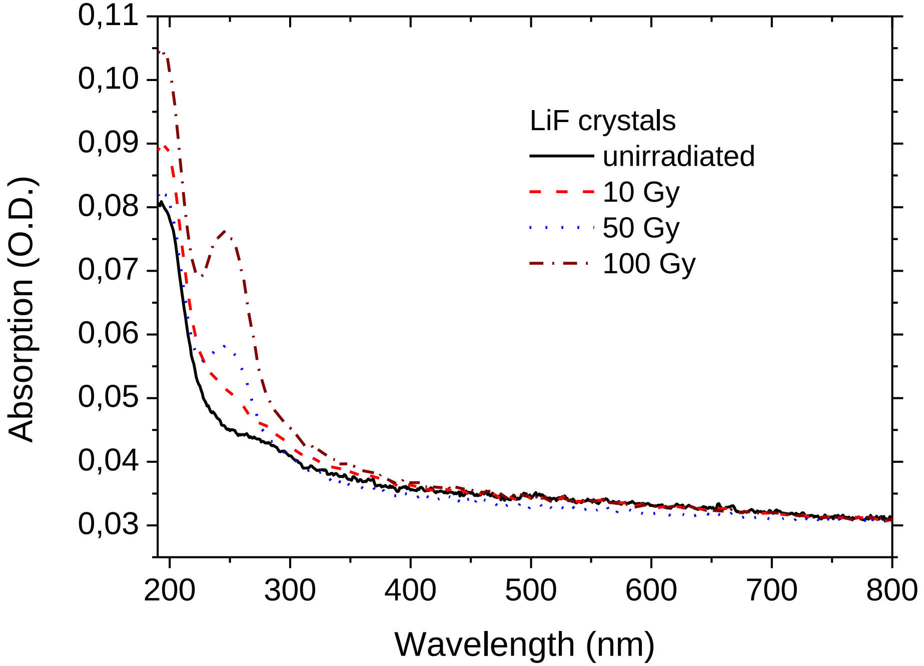
Nominally pure, commercially available, LiF crystals (5x5x0.5) mm^3, polished on both sides, were irradiated under full electronic equilibrium conditions.

- 6 MV X-ray clinical beam (Tom Baker Cancer Center, Calgary, Canada)
- Dose-rate 4.66 Gy/min
- Doses: 1, 10, 20, 50 and 100 Gy
- Dose accuracy +/- 2 %



- A (10x10) cm^2 field size was set for all the irradiations.
- LiF crystals were positioned at the center of the square radiation field.
- All the doses refer to doses to water.

Optical absorption measurements



The F absorption band, peaked at around 248 nm, is clearly observed for the LiF crystals irradiated at the highest doses (50 and 100 Gy).
The M absorption band located at around 450 nm, is not clearly detected even for the highest irradiation doses used in this investigation.

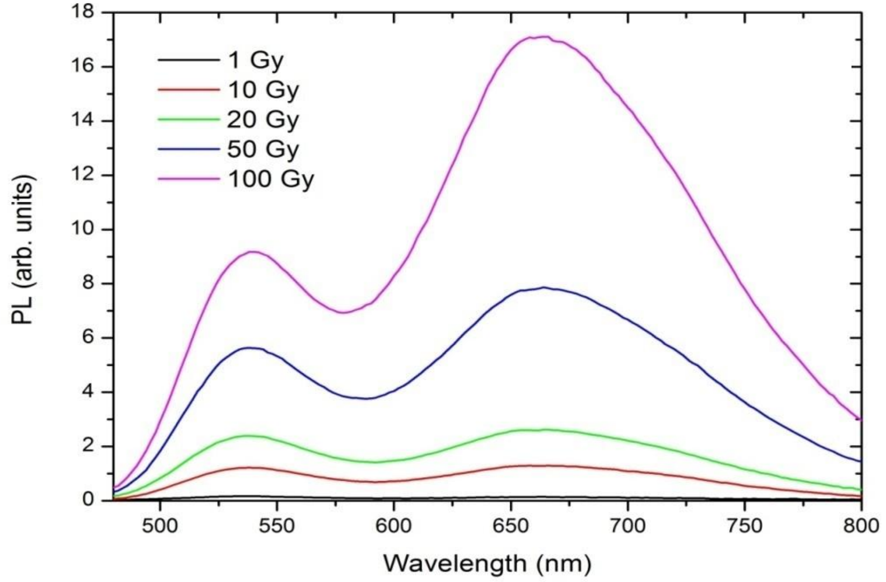
From the **Smakula** formula

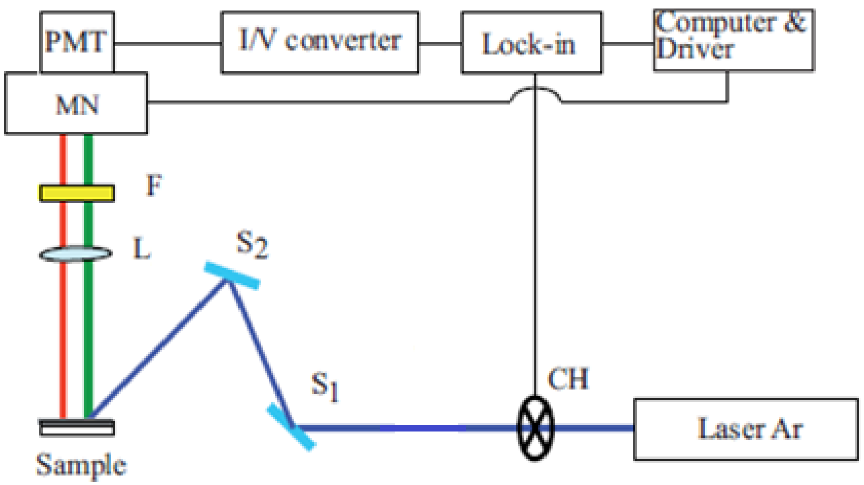
$$N\ (cm^{-3}) \times f = 0.87 \times 10^{17}\ [n/(n^2+2)^2] \times \alpha(cm^{-1}) \times FWHM(eV)$$

Dose (Gy)	F concentration (cm^{-3})
50	1.25×10^{16}
100	1.95×10^{16}

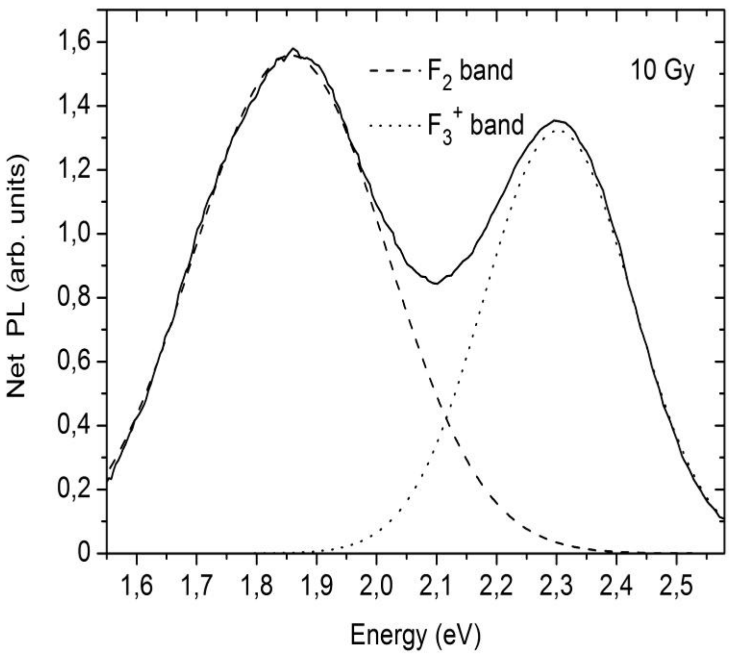
For the M band, the absorption signal is comparable with the measurement noise.

PL measurements



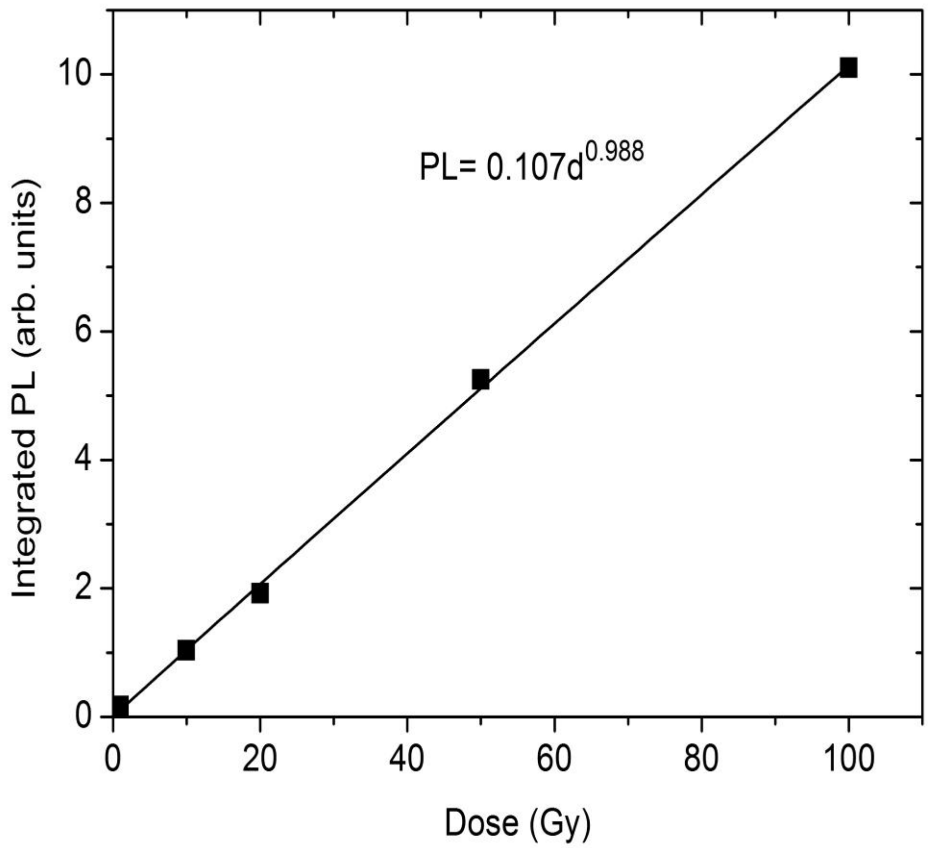


PL spectra excited at 457.9 nm. Each spectrum, obtained by subtracting the PL spectrum of an unirradiated LiF crystal, presents the two characteristic broad emission bands, due to the aggregate F_2 and F_3^+ defects, centred around 678 and 541 nm, respectively.



Integrated PL vs Dose by laser spectroscopy

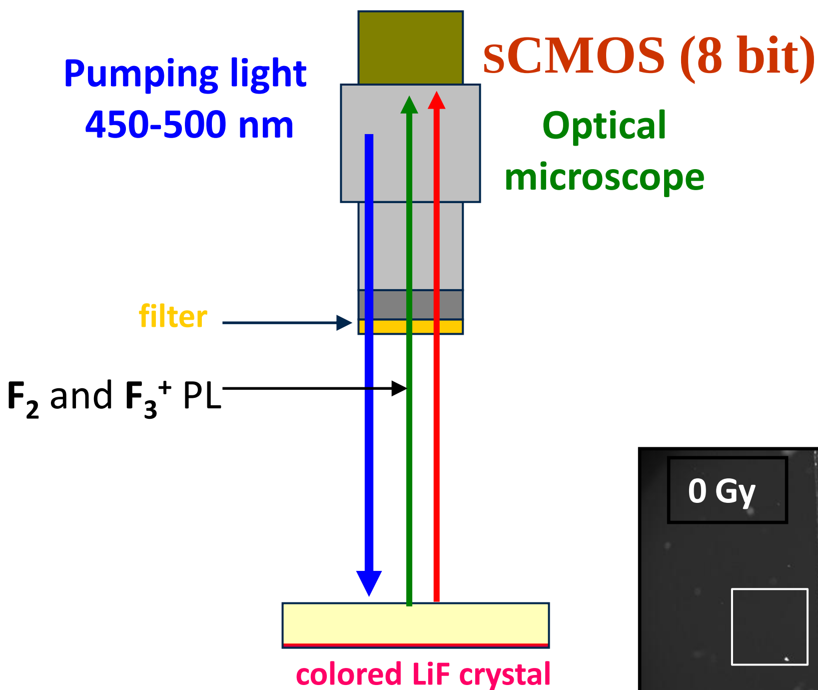
The Integrated F_2 and F_3^+ PL signal shows a linear behaviour as function of the adsorbed dose in the investigated conditions (exponent value of 0.99).

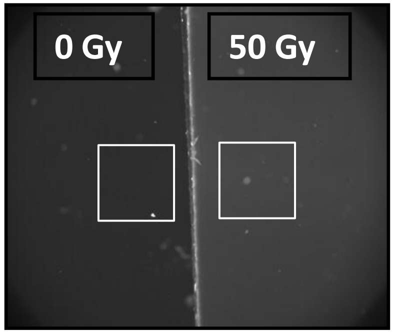


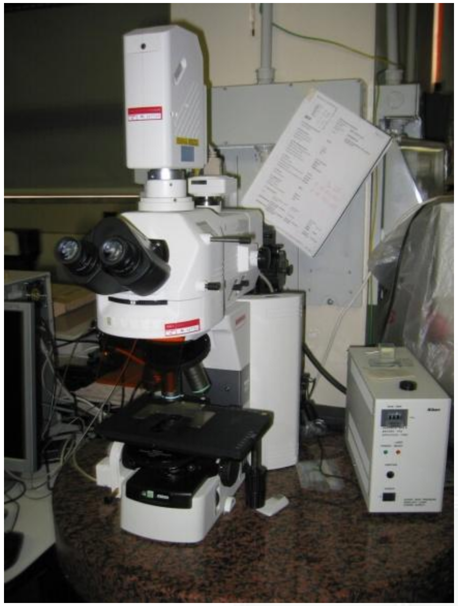
Fluorescence microscopy measurements

F_2 and F_3^+ PL integrated intensity was measured using a conventional fluorescence optical microscope under blue lamp illumination.

An unirradiated LiF crystal was always positioned side by side close to the irradiated sample. Optical images of the irradiated LiF crystals were sequentially acquired under this arrangement in identical experimental conditions. For each image, the integrated PL signals from two identical square areas were acquired.



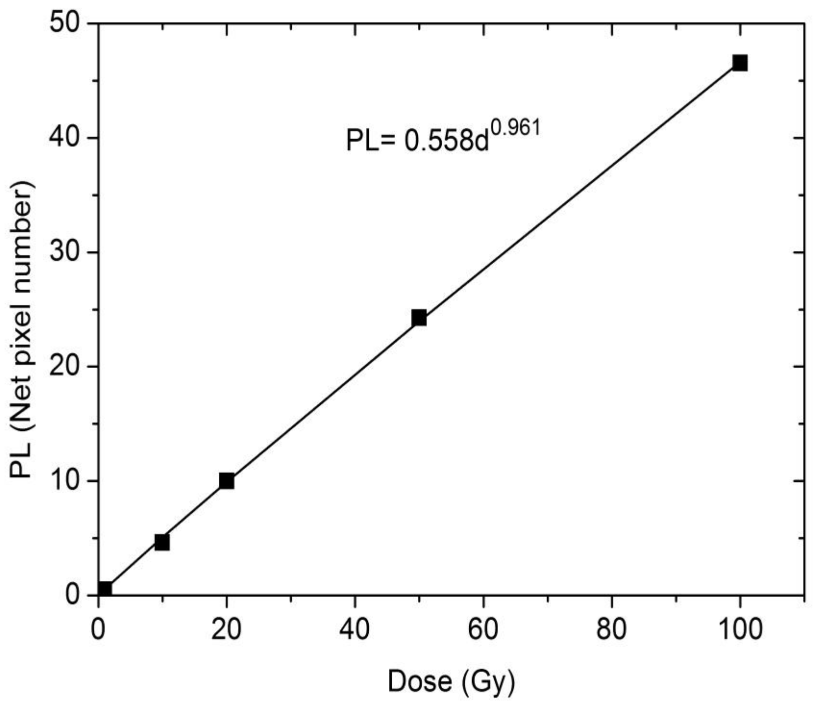


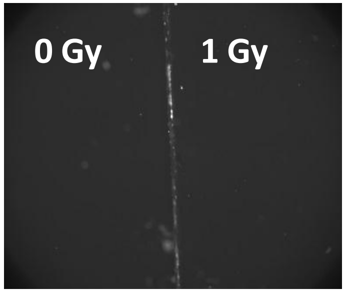


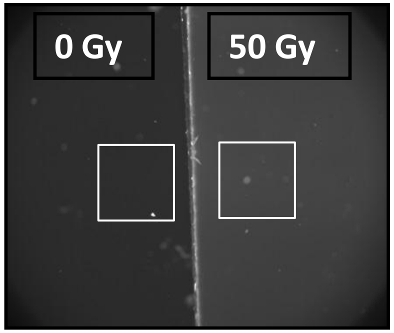
Fluorescence Microscope Nikon Eclipse 80-i, s-CMOS camera Andor NEO.

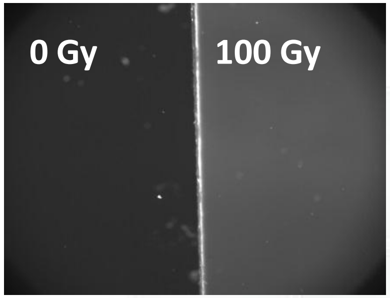
Net Integrated PL vs Dose

The subtraction of the two integrated PL signals determines the “Net integrated PL” of each irradiated LiF crystal. Again the Net integrated PL as a function of the irradiation dose shows a linear behaviour in the investigated dose range, as evidenced by the linear best fit (exponent 0.96).









Similar results were obtained for 5 MV X-ray clinical beam irradiation (S. M. Hospital, Terni).

Conclusions

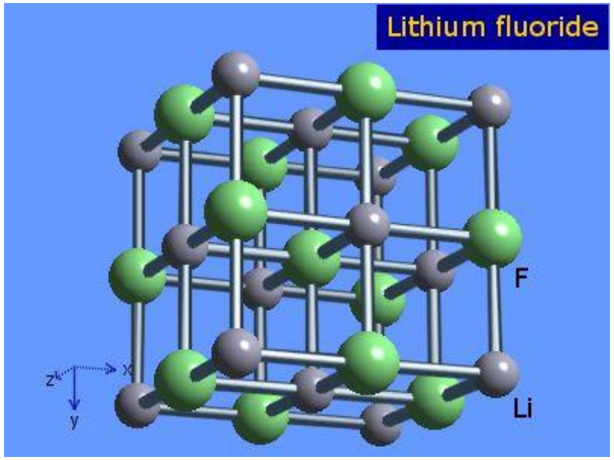
The use of nominally pure LiF crystals as dosimeters based on optical reading of F_2 and F_3^+ PL, in the clinically relevant dose range, has been investigated for 6 MV x-rays.

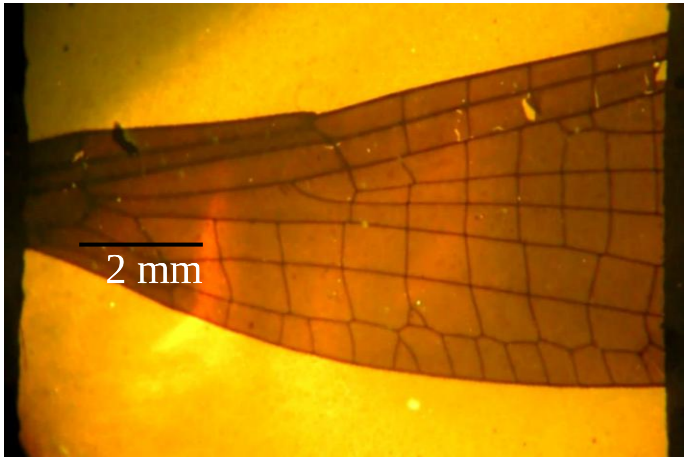
The linearity of the integrated PL response, due to F_2 and F_3^+ eletronic defects, as function of irradiation dose, derived from the laser induced visible PL spectra is consistent with the optical response detected with a fluorescence microscope.

The linearity (desirable feature of any radiation detector) was obtained with a good reproducibility (within 4%) of PL measurements.

Re-usability of LiF crystals after thermal annealing and LiF crystal-batch reproducibility require additional investigation. Further work is in progress to investigate the potential role of dopant.

These preliminary results grant further investigation of nominally pure LiF crystals for clinical dosimetry.





Thanks for your attention