Visible photoluminescence of color centers in LiF crystals for advanced diagnostics of 18 and 27 MeV proton beams

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ABSTRACT

Solid-state radiation detectors based on the visible photoluminescence of radiation-induced \textit{F}_2 and \textit{F}_3\textsuperscript{+} color centers in lithium fluoride crystals have been used for advanced diagnostics of 18 and 27 MeV proton beams, produced by the TOP-IMPLART linear accelerator, which is under development for protontherapy applications at ENEA C.R. Frascati, Italy. Visible fluorescence microscopy was successfully used to read the latent proton beam images stored in the lithium fluoride crystals, thanks to high emission efficiency of the \textit{F}_2 and \textit{F}_3\textsuperscript{+} color centers obtained by simultaneous optical excitation in the blue spectral range. High intrinsic spatial resolution and wide dynamic range of these novel LiF detectors allow obtaining two-dimensional images of both the beam transverse intensity distribution and of the Bragg curve. By using a simple defect formation model that takes into account the energy released in the material and the saturation of defect concentration, not only the two-dimensional dose map was obtained from the beam transverse intensity distribution image, but also the full Bragg curve was reconstructed, allowing the thorough characterization of proton beams produced by the accelerator.

1. Introduction

Lithium fluoride (LiF) is a practically not hygroscopic alkali halide that can host laser-active electronic defects, known as color centers (CCs), characterized by wide tunability and good stability even at room temperature (RT). Such CCs can be created by several kinds of ionizing radiation (X-rays, γ-rays, electrons, neutrons, protons, α-particles and heavier ions), the main ones being the primary F center (an anionic vacancy occupied by an electron) and the aggregate \textit{F}_2 and \textit{F}_3\textsuperscript{+} CCs (two electrons bound to two and three anion vacancies, respectively). The F center has an optical absorption band peaked at a wavelength of about 248 nm, but its photoluminescence (PL) has never been detected unambiguously (Baldacchini et al., 1993). On the contrary, by optically pumping the \textit{F}_2 and \textit{F}_3\textsuperscript{+} centers in their almost overlapping absorption band centered at about 450 nm (Nahum and Wiegand, 1967), they simultaneously emit broad PL bands peaked at 678 and 541 nm, respectively (Baldacchini et al., 2000). Due to these peculiar physical and optical properties, CC-based luminescent LiF solid-state detectors are widely used in optoelectronics (Ter-Mikirtychev and Tsuboi, 1996), integrated optics (Montereali et al., 2001) as well as in dosimetry, in both pure (McLaughlin et al., 1980) and doped (Lakshmanan et al., 1996) form.

Recently, the use of protons in oncological radiotherapy has seen a remarkable growth because they lose most of their energy at the end of their path in tissue, called Bragg peak, with modest lateral diffusion, thus preserving the surrounding healthy organs (Tamborini et al., 2016). In the framework of the TOP-IMPLART project (Ronsivalle et al., 2011), a 150 MeV proton accelerator, designed as a sequence of linear accelerating modules, is under development at ENEA C.R. Frascati, aiming at using it for protontherapy applications. We have started studying the optical properties of CCs induced in LiF by low-energy protons (Piccinini et al., 2014, 2015) with the purpose of performing the TOP-IMPLART proton beam diagnostics during the accelerator development, using CCs-based LiF radiation detectors for imaging and dosimetry under different operation conditions (Piccinini et al., 2017a).

An advantageous application of these solid-state LiF-based radiation detectors is the possibility of imaging not only the proton beam transverse intensity distribution, but also the Bragg curve. In this paper we present the beam characterization results obtained from PL images of the 18 and 27 MeV proton beams transverse intensity distribution and of their Bragg curves stored in LiF crystals. The images were processed by applying a CC formation model that allowed relating the PL intensity...
to the absorbed dose and thus reconstructing two-dimensional (2D) beam transverse dose maps and best-fitting the whole Bragg curve to obtain the main proton beam parameters.

2. Materials and methods

In this work commercially available (10 × 10) mm², 1 mm thick LiF crystals polished on both faces were used as radiation detectors. When protons enter the LiF crystal, they release energy and create stable F₂ and F₃⁺ CCs, whose concentrations are proportional to the energy deposited in the material. By exposing one of the polished crystal faces perpendicularly to the beam propagation direction, the 2D PL image of the transversal proton beam intensity distribution could be stored in the LiF detector (see Fig. 1). After irradiation, the stored image was read by the fluorescence microscope Nikon Eclipse 80-i, equipped with a 2x objective and a Hg lamp, whose blue emission, peaked at 434 nm, simultaneously excited the PL of the F₂ and F₃⁺ CCs (Baldacchini et al., 2000), while an Andor Neo s-CMOS camera acquired the PL images with an 11-bit dynamic range.

By exposing the 1 mm thick LiF crystal side perpendicularly to the impinging protons, when the beam penetrates the crystal it releases its energy and thus creates F₂ and F₃⁺ CCs, whose local concentrations are directly proportional to the linear energy transfer (LET) curve, also called the Bragg curve, provided saturation has not been reached (Piccinini et al., 2014). After exposure, the fluorescence microscope was used to acquire the PL image of the spatial distribution with depth of the CCs in the crystals. The PL intensity exhibited a strong increase at a defined distance from the crystal edge; it is representative of the Bragg peak position, that corresponds to the maximum energy deposited by the proton beam (see Fig. 2). After selecting a region of interest (r.o.i.) in the image, the experimental PL Bragg curve was obtained by integrating transversally to the proton beam propagation direction the PL intensity within the r.o.i. by means of ImageJ software (ImageJ v.1.47 and National I) (see Fig. 3).

All irradiations were performed in air at room temperature and the LiF crystals were placed at 10 mm from the accelerator 50 μm-thick Titanium exit window. The proton beam produced by the TOP-IMPLART accelerator is pulsed; for both the 18 and 27 MeV beams 2400 pulses were delivered to the LiF crystals with a charge of 64 pC/pulse at a repetition frequency of 10 Hz.

3. Results and discussion

Fig. 1 shows the PL image of a 18 MeV proton beam stored by radiation-induced CCs, obtained by exposing one of the polished LiF crystal faces perpendicularly to the beam propagation direction.

Fig. 1. PL image of the 18 MeV proton beam transversal intensity distribution stored in a 1 mm-thick LiF crystal at an average dose of 1.8 × 10⁴ Gy.

Fig. 2. PL image of the 18 MeV Bragg curve stored in a LiF crystal.

According to our investigations, the integrated PL signal, obtained from the fluorescence images of the proton irradiated spots, as a function of the dose deposited by 3 and 7 MeV proton beams in 1 μm thick LiF films, shows a linear behavior from 10³ Gy, extending up to three orders of magnitude of the dose, while at the highest doses CCs saturation effects start occurring, thus causing a sub-linear behavior (Piccinini et al., 2015).

Such a PL response behavior can be reproduced by a linear-model approach, assuming the volume density of CCs generated by ionizing radiation to be locally proportional to the amount of deposited-energy density, but including also a suitable saturation mechanism. Such a model was introduced by Soshea and co-workers to describe the formation of CCs in MgO (Soshea et al., 1958), where ionizing radiation is supposed to mediate, besides creation, also annihilation of CCs. In ref (Piccinini et al., 2017b). this model was successfully applied to best fit the PL behavior of ref. (Piccinini et al., 2015), in which the integrated PL intensity (Iₚ) is related to the dose (D) by the equation:

\[
Iₚ = A \left[ 1 - \exp \left( - \frac{D}{D_{sat}} \right) \right]
\]

where the saturation dose (D_{sat}) is defined as a threshold dose value above which saturation begins to be evident and A is a normalization factor strictly dependent on the arbitrary measurements units of the PL.

Equation (1) can also be used, as explained below, to perform the
best fit of the experimental PL Bragg curve obtained by averaging transversally to the 18 MeV proton beam propagation direction \( z \) the PL intensity found within the \((2300x100) \mu m^2\) r.o.i. of the image shown in Fig. 2. It was acquired by the fluorescence microscope from the top face of the LiF crystal, whose 1 mm-thick side was exposed perpendicularly to the impinging protons. The PL Bragg curve is shown in Fig. 3 together with its best-fitting theoretical curve obtained by taking into account that in equation (1) the dose depth distribution \( D(z) \) is related to the LET curve \( L(z) \) through:

\[
D(z) = L(z) \Phi(z) / \rho \tag{2}
\]

where \( \Phi \) is the proton fluence and \( \rho \) is the LiF density \( (\rho = 2.635 \, g/cm^3 \) (Patnaik, 2002)).

The LET curves were simulated by SRIM software (Ziegler et al., 2010) and the experimental PL profile was satisfactorily best fitted by processing SRIM output curves in MATLAB (MathWorks 2010 v., 2010), provided spread of the proton-beam energy (modeled with a Gaussian distribution) was assumed with three fit parameters to be found via least-squares minimization: the mean energy \( \langle E \rangle \), the standard deviation \( \sigma_E \) of the distribution and the \( D_{sat}/D_{sat} \) ratio, where \( D_{sat} \) is the dose at the entry face of the LiF crystal (Nichelatti et al., 2017).

By using the resulting best-fitting values of \( \langle E \rangle \), \( \sigma_E \) and \( D_{sat}/D_{sat} \), together with the available experimental value of proton fluence \( \Phi \), a few other useful irradiation parameters could be evaluated. From the LET values, given by SRIM, it was possible to estimate \( D_{sat} \) by specializing equation (2) into \( D_{sat} = \Phi L_{sat} / \rho \). Then \( D_{sat} \) was estimated by substituting \( D_{sat} \) into \( D_{sat}/D_{sat} \) and also the dose at the Bragg peak \( (D_B) \) was estimated by using the Bragg peak LET values given by SRIM for the corresponding \( \langle E \rangle \) and \( \sigma_E \) and by applying once more equation (2). All the obtained proton beam parameter values are reported in Table 1 and the dose profile with depth is reported in Fig. 3 (dashed curve).

This PL Bragg curve analysis was applied also to a 27 MeV proton beam. During the commissioning of the accelerator a small fraction of the beam was not accelerated up to 27 MeV, thus the Bragg curve was constituted by several lower energy components. Fig. 4 shows the PL image stored in the LiF crystal, where several energy components are clearly visible, as several Bragg peaks are present, and the Bragg curve profile corresponding to the selected r.o.i. is reported in Fig. 5. Due to the presence of the lower-energy components, the best fit of the 27 MeV component in the PL Bragg curve could be performed only considering the part after the lower-energy Bragg peaks and the best-fitting values were found to be \( \langle E \rangle = (27.5 \pm 0.1) \) MeV and \( \sigma_E = (219 \pm 7) \) keV. In order to highlight the presence of the lower-energy peaks, the selected r.o.i. was set at the beam side, where the fluence of the 27 MeV component was much lower than at the center, so the best fit could be performed using the first-order linear approximation of equation (1), for \( D \propto D_{sat} \); in this case also \( D_{sat} \propto D_{sat} \), so the only fit parameters were \( \langle E \rangle \) and \( \sigma_E \), and the dose profile with depth, reported in Fig. 5, is coincident with the best fit curve.

It can be noted that a bump is observed in the experimental PL curves of both Figs. 3 and 5. It is an artifact due to light scattering at the unpolished 1 mm-thick crystal side exposed perpendicularly to the impinging protons.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle E \rangle )</td>
<td>( (18.24 \pm 0.05) ) MeV</td>
</tr>
<tr>
<td>( \sigma_E )</td>
<td>( (143 \pm 5) ) keV</td>
</tr>
<tr>
<td>( D_{sat}/D_{sat} )</td>
<td>( (0.612 \pm 0.004) )</td>
</tr>
<tr>
<td>( D_{sat} )</td>
<td>( (0.80 \pm 0.04) \times 10^5 ) Gy</td>
</tr>
<tr>
<td>( D_{sat} )</td>
<td>( (1.31 \pm 0.07) \times 10^5 ) Gy</td>
</tr>
<tr>
<td>( D_{BP} )</td>
<td>( (4.11 \pm 0.19) \times 10^6 ) Gy</td>
</tr>
</tbody>
</table>

Equation (1) was exploited not only to perform the best fit of the experimental PL Bragg curve, but also to analyze the PL image of the beam transverse intensity distribution (see Fig. 1). In fact, equation (1) can be inverted to give:

\[
D = -D_{sat} \ln \left( \frac{I}{I_{sat}} \right) / A \tag{3}
\]

By applying equation (3) to the image of Fig. 1, the dose can be determined as a function of the PL intensity in the form of a bi-dimensional \((x, y)\)-distribution, with both \( D \) and \( I_{sat} \) functions of the surface coordinates \((x, y)\). When analyzing the bi-dimensional PL image to obtain its dose distribution, it should be pointed out that the parameter \( A \) in equation (3) is generally different from that obtained from the best fit of the PL behavior of ref. (Piccinini et al., 2015); however, a numerical approach can be applied to recover its value (Piccinini et al., 2017b). In ref (Piccinini et al., 2017b), equation (3) was successfully applied to obtain a dose-map from the PL image of a 3 MeV proton beam stored in a 0.8 \( \mu \)m thick LiF film.

The PL image of Fig. 1 is a 18 MeV proton beam stored by a 1 mm thick LiF crystal irradiated with a dose of \( 1.8 \times 10^4 \) Gy. The image is an 11-bit-depth 1850x1300 pixel photo of the visible luminescence emitted by the irradiated LiF crystal acquired with the fluorescence microscope and the s-CMOS camera. The PL intensity \( I_j \) \((j = 1, \ldots,\)
equating the surface integral equation (3) to the measured average dose of aggrate CCs in LiF at 3 and 7 MeV (Piccinini et al., 2017b) and allowed reading instrument. Bragg curve by using a conventional optical images of both the beam transverse intensity distribution and of the occurring. The same model has been successfully used at 18 and 27 MeV correction for higher doses where a sub-linear PL response starts occurring. This model has been successfully used at 18 and 27 MeV to determine a linear-proportionality law between the PL intensity and the absorbed dose below a certain saturation dose, including also a dynamic range, together with the good efficiency of visible emission of short-wavelength laser excitation and good linearity of the PL Bragg curve as described above) and by knowing the effective image pixel size to be 3.26 × 3.26 μm², allowed obtaining a dose-map, after a suitable value for A (A = 394.28 a.u.) was found numerically by equating the surface integral equation (3) to the measured average dose of 1.8 × 10⁶ Gy; in this way the correctness of the retrieved dose scale was assured. The resulting dose-map is shown in Fig. 6 as a 2D distribution.

4. Conclusions

Solid-state radiation detectors based on the photoluminescence of radiation-induced color centers in LiF crystals have been demonstrated to be good candidates for advanced diagnostics of low-energy proton beams, by exploiting their high intrinsic spatial resolution and wide dynamic range, together with the good efficiency of visible emission of F₂ and F₃⁻ CCs. These features allowed obtaining two-dimensional images of the beam transverse intensity distribution and of the Bragg curve by using a conventional optical fluorescence microscope as reading instrument.

A theoretical model was used to describe the formation of the aggregate CCs in LiF at 3 and 7 MeV (Piccinini et al., 2017b) and allowed to determine a linear-proportionality law between the PL intensity and the absorbed dose below a certain saturation dose, including also a correction for higher doses where a sub-linear PL response starts occurring. The same model has been successfully used at 18 and 27 MeV proton energies to process the beam PL images stored in the LiF crystals, in order to theoretically reproduce the entire PL Bragg curve and to obtain high resolution transversal beam dose-maps. They allowed to extract from it useful information regarding the beam itself and a few irradiation parameters, such as the beam energy, its spread and the absorbed dose at any chosen depth in the material.

An improved theoretical model is being developed to best fit also the entire PL Bragg curve of multi-component energetic beams and further research is being carried on regarding the possibility of using of LiF-based devices as radiation detectors in oncological protontherapy.

Acknowledgements

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References


Fig. 6. Dose-map obtained from the image of Fig. 1 by using the procedure described in the text.

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1850 (j = 1, ..., 1300) of each pixel was acquired within MATLAB as a 1850×1300 matrix. Applying equation (3) to each pixel of such a matrix, with the value D_{sat} = (1.3 ± 0.1)×10⁶ Gy (obtained by best-fitting the PL Bragg curve as described above) and by knowing the effective image pixel size to be 3.26 × 3.26 μm², allowed obtaining a dose-map, after a suitable value for A (A = 394.28 a.u.) was found numerically by equating the surface integral equation (3) to the measured average dose of 1.8 × 10⁶ Gy; in this way the correctness of the retrieved dose scale was assured. The resulting dose-map is shown in Fig. 6 as a 2D distribution.

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