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Visible photoluminescence of aggregate colour centres in lithium fluoride thin films for low-energy proton beam radiation detectors at high doses

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ABSTRACT

Colour centres (CCs) in lithium fluoride (LiF) are well known for application in tuneable lasers and dosimeters. The visible photoluminescence (PL) of radiation-induced, broad-band light-emitting aggregate CCs in LiF crystals and films has been proposed for high spatial resolution X-ray imaging; use of LiF-based detectors has been recently successfully extended to advanced diagnostics of low-energy proton beams. After exposure, transversal dose mapping was obtained on LiF films by acquiring the visible PL image of the irradiated spots in a fluorescence microscope under blue-light pumping.

Irradiation of thermally evaporated LiF thin films with a proton beam of 3 MeV nominal energy, produced by a linear accelerator, in the fluence range of 10^{11}–10^{15} protons/cm^2, induces the formation of stable CCs, mainly the primary F centre and the aggregate F_2 and F_3^+ defects. A comparison with irradiations performed at 7 MeV shows that the spectrally integrated PL as a function of the absorbed dose is independent on the selected beam energy, at least as far as typical LiF film thicknesses are concerned. The PL behaviour vs. dose can be described by a linear growth which covers up to three order of magnitude, followed by saturation at high values ($> \approx 10^5$ Gy). The spectral contributions of F_2 and F_3^+ CCs to the detected PL, in the red and in the green respectively, under laser pumping were carefully analysed in order to investigate behaviour differences of these defects at high doses.

1. Introduction

Luminescent properties of point defects in insulating materials are widely used for radiation detectors and dosimetry [1]. Among them, the photoluminescence (PL) of radiation-induced colour centres (CCs) in lithium fluoride (LiF) has been exploited for applications in optically-pumped light-emitting miniaturised devices [2–5] and tuneable solid-state lasers [6]. Various kinds of ionising radiations generate stable primary and aggregate defects in LiF crystals [7] and thin films [8]. The simplest defect that can be created is the so-called primary F centre, which is formed when a negatively charged ion is dislocated in the crystal lattice, leaving an electron trapped in a positively charged vacancy; the PL from F centres was not unambiguously observed up to now. On the other hand, broad-band laser-active F_2 and F_3^+ CCs, consisting of two electrons bound to two and three anion vacancies, respectively, have the peculiarity to possess almost overlapped absorption bands at about 450 nm, generally called M band [9]. They are stable at room temperature (RT) and under optical excitation in this spectral range, they simultaneously emit broad PL emission bands in the red (F_2) and green (F_3^+), peaking at about 540 and 680 nm, respectively [9,10].

LiF crystals and novel LiF thin-film radiation imaging detectors, based on the exploitation of the peculiar PL properties of the radiation-induced F_2 and F_3^+ defects, have been proposed for high-spatial resolution soft X-ray imaging [11], and successfully tested at different photon energies [12] from the extreme ultraviolet to hard X-rays.

Among the main advantages of the LiF radiation detectors, very high intrinsic spatial resolution, large field of view and wide dynamic range are worth being cited. Moreover, these solid-state radiation detectors are easy to handle, being not sensitive to ambient light, and no development process is needed after irradiation. In the last years, their use was successfully extended to advanced diagnostics of low-energy proton beams [13–15] produced by a linear accelerator (LINAC) under development at ENEA C.R. Frascati for radiobiology and radiotherapy.

On the other hand, use of low-penetrating elementary particles is particularly interesting in LiF crystals because it makes possible to

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prepare thin coloured layers with depths of a few micrometres and high concentration of defects located close to the surface of the crystalline material [16,17]; active optical waveguide fabrication was demonstrated by using He^+ ions [18].

A systematic investigation of the optical properties of CCs induced in LiF crystals and thin films by proton beams of nominal energies 3 and 7 MeV in the fluence range of 10^{11}–10^{15} protons/cm^2 is being performed [13]. After exposure to proton beams, the latent images stored in the LiF thin layers by local formation of active electronic defects can be read with a conventional optical fluorescence microscope. The recording of the transversal proton-beam fluence profiles on LiF were obtained by acquiring the visible PL image of the irradiated spots under blue-light pumping. In LiF films it was found that the spectrally integrated PL response as a function of the dose is independent on the selected beam energy [14]. It consists of a linear growth, which covers up to three order of magnitude within the investigated range, followed by saturation at highest values ($> \approx 10^5$ Gy); this behaviour can be described by a suitable defect formation model, which also allows for a two-dimensional dose-mapping reconstruction [15].

The PL response is ascribed to the simultaneous excitation of both kinds of optically active F_2 and F_3^+ CCs in the M absorption band. Despite of film low thickness, laser induced PL spectra are very effective to probe the stable formation of F_2 and F_3^+ defects in irradiated LiF thin layers. In this work, their distinctive contributions to the PL spectra, measured under laser pumping at 458 nm, were carefully analysed and reported as a function of dose for the first time, also to study differences in their behaviour at high doses.

2. Materials and methods

The samples were polycrystalline LiF thin films, about 1 μm thick, grown by thermal evaporation on glass substrates [8] kept at a constant temperature of 300 °C during the deposition process, which was performed in a vacuum chamber at a pressure below 1 mPa, at the Solid State Lasers 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. The substrates were mounted on a rotating sample holder in order to obtain a better uniformity.

The optical reflectance and transmittance spectra of one of these LiF films on glass substrate and of a twin bare glass substrate were measured at a UV–Vis–NIR Perkin-Elmer Lambda 900 spectrophotometer in the wavelength range from 190 nm to 1600 nm. After deriving the wavelength-dependent optical constants of the bare substrate with a fully analytical method [19], a best-fitting procedure relying on a non-ideal layer theoretical model [20] allowed estimating some physical and geometric parameters of the film from the measured spectra, besides the refractive index and extinction coefficient dispersions of its material.

Proton beams of nominal energies 3 and 7 MeV were used to irradiate the LiF films. They were produced by a LINAC (PL7 model by ACCSYS-HITACHI) working as the injector of the prototype of a medium-energy proton accelerator for protontherapy, named TOP-IMPLART [21], designed as a sequence of linear accelerating modules and under development at ENEA C.R. Frascati. The films were placed in air perpendicularly to the proton beams, at a distance of 10 mm from the exit of the machine beamline, consisting of a 50 μm thick kapton window. The average beam current was 1 μA in 60 μs-long pulses at a repetition rate of 50 Hz. The irradiation fluence covered the range of 10^{11}–10^{15} protons/cm^2 by varying the total number of pulses delivered to different LiF samples.

The PL spectra of the irradiated spots on LiF films were measured at RT by pumping in a continuous-wave regime with the 457.9 nm line of an Argon laser, which allows to simultaneously excite the Stokes-shifted green and red emissions of F_3^+ and F_2 CCs [10]. The PL signal was spectrally filtered by a monochromator and detected by means of a photomultiplier with lock-in technique. The emission spectra were acquired in the wavelength range between 480 nm and 800 nm in order to measure the spectral contributions of F_2 and F_3^+ defects in the visible; all the spectra were corrected for the instrumental calibration.

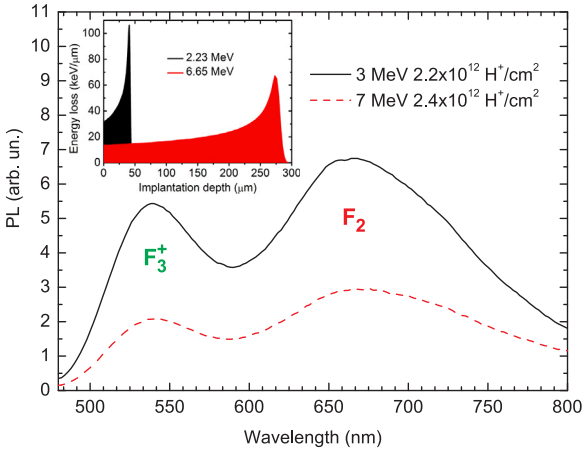

Fig. 1. Photoluminescence spectra of LiF films about 1 μm thick thermally evaporated on glass substrate and irradiated by 3 and 7 MeV proton beams at a fluence around 2.3×10^{12} protons/cm^2, measured at RT under laser pumping at 457.9 nm. Inset: SRIM simulation of the energy loss as a function of the proton implantation depth in LiF for beams of energy 2.23 and 6.65 MeV.

3. Results and discussion

Fig. 1 shows the laser-excited PL spectra of two LiF thin films, irradiated by proton beams of different nominal energies, 3 and 7 MeV, with similar fluence. They consist of two broad emission bands peaked at 540 nm and 680 nm and ascribed to F_3^+ and F_2 centres, respectively [9,10]. The PL intensity was found to be higher in the LiF thin film coloured with protons at lower energy, both for F_2 and F_3^+ PL bands [13]. This behaviour can be explained by simulations of proton energy loss in LiF, performed with SRIM software [22]. They demonstrate that the effective energies of protons impinging the LiF target, after crossing the 50 μm kapton window and air, are 2.23 and 6.65 MeV, with estimated implantation depths of about 45 and 300 μm, respectively. The inset in Fig. 1 reports the energy loss calculated by SRIM as a function of the implantation depth in LiF for the two proton beam energies. The linear energy transfer (LET) continuously increases with depth, reaching the maximum value about at the end of the implantation path; this maximum is called the Bragg peak and its position depends on both proton energy and material density [13,16,17,22]. For the considered energies, the LiF film thickness of about 1 μm is much lower than the estimated maximum proton implantation depth, so that the LET can be considered constant within the LiF layer (see inset in Fig. 1). The radiation-induced CCs are located in the film, within which only a small fraction of the total proton energy is released, the remaining being deposited in the glass substrate. Such a fraction decreases for increasing proton energy, so that it is lower for 7 MeV protons than for 3 MeV (see inset in Fig. 1). According to SRIM simulations in LiF crystal, the LET values at the entrance face of the material are 30.8 and 13.4 eV/nm for the proton energies of 2.23 and 6.65 MeV, respectively. In case of a LiF film whose mass density is lower than bulk, these LET values scale proportionally to the material packing density. Fig. 2 shows the LET values as a function of the proton energy in the range extending from 0.5 to 16 MeV as derived from SRIM simulation in LiF. At lower energies, its behaviour is strongly non-linear, and the target becomes progressively more “transparent” at higher particle velocities [16].

Fig. 3 shows the experimental reflectance and transmittance