Journal of Luminescence 170 (2016) 761–769

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Photoluminescence of colour centres in lithium fluoride thin films: From solid-state miniaturised light sources to novel radiation imaging detectors

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ARTICLE INFO

Article history:
Received 15 May 2015
Received in revised form
27 July 2015
Accepted 28 July 2015
Available online 11 August 2015

Keywords:
Colour centres
Photoluminescence
Thin films
X-ray imaging
Radiation effects

ABSTRACT

Luminescence properties of point defects in insulating materials are successfully used for solid state light sources and radiation detectors. Among them, colour centres in lithium fluoride, LiF, are well known for their application in tuneable lasers and dosimeters. Broad-band light-emitting F_2 and F_3^+ electronic defects, stable at room temperature, are produced in LiF crystals and films by different kinds of radiation. Under blue optical pumping in their overlapping absorption bands, the efficient photoluminescence spans over the green–red visible spectral range. Novel LiF thin-film radiation imaging detectors based on the exploitation of the peculiar spectral characteristics of F_2 and F_3^+ defects and of the optical properties and radiation sensitivity of the LiF material have been proposed and successfully tested for extreme ultraviolet radiation, soft and hard X-ray imaging, including micro-radiography of biological objects, even for *in vivo* samples. After exposure to X-rays, the latent images stored in the LiF thin layers by local formation of active defects are read with conventional and advanced optical fluorescence microscopes. Among the main advantages of the LiF thin-film imaging detectors, there are intrinsic very high spatial resolution, large field of view and wide dynamic range. Moreover, these solid state radiation detectors are easy to handle, as insensitive to ambient light, and no development process is needed. Recently their use has been extended to proton beam advanced diagnostics. In this paper, a short review of their properties, results and applications in X-ray biological imaging and proton dose-mapping is presented, underlying the great versatility and potentialities offered by LiF thin films, whose photoluminescence response can be improved through the choice of suitable substrates and growth conditions.

1. Introduction

Luminescence properties of point defects in insulating materials [1] are successfully used for solid state light sources and lasers [2] as well as radiation detectors [3]. Among them, radiation-induced colour centres (CCs) in lithium fluoride, LiF, [4] find applications in solid-state tuneable CC lasers [5,6], broad-band miniaturised light sources [6–8] and dosimeters [9,10]. Their spectral properties have been successfully exploited in novel, high spatial resolution, X-ray radiation imaging detectors, based on the optical reading of photoluminescence (PL) radiated from F_2 and F_3^+ aggregate electronic defects in LiF crystals and thin films [11–15].

These laser-active centres, consisting of two electrons bound to two and three adjacent anion vacancies, respectively, possess almost overlapping absorption bands peaked at ~450 nm, generally known as a whole as M band [4], and differently Stokes-shifted broad photoemission bands centred at 678 nm and 541 nm [16], respectively. Their spectral characteristics and high emission efficiencies [5], even at room temperature (RT), combined with the capability to grow good optical-quality LiF thin films on different substrates by thermal evaporation [7], make them suitable for the development of fully dielectric red-emitting (F_2) optical micro-cavities [17,18], as well as versatile high-spatial resolution radiation imaging detectors of enhanced sensitivity [15], where the atomic-scale radiation-induced defects are utilised as minimum luminescent units.

For almost 120 years, X-ray imaging played a major role in medical diagnostics and had an important impact on biological research. Accomplishing imaging in the extreme ultraviolet (EUV), soft and hard X-ray spectral ranges (photon energies from 20 eV to 60 keV), with high spatial resolution across a wide field of view, is considered a topical task nowadays [19]. In particular, it is of great interest the spectral region between the *K* shell X-ray absorption edges of carbon and oxygen, the (280–530) eV energy interval,

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http://dx.doi.org/10.1016/j.jlumin.2015.07.052
0022-2313/

known as the Water-Window, where water is much less absorbing than organic compounds, such as proteins and carbohydrates, containing carbon. Thus, X-ray micro-radiographies can be obtained of specimens containing water with a natural contrast [20], like for biological samples in life science.

Among the main peculiarities of the luminescent LiF-film solid-state radiation imaging detectors, noteworthy ones are their very high intrinsic spatial resolution and wide dynamic range. Moreover, being they insensitive to ambient light and no development process being needed, they are quite easy to handle. As a matter of fact, after X-ray exposure, the latent images stored in the LiF thin layers by the local formation of stable aggregate CCs are directly read with fluorescence optical microscopy techniques.

Lens-less soft X-ray microscopy of biological objects in absorption contrast [11], even of *in vivo* specimens [21], was successfully performed under vacuum with intense soft X-ray laser-driven plasma sources by using LiF crystals and thin films as fluorescent radiographic plates in contact mode. High-quality, well-contrasted soft X-ray micro-radiographies of biological samples and metallic meshes were obtained, across a large field of view (larger than 1 cm^2) with typical spatial resolution down to 250 nm, by using conventional and confocal laser fluorescence microscopy as reading techniques; resolution values down to 80 nm [22] were demonstrated in good optical-quality thermally-evaporated LiF films by scanning near-field optical microscopy.

Solid-state LiF thin-film radiation imaging detectors were tested also for X-ray energies up to about 10 keV [13], using compact X-ray tubes in different configurations, and with hard X-rays from a synchrotron white beam up to 60 keV [14]. Although the X-ray attenuation lengths at these energies are longer than the typical thickness of thin film (0.1–3 μm) radiation detectors, it is amazing to find that lens-less X-ray imaging at very high spatial resolution can be achieved within reasonable exposure times. By exploiting synchrotron source coherence and phase-contrast mechanisms [23], in-line coherent diffraction imaging (CDI) experiments with a white beam were successfully reported for the first time [14] at high X-ray energies also on LiF films. Similar phase-contrast imaging experiments were also performed on LiF crystals and thin films by means of monochromatic coherent radiation at very short wavelengths in a soft X-ray free-electron laser facility [24].

Recently, large-area polycrystalline LiF thin films of correct stoichiometry were grown by thermal evaporation on a glass disc-type plate (diameter 80 mm) for accurate X-ray two-dimensional (2D) dose-imaging detectors [25]; they are stable at RT and can be re-used after annealing at 400 °C for an half-hour. Although their sensitivity at 8 keV was found to be less than that of commercially available Ag-activated phosphate glass slabs of higher thickness, they could be suitable for X-ray radiation diagnostics and clinical radiotherapy.

LiF thin-film radiation detectors allow for great versatility, since the material is sensitive to almost any kind of radiation, including charged particles. Recently, their use has been proposed and successfully extended to low-energy proton beam advanced diagnostics [26]. Accurate accumulated 2D dose distribution with high spatial resolution over large areas and a wide dynamic range, covering at least three orders of magnitude of doses, together with non destructive optical fluorescence readout, were successfully demonstrated for the first time by using low-energy proton beams, with the main challenge of application in clinical adrotherapy.

Thermally evaporated, optically transparent LiF thin films are compatible with several kinds of substrates [7], a peculiarity which increases the versatility of LiF-based radiation imaging detectors, so that they can be integrated in different experimental apparatus and configurations. The broad-band PL response and the emission intensities of CCs hosted in the LiF film matrix can be directionally and spectrally controlled through the appropriate choice of reflecting substrates [27,28] and multi-layer designs [15,17,28]; moreover, the radiation sensitivity of polycrystalline LiF films could be further enhanced by tailoring their micro-structural properties through control of their growing conditions [29].

In this paper, a short review of the properties of such detectors, results and applications, with some emphasis on X-ray biological imaging and proton dose-mapping, is presented, underlying the great versatility and potentialities offered by LiF thin films.

2. Optical spectroscopy of F_2 and F_3^+ point defects in irradiated LiF films

LiF possesses the largest band gap, greater than 14 eV, of any solid in natural form; its high optical transparency is particularly suitable for the investigation of lattice defect spectral features by optical spectroscopy and advanced fluorescence microscopy techniques. Unlike other alkali halides, CCs can be created in LiF only by ionising radiation. The radiation-induced point defects mainly consist of primary F centres (an electron bound to a fluorine vacancy) and aggregate F_2 and F_3^+ electronic defects, whose absolute and relative concentrations depend on the specific radiation type and irradiation conditions.

The main spectral characteristics of F_2 and F_3^+ point defects in LiF [4,16], i.e. broad optical absorption and Stokes-shifted broad PL bands, are typical of CCs in alkali halides and quite well known from the literature [30]. With respect to other alkali halides, a peculiarity of radiation effects in LiF is the stability of these point defects even at RT and the formation of high densities of F_3^+ centres, together with F and F_2 defects [4].

Laser-induced optical-fluorescence scanning microscopies in far-field confocal configurations [31] as well as in near-field [32], were successfully used to gather information about radiation effects and 2D and 3D mapping of F_2 and F_3^+ performed in the framework of research and development activities about micro- and nano-fabrication techniques for active optically confined structures, based on LiF thin films, for the realisation of miniaturised broad-band optical emitters, amplifiers and lasers operating in the visible spectral range [7].

In principle, the intrinsic spatial resolution of LiF is limited only by the size of point defects, which is at atomic scale. This means that such a resolution could be below a few nanometres [33], since the lattice constant of LiF is only 0.2013 nm, the shortest of any alkali halide crystal. In practise, the actual spatial resolution is essentially limited by the microscope and technique utilised for PL detection in the optical readout process.

The large Stokes shift between optical absorption and PL peaks of F_2 and F_3^+ defects is due to the equilibrium nuclear coordinates, which are significantly different in the optical excited state than they are in the fundamental one [30]; this fact depends on the specific defect configuration and host matrix. Due to the strong electron–phonon coupling to the lattice, the absorption and emission bands are homogeneously broadened. The spectral features of the F absorption band, peaked at 248 nm in LiF crystals, are well known from the literature [30]. Due to the full overlapping of the F_2 and F_3^+ absorption bands, the situation is more complex for these two kinds of point defects. Indeed, different values of absorption peak positions and band widths are found in the literature. Reference values are reported in Table 1 according to [16]; the corresponding F_2 and F_3^+ absorption and emission bands, sketched as normalised Gaussians, are shown in Fig. 1.

So far no luminescence unambiguously originating from the primary F centre in LiF has been detected under optical pumping. On the contrary, laser induced PL spectra are very effective to probe the stable formation of F_2 and F_3^+ defects in irradiated LiF films, due to the simultaneous excitation of both kinds of optically