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Versatile lithium fluoride thin-film solid-state detectors for nanoscale radiation imaging

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Summary. — Point defects in insulating materials are successfully used for radiation detectors. Among them, colour centres in lithium fluoride (LiF) are well known for application in dosimeters and in light-emitting devices and lasers. LiF thin-film detectors for extreme ultraviolet radiation, soft and hard X-rays, based on photoluminescence from aggregate electronic defects, are currently under development for imaging application with laboratory radiation sources, *e.g.* laser-driven plasma sources and conventional X-ray tubes, as well as large-scale facilities, *e.g.* synchrotrons and free-electron lasers. Among the peculiarities of these detectors, noteworthy ones are the very high intrinsic spatial resolution ($< 100\,\mathrm{nm}$) across a large field of view ($> 1\,\mathrm{cm}^2$) and the wide dynamic range. Moreover, they are insensitive to ambient light and no development process is needed. The latent images stored in the LiF thin layer can be read with fluorescence optical microscopy techniques. These detectors prove to be highly versatile, as LiF is sensitive to almost any kind of radiation, including charged particles and neutrons, and can be grown in the form of polycrystalline thin films, whose photoluminescence response can be tailored trough the control of the growth conditions.

PACS 42.79.Pw – Imaging detectors and sensors.
PACS 61.72.jn – Color centers.
PACS 61.80.-x – Physical radiation effects, radiation damage.
PACS 78.55.Fv – Solid alkali halides.

1. – Introduction

Point defects—impurity ions, colour centres (CCs), etc.—in insulating materials [1,2] are successfully used for radiation detectors [3]. Although impressive advances in

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electronic design and direct-detection materials continue to drive progress in the development of radiation imaging detectors, the role of luminescent materials is still of great relevance in this field [4]. Among them, LiF crystals and films containing CCs are well known for application in dosimeters [5], in miniaturised light-emitting devices [6] and in tuneable solid-state lasers [7]. Electronic defects are produced in LiF by different kinds of ionising radiation, such as charged particles, as well as energetic photons, like X-rays [8] and γ-rays [9]. Broad-band visible-emitting aggregate CCs are efficiently created in LiF thin films by low-penetrating particles [6]. At ENEA C. R. Frascati, novel LiF imaging detectors for extreme ultraviolet (EUV) radiation and soft X-rays (SXRs), based on visible photoluminescence (PL) from optically active CCs produced in a very thin surface layer of LiF crystals and films, were lately proposed [10, 11] and investigated in EUV lithography and SXR direct writing [12] for recording light-emitting micro- and nano-patterns. Lens-less X-ray microscopy experiments in absorption contrast of biological samples [11], even *in vivo* specimens [13], and of very thin materials and devices that are partially transparent to soft X-rays [14], were successfully performed under vacuum with intense SXR laser-driven plasma sources in contact mode. Lens-less phase-contrast imaging of geometric masks was used for the characterisation of monochromatic X-ray laser beams in the EUV—see [15] for an overview. High-quality, well-contrasted micro-radiographies of biological samples and metallic meshes were obtained across a large field of view ($> 1\,\mathrm{cm}^2$) with typical spatial resolution down to 250 nm by using confocal laser fluorescence microscopy as reading technique; resolutions values down to 80 nm [16] were demonstrated with scanning near-field optical microscopy (SNOM).

Solid-state LiF imaging detectors based on polished single crystals and transparent polycrystalline thin films thermally evaporated on several kinds of substrates were tested also at higher X-ray energies, up to 10 keV [17], using compact X-ray tubes in different configurations [18], and with hard X-rays from a synchrotron white beam up to 60 keV [19]. Although the X-ray attenuation lengths at these energies are higher than the typical thickness (200–2000 nm) of the used LiF thin film detectors, lens-less X-ray imaging at very high spatial resolution can be performed with reasonable exposure times. LiF thin films, which are compatible with several substrates [6], increase the versatility and easiness of use of radiation imaging detectors, which can be integrated in different experimental apparatus' and configurations. Moreover their PL response, which is directly related to radiation sensitivity, can be enhanced trough the appropriate choice of substrates and multi-layer designs [20], and by tailoring the micro-structural properties of polycrystalline LiF films through the control of the growth conditions [21].

2. – LiF film radiation imaging detectors based on PL from CCs

LiF has several peculiar material characteristics. In spite of its typical ionic structure, the crystal is resistant to moisture and is relatively hard. It is characterised by a face-centred cubic structure, with the nearest-neighbour distance equal to 0.2013 nm, which is the shortest among alkali halides. It is transparent in the wavelength range from 120 nm to 7 μm and is sensitive to almost any kind of ionising radiation. CCs can be permanently produced in LiF; they efficiently emit light in the visible and near infrared spectral ranges, even at room temperature, under selective optical excitation. Some CCs, among them the F_2 and F_3^+ defects—consisting of two electrons bound to two and three anion vacancies, respectively—are stable, with broad absorption and emission bands in the visible spectral range. In particular, these two kinds of aggregate point defects possess almost mutually overlapping optical absorption bands located at about 450 nm, known as the M-band [9],

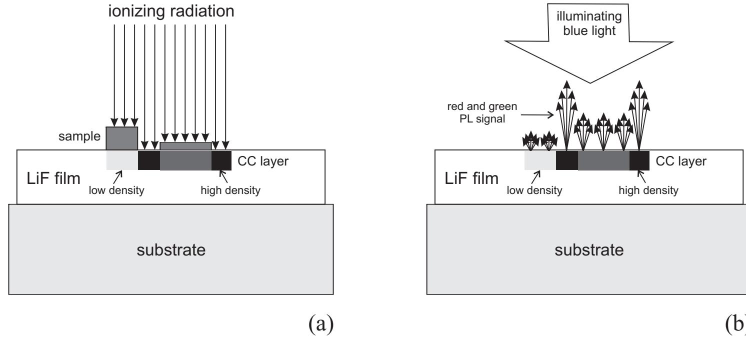

Fig. 1. – Scheme of LiF plate operation as imaging detector in a X-ray contact microscopy experiment. (a) Contact X-ray imaging configuration and CC formation in a LiF film detector during the exposure process. (b) Visible PL of CCs in the LiF film detector under blue-light illumination during the reading process.

and exhibit intense and broad Stokes-shifted PL bands, peaked in the red (F_2) and green (F_3^+) spectral ranges. Polycrystalline LiF films can be grown by thermal evaporation under vacuum on different materials; their thickness can be controlled in a wide range extending from a few hundred nanometers to a few microns [6]. They offer the advantage of compatibility with amorphous and crystalline substrates, the possibility to grow multi-layered structures of different materials in order to functionalise their emission properties, and the control of dopant concentration by versatile preparation techniques [6].

2·1. *Principle of operation.* – The use of LiF in radiation imaging is depicted in fig. 1 for contact-mode operation, which is the simplest approach to X-ray microscopy [22], as it does not need any optical system for X-ray manipulation. The investigated samples are placed in close contact with the LiF detector surface and are exposed to X-rays, see fig. 1(a); the irradiation produces a layer of stable CCs, whose local concentration is proportional to the absorbed dose, which in turn depends on the transparency of the sample. More absorbing parts of the specimen correspond to lower CC densities in the colored layer, while less absorbing parts induce higher CC densities. After exposure, the investigated sample is removed and the latent image stored in the LiF film is read by illuminating it with blue light and detecting the red and green PL emitted by F_2 and F_3^+ CCs, see fig. 1(b). The optical readout process of LiF plates can be directly performed by means of a conventional optical fluorescence microscope, which has to be equipped with a blue-light pump, such as a filtered lamp or a blue LED or a blue laser, spectrally centered around the peak wavelength of the M-band to simultaneously excite F_2 and F_3^+ defects.

LiF-based imaging detectors can be exposed to ambient light before and after irradiation without any problem; they need no development procedure, and can preserve images for a very long time—several years or even more. PL detection as reading optical process represents a dramatic breakthrough to direct radiation imaging. The high quantum efficiency [7] of broad red and green photoemission bands from F_2 and F_3^+ defects, when simultaneously excited, allow for the use of optical fluorescence microscopy as a fast and low-cost reading technique. The PL signal readout process of the LiF-based imaging detectors is particularly simple and efficient. Moreover, with proper laser excitation sources and time-resolved detection systems, PL sensitivity can become virtually unlimited: under suitable conditions, even a single luminescent CC in the sample can be in principle detected.

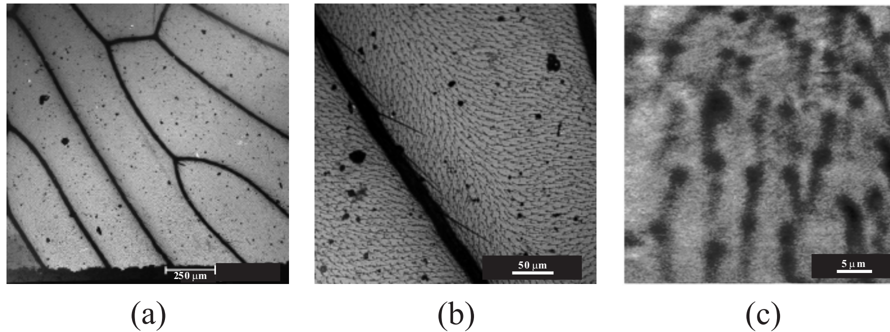

Fig. 2. – (a,b) Confocal fluorescence image of a X-ray micro-radiography of a mosquito (*Diptera*) wing stored in a thin LiF film (Si substrate) at two different magnification levels. (c) SNOM fluorescence image of a detail of the wing.

Among the main features of a LiF-based detector, let us also cite its large field of view and wide dynamic range combined with intrinsic high spatial resolution, which is in principle limited only by the point-defect size, that is, at the atomic scale [23]. In practice, the spatial resolution is essentially limited by the reading-device optics and by the technique utilised for PL detection during the reading process.

2˙2. *Some peculiarities of radiation detectors based on PL from CCs in LiF*. – LiF thin films allow to directly produce thin coloured layers also when deep-penetration energetic radiation is used; this is practically accomplished by limiting the coloured layer through the choice of a suitable film thickness.

LiF films can be grown on extended areas—up to several cm^2—hence the dimensions of the sensitive area can be large. The consequent wide field of view is also allowed by the optical readout process of the LiF detector. By changing the observation parameters of the microscope, images at different magnification levels can be easily read, as shown in fig. 2. In it, the micro-radiography of a mosquito (*Diptera*) wing, stored in a thin LiF film thermally evaporated on a Si substrate [11], is shown. The specimen, put in close contact with the LiF film, was irradiated under vacuum with SXRs emitted by a laser-plasma source developed at ENEA Excimer Laboratory in Frascati. The X-ray micro-radiography was read with a confocal laser scanning microscope (CLSM) in fluorescence mode at two different magnification levels, see fig. 2(a) and (b). Figure 2(c) is a SNOM fluorescence image of a detail where wing hairs are well defined. It should be pointed out that it was possible to acquire the SNOM image a long time—a few months—after the micrograph had been recorded thanks to the good stability of F_2 and F_3^+ centres at room temperature. Figure 2 demonstrates the great versatility of the LiF-film detector, able to store a rich level of detail that is available at the desired scale and field of view by using suitable instruments.

2˙3. *Increased radiation sensitivity of LiF films*. – The main characteristics of the as deposited LiF films—including surface morphology, degree of crystallinity, preferred orientation, compactness, etc.—strongly depend on the nature of the substrate and the growth conditions [6], in particular on the substrate temperature and the film total thickness. The formation efficiency of primary F centres and visible-emitting F_2 and F_3^+ aggregate defects is usually higher in polycrystalline LiF films than in single crystals and is influenced by the peculiar structure of LiF films [21]. The surface-to-volume ratio

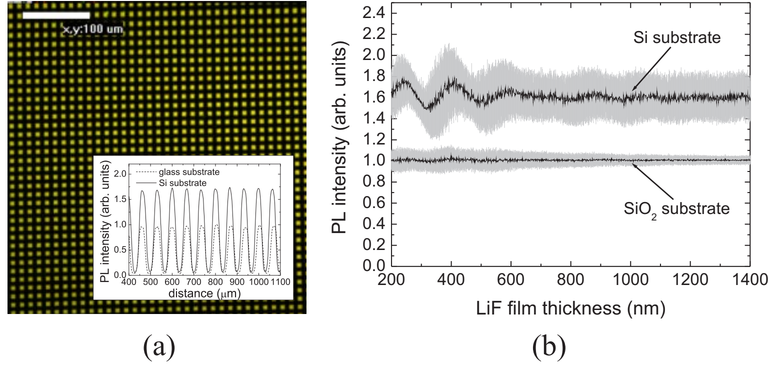

Fig. 3. – (a) CLSM fluorescence image of the X-ray contact micro-radiography of a nickel mesh on LiF film (thickness of about $1\,\mu$m) on Si substrate. In the inset, PL intensity profiles along a line of it that intercepts the bright dot centres, and an analogous profile obtained in a similar manner for the case of a glass substrate. (b) Theoretical simulation of the PL intensity of a LiF film over a Si and SiO_2 substrate *vs.* film thickness—the grey bands represent the uncertainties deduced with a Montecarlo approach (more details in the text).

and the film compactness are thought to play a relevant role because they establish the density of the grain boundaries, which act as a source of vacancies during the CC formation and stabilisation processes. As a consequence, the sensitivity to X-rays of LiF-film–based detectors is higher than of single crystals [24] and a further enhancement, up to an order of magnitude, is achieved by choosing a suitable substrate material and selecting a proper film thickness in the layered imaging detector, that is, by taking into account light confinement effects [20, 25]. It is also possible to realise vertical multilayer structures in order to increase the collection efficiency of the PL signal emitted by CCs during the reading process [26] and, consequently, the sensitivity of the LiF-film–based detectors. If needed, a cover layer can be deposited on the LiF film in order to protect it from powder or other potentially dangerous agents, such as water and organic liquids of living cells.

Perhaps the most elementary example of light-confining structure consists of a distribution of CCs within a LiF film over a reflective substrate, whose purpose if to redirect the otherwise lost fraction of PL towards the detection system (assumed to be in the LiF film side). In the case of F_2 and F_3^+ CCs in a LiF film, a Si substrate provides a sensible increase of performances as compared to a SiO_2 substrate. This fact has been demonstrated by comparing the PL intensities coming from two LiF thin films grown in the same evaporation run on a glass and a Si substrate, respectively, after X-ray irradiation under the same conditions with a laser-plasma source developed at Tor Vergata University in Rome. During irradiation, identical metallic meshes were placed in contact with the LiF film surface. The confocal fluorescence image stored in the LiF film detector on Si is shown in fig. 3(a), where the dark areas correspond to the nickel mesh wires—they are opaque to the incident X-rays. In the inset, the PL spatial profiles are shown for the colored LiF films on both the substrates. The integrated PL signal measured on the LiF film on Si is higher than the one collected from the LiF film on glass and the ratio of their intensities is 1.76 ± 0.11.

These experimental results satisfactorily agree with theoretical predictions about the PL intensity radiated from an entirely coloured LiF film placed over SiO_2 and Si substrates. By using our fully analytical approach [26], the outcoupled PL could be theoret-

TABLE I. – *Schematic comparison of LiF-based detectors with respect to the standard ones, excluding electronic devices.*

	LiF-based imaging detectors	Photographic films	Photoresist	Phosphor-based imaging plates
Soft X-rays	+	+	+	−
Hard X-rays	+	+	−	++ (linear response)
Reading technique	Optical (PL)	Optical (OD)	AFM	Optical (OSL)
No development	+	−	−	+
No light sensitivity	+	−	+	−
Image stability	+	+	+	− (fading)
Spatial resolution	++	+	++	+
Dynamic range	+	+	−	+
Wide field	+	+	−	+

ically estimated as a function of the film thickness; the results are shown in fig. 3(b) for both the substrates. To evaluate total PL, the PL spectral distributions of F_2 and F_3^+ centres [6] and the presence of red (562–1000 nm) and green (499–529 nm) bandpass filters in front of the NA = 0.13 CLSM objective were duly taken into account. Because some of the simulation parameters are very critical, such as refractive indices and the exact LiF thickness, we associated uncertainties to them and adopted a Montecarlo approach: the simulation parameters were made randomly and independently vary 100 times within assigned limits and PL integrated intensity *vs.* thickness curves were calculated at each of these 100 iterations. The average curves and their standard deviations, shown as grey confidence bands in fig. 3(b), were eventually evaluated from the set of 100 stored curves for each substrate material. The complex refractive-index dispersion curves to which the random uncertainties were applied were literature ones [27]. The limits of the applied random uncertainties were: ±0.05 for the refractive indices, ±0.001 for the extinction coefficients, ±10% for the LiF thickness (however never smaller than 10 nm or larger than 50 nm). From the curves shown in fig. 3(b), the foreseen PL intensities corresponding to a LiF thickness of 1 μm are (1.60 ± 0.22) a.u. for the Si substrate and (1.00 ± 0.05) a.u. for the SiO_2 substrate. Therefore, the PL intensity coming from the Si-substrate sample is 1.60 ± 0.30 times higher than that coming from the SiO_2-substrate sample. This result well agrees with the experimentally found ratio.

3. – Comparison of LiF films with other solid-state detectors for imaging applications

The LiF-based detectors are easy to handle, as they are insensitive to ambient light, contrarily to widely used X-ray photographic films. Still more practical, they do not need any development process after exposure to X-rays, contrarily to other imaging X-ray detectors, like photographic films and Poly-Metyl-MetAchrilate (PMMA) photoresist ones. The intrinsic LiF radiation-imaging spatial resolution is in principle limited only by the involved point-defect size, that is, at the atomic scale. High spatial-resolution polymeric photoresists have a very poor dynamic range; moreover, after irradiation, they need chemical development that can strongly influence the quality of the image, stored as a relief map, and allow for a very limited field of view because the reading process

is based on an atomic force microscope. Standard imaging detectors—like photographic films, image plates and CCDs—have a low spatial resolution limited by the size of the grains or pixels, respectively, and they do not allow to obtain images with high spatial resolution by using lens-less contact X-ray microscopy. This limitation forced X-ray imaging technology to adopt very complicated and sophisticated irradiation techniques, not easy to use in research laboratories for life sciences. A LiF-based detector can store the latent image of the sample for a very long time—several years or even longer; the X-ray micro-radiography can be read many times, contrarily to phosphor imaging-plates that are currently used at the highest X-ray energies and suffer from fading effects. It is important to state that the optically stimulated luminescence (OSL) processes, which are at the basis of these widely used X-ray detectors, differ from the PL processes utilised in our LiF-based detectors. OSL relies on the optically induced transitions of electronic charge between radiation-induced defect centres [28], while for PL from CCs the electronic transitions are localised around the same defects, as described by the basic four-energy levels scheme [2]. Table I provides a schematic comparison among the mentioned detectors; the plus and minus signs stand for positive and negative features, respectively.

4. – Conclusions

The peculiarities of versatile solid-state LiF film radiation-imaging detectors, based on PL from CCs and characterised by intrinsic high spatial resolution, have been described and compared with those of common X-ray detectors. The advantages offered by the use of these thin films, with emphasis on the enhanced radiation sensitivity offered by optimising their optical design to increase the effective PL collection efficiency, have been highlighted. Control of the polycrystalline properties for the stabilisation of radiation-induced defects can be further exploited to increase the PL response, in order to reduce exposure times in X-ray imaging experiments, even for *in vivo* biological specimens. Further applications to charged particles and neutron imaging can be foreseen.

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