POINT DEFECTS IN LITHIUM FLUORIDE FILMS INDUCED BY GAMMA IRRADIATION

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Pure and doped lithium fluoride (LiF) crystals are well-known dosimeter materials. In this work we report the preliminary results about a careful optical characterisation of polycrystalline LiF films thermally evaporated on fused silica substrates and gamma-irradiated at several doses up to 10^6 Gy in air. Gamma irradiation of LiF films gives rise to stable formation of primary and aggregate defects. Among them, F centres give rise to the absorption band peaked at 245 nm, while F_2 and F_3^+ centres are responsible for the absorption in the blue region and for stable and intense green (F_3^+) and red (F_2) photoluminescence at room temperature. Photoluminescence spectra were measured with both a commercial and a laboratory apparatus. A simplified set-up for optically stimulated luminescence reading was tested. The results are encouraging to propose LiF film on fused silica substrate as dosimeter for gamma irradiation.

1 Introduction

Many radiation-sensitive thermoluminescent (TL) and colour-forming solid-state dielectric and transparent compounds are utilised for radiation dosimetry [1]. Among them Lithium Fluoride (LiF) is one of the most used and investigated in different forms. Pure [2] and doped [3] LiF crystals are well-known dosimeter materials. Recently new radiation detectors based on dispersion of microcrystalline LiF in polymer matrix for gamma and electrons high-dose dosimetry have been proposed [4], as well polycrystalline LiF films, directly grown on silicon substrate, as nuclear sensors for neutrons [5].

The great interest for new radiation detectors based on this material prompted us to a careful investigation of the optical properties of gamma irradiated LiF films. In this paper, we report preliminary results of the optical characterisation of gamma-irradiated polycrystalline LiF films thermally evaporated on fused silica substrates. Gamma irradiation of LiF gives rise to stable formation of primary and aggregate electronic defects, known as colour centres (CCs), consisting in anionic lattice vacancies occupied by electrons [6]. Their formation induces discrete optical absorption bands, generally located in the visible spectral region. Among alkali halides, LiF films are interesting for several applications [7], because this material is practically not-hygroscopic and it can host point defects that are stable at room temperature (RT). Several of them are optically active CCs emitting in a broad wavelength range in the visible and near infrared [8]. The high efficiencies of green and red photoemissions from the F_3^+ and F_2 defects (two electrons bound to three and two adiacent anion vacancies, respectively), when excited in their almost overlapping absorption bands located around 450 nm allows to utilize Optically Stimulated Luminescence (OSL) as useful method of dosimetry for this inorganic crystalline material [9].

2 Experimental

Polycrystalline LiF films, 3 μm thick, have been deposited by thermal evaporation on radiation hard fused silica substrates, kept at 250°C during the growth, in the Solid State Laboratory of ENEA Frascati. Their structural, morphological and optical properties are strongly dependent on the nature of the substrate and on the main deposition parameters, i.e. substrate temperature, thickness and evaporation rate [7]. The films have been exposed to gamma radiation from a ^{60}Co source at the *Calliope* plant of ENEA-Casaccia (Rome) [10] at several doses ranging from 10^3 to 10^6 Gy in air, with the same dose-rate of 2.4 kGy/s.

Optical reflectance and transmittance spectra of the films before and after irradiation have been measured at normal incidence with a Perkin-Elmer λ-19 spectrophotometer in the spectral range 190 - 850 nm.

Photoluminescence spectra of F_2 and F_3^+ centres were measured with both a commercial Jobin Yvon Fluorolog-3 spectrofluorimeter adopting a front-face detecting geometry, and a laboratory set-up, where the luminescence has been excited by the 458 nm line of an Argon laser, spectrally analysed by a monochromator and detected by a photomultiplier with a lock-in technique.

A simplified OSL reading set-up has been arranged to measure the integrated red photo-emitted light from LiF films irradiated at different doses. The excitation source was a light emitting diode (LED) King Bright 53 MBD, whose broad emission (Fig.1), peaked at 440 nm, overlaps quite well the F_2 and F_3^+ centres absorption bands as known from the literature [11] and outlined in Fig. 1 as normalised gaussian bands. The emitted red light was filtered by an open-slit monochromator coupled with a glass band-pass filter Shott RG630.

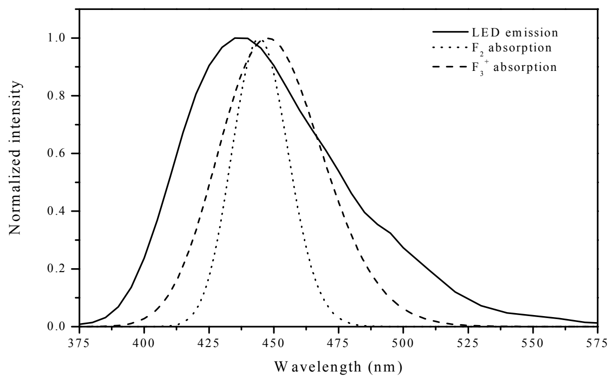

Figure 1. Emission spectrum (solid) of the LED King Bright 53 MBD used as excitation source in the simplified OSL set-up superimposed to the F_2 (dotted) and F_3^+ (dashed) centres absorption bands as known from the literature and outlined as normalised gaussian bands.

3 Results and discussion

Gamma irradiation of LiF induces the stable formation of primary and aggregate CCs, which generally coexist with often overlapping absorption bands. Among them, the F centres gives rise to an absorption band peaked at about 245 nm; the F_2 and F_3^+ centres are responsible for the so called M absorption band at about 450 nm [6]. Their contributions are clearly distinguishable by comparing the transmittance spectra of a LiF film before and after $1.16*10^5$ Gy of gamma irradiation, see Fig. 2. These two main absorption bands are superimposed to the film interference pattern. The transmittance spectra of the bare silica substrate before and after gamma irradiation at the same dose are also reported. Up to now, no luminescence originating unambiguously from the F centre in LiF has been detected. On the other hand the F_2 and F_3^+ centres are responsible for stable and intense green (F_3^+) and red (F_2) photoluminescence at RT when excited in a broad wavelength range around 450 nm, as measured also in thin films irradiated by low-energy electron beams [12]. A typical RT photoluminescence spectrum excited with the 458 nm line of an Argon laser is shown in Fig. 3 for the gamma coloured LiF film of Fig. 2. After instrumental response calibration, it has been resolved into the sum of two gaussian bands ascribed to F_2 and F_3^+ defects with peaks and half-widths in good agreement with the literature [11].

A similar photoemission spectrum of the same irradiated LiF film has been obtained by a commercial spectrofluorometer, as shown in Fig. 4.

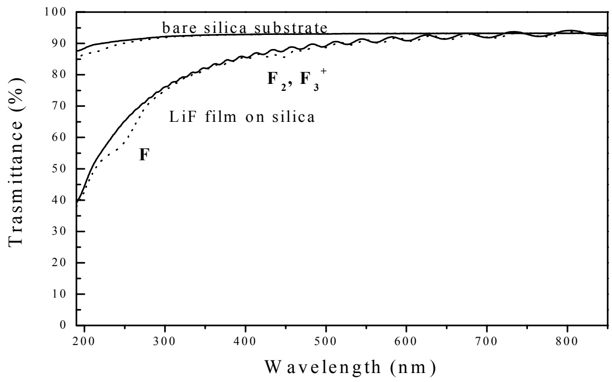

Figure 2. RT transmittance spectra at normal incidence of a 3 μm thick LiF film thermally evaporated on a silica substrate before (solid) and after (dotted) gamma irradiation with a dose of 1.16*10^5 Gy. The transmittance spectra of the bare silica substrate before (solid) and after (dotted) gamma irradiation at the same dose are reported for comparison.

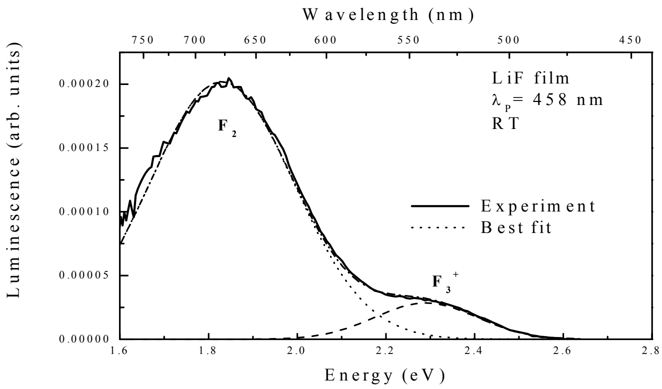

Figure 3. RT photoluminescence spectrum excited with the 458 nm line of an Argon laser of the gamma coloured LiF film, whose transmittance spectrum is shown in Fig. 2.

A similar photoemission spectrum of the same irradiated LiF film has been obtained by a commercial spectrofluorometer, as shown in Fig. 4. The excitation wavelength of 458 nm was provided by a xenon lamp filtered by a monochromator. The broad visible emission bands ascribed to F_2 and F_3^+ defects are again observable, although the ratio of their intensities is different from the one of Fig. 3. The complex optical behaviour of the F_3^+ centres with respect to the F_2 ones should be taken into account for the comprehension of the observed results.

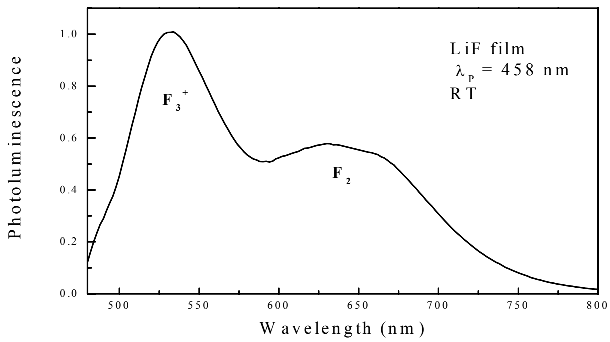

Figure 4. RT photoluminescence spectrum excited at the wavelength of 458 nm of the gamma coloured LiF film of Fig. 2 as measured by a commercial spectrofluorometer.

As a matter of fact, the ratio between the emission intensities of F_3^+ and F_2 defects depends not only on the defect concentrations, but also on the pumping intensity. Indeed, under continuous optical pumping, the F_3^+ luminescence increases sub-linearly as a function of the exciting power due to the presence of a metastable state, which strongly influences the optical behaviour of this defect [13]. As a consequence an appreciable quenching of the F_3^+ luminescence is observed even at low pumping power densities.

Figure 5 shows the luminescence signal of 4 specimens irradiated at different doses, ranging from 10^3 to 10^6 Gy, measured with the simplified OSL set-up. This set-up exhibits a superior signal/noise ratio (also reported in figure): no signal was detected for the sample irradiated at 10^3 Gy with the other considered equipments. The trend of the signal with the dose results sub-linear. The accurate spectrophotometric characterisation of the not-irradiated [14], and the two more irradiated [15] specimens allows to estimate the defect concentrations, showing that the lack of a linear response at the highest doses seems due to a reduction in the active defects formation mechanisms rather than to concentration quenching phenomena. Further investigations are under way to exploit these aspects.

4 Conclusions

Polycrystalline LiF thin films, only 3 µm thick, thermally evaporated on fused silica substrates have been optically characterised before and after gamma irradiation in the 10^3 - 10^6 Gy dose range. Gamma irradiation of LiF films gives rise to the stable formation of primary F centres and aggregate F_2 and F_3^+ centres, which emit efficient red and green photoluminescence, respectively. Their visible emission spectra have been measured at RT by different equipments. The one exhibiting the best signal to noise ratio is a simplified luminescence set-up where the light pumping is performed with a blue LED. The trend of luminescence versus absorbed doses results sub-linear; the film optical characterisation indicates at high doses a reduction in the active defects formation rather than a concentration quenching phenomena. The sensitivity of this simplified set-up will be improved in the next future in order to extend the readout to lower doses.

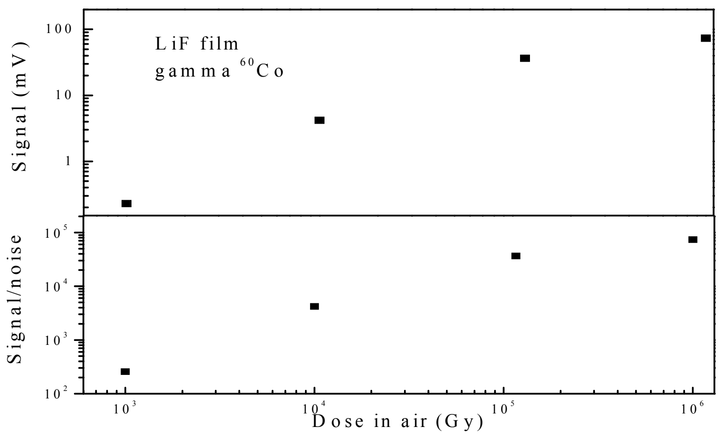

Figure 5. Top: red photoluminescence signal measured by the simplified luminescence set-up for LiF films coloured at different doses; the error is smaller than the symbol. Bottom: signal to noise ratio.

Unlike TL, OSL at RT does not anneal the luminescent defects, and the non-destructive readout by light can be used for archival dosimetry and imaging applications. The thin film geometry supplies either single integrated dose readings or two-dimensional radiographic images. The preliminary results are encouraging to consider LiF films as sensors in compact, cheap and versatile radiation detectors.

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