Visible photoluminescence in coloured Lithium Fluoride under ultra-violet continuous wave excitation

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Abstract. The γ-coloured Lithium Fluoride crystals visible fluorescence at room temperature was measured under excitation with ultra-violet continuous wave light at λ = 244 nm from a frequency-doubled Ar⁺-ion laser. The excitation wavelength lies close to the peak of the F-centre absorption band for LiF, and the visible luminescence spectrum consists of two broad emission bands, assigned to F⁺ and F₂ centres in LiF. The luminescence spectrum changes in a short time after start of illumination. The main effect of 244 nm laser illumination is the observed change in the F₂ emission band intensity, which is strongly and permanently bleached by the CW UV light at 244 nm as soon as it illuminates the crystal. The time evolution of the fluorescence signals can be measured, and the corresponding curves were fitted by a single exponential decay, resulting in characteristic time constants of ≈ 9 s and ≈ 30 s for the F₂ and F⁺ bands, respectively. The reported effects support previous work about UV laser illumination in the F-band absorption peak as an effective method to control the ratio of F₂ to F⁺ centres in LiF, due to permanent bleaching of the former ones.

1. Introduction

Lithium Fluoride presents a few characteristics that differ from other alkali halides, since, e.g., it is almost non hygroscopic and crystals are very hard to cleave. Additive colouration of LiF crystals is not effective; however, it is possible to produce colour centres by irradiation with X-rays, γ-rays, electrons or ionized particles beams and even by means of high power laser pulses. Many colour centre absorption bands have been observed in coloured LiF crystals, and several of them were associated to F-centres and F-aggregate centres [1].

The F-centre in LiF presents an absorption band in the ultra violet (UV) spectral region, centred at 248 nm (5.0 eV) when measured at room temperature (RT). One of the most intriguing optical characteristics of coloured LiF is that the F-centre emission band has not yet been assigned. From Mollwo-Ivey Law, the emission band should lie at around (≈ 900 – 910 nm) [2]. Some experiments, which used direct pulsed laser pumping in the F-band at 248 nm, found an
emission band, centred at 910 nm [3], which is superimposed to that assigned to the $F_2^+$ centre emission.

Photoluminescence in LiF has been studied by exciting through conventional broad-band c.w. (continuous wave) sources, followed by filters or monochromators, and the results usually show the interdependence of $F_2$ and $F_3^+$ luminescence bands. Some experiments with UV light (248, 315 nm) pointed to $F_2$ and $F_3^+$ emission bands. However, such first experiments were performed with low fluence light, and their results mainly show differences in emission spectra related to the crystal growth and irradiation techniques [4]. In any case, no evidence of the permanent bleaching of these centres has been observed. In fact, the regenerative optical pumping cycle of $F_2$ and $F_3^+$ centres is important for their use in colour centre lasers.

Recently, due to studies of waveguides and optical gain in LiF crystals and films [5, 6], there has been a renewed interest in the optical emission properties of LiF. Grating assisted laser emission using femtosecond pulses to record the grating structures in LiF crystals were also reported [7, 8]. Low power UV c.w. laser light was also used to record submicrometric patterns on $\gamma$- and soft X-rays coloured crystals and films [9, 10, 11, 12]. In those papers, the authors also observed a permanent bleaching of $F_2$ centre emission in contrast to that of $F_3^+$ centres as a consequence of the UV illumination, which can lead to laser action in the green region of the spectrum.

2. Experimental details

The LiF crystals used in the experiments were grown and coloured by $\gamma$-rays at the Institute of Molecular and Atomic Physics, Minsk (Belarus); after irradiation, their colour ranges from light yellow to dark red, depending on the dose received ($\approx 10^6 - 10^7$ R).

Photoluminescence experiments were performed at RT using an Ar$^+$ ion laser (Spectra Physics) with an intracavity frequency doubler based on BBO crystal (GWU Lasertechnik) operating at 244 nm, which is normally used to record fibre Bragg gratings at the Physics Department, University of Aveiro (Portugal). Profiting from the recording set-up, prior to the sample the laser beam is deflected by a 460 nm pitch phase mask (Ibsen Photonics), so that only UV light impinges on the crystal. The laser power is measured with a thermal detector placed in front of the phase mask. Light emitted from the crystal is collected by a 400 $\mu$m diameter fibre optic placed close to the illuminated spot. Photoluminescence spectra and time evolution of the emission signals are acquired by using an Ocean Optics Mini-Spectrometer (USB4000) and their specific SpectraSuite software package in fast acquisition mode.

Due to the transient characteristics of the photoluminescence, the exciting and collecting geometry is first aligned by using one spot in the crystal surface. The sample is then moved with a micrometric translation stage, with the laser beam stopped, so that another spot can be illuminated to acquire the initial emission spectrum as soon as illumination begins. A final photoluminescence spectrum, after the established illumination period, is also measured. After that, again with the beam stopped, the coloured crystal is moved to another position in order to obtain the fluorescence time evolution. The total time from the opening of the exciting laser beam to the final photoluminescence spectrum acquisition is in the order of a few seconds, ($\approx 2 - 5$) s.

Optical transmittance spectra of the used crystals were measured at RT by using a Lambda 950 Perkin-Elmer spectrophotometer in the NUV and VIS spectral range, extending from 290 to 800 nm at a wavelength resolution of 2 nm. Photoluminescence spectra were also performed at RT with the same spectral resolution with an ISA-SPEX Jobin Yvon Fluorolog-3 spectrofluorometer equipped with a 450 W Xenon lamp and a solid-sample holder in front face detecting geometry, where the emitted signal is collected at an angle of 20° with respect to the normal direction of the sample surface, coincident with the exciting beam direction. A proper mask was used to select illuminated or non illuminated areas of the crystal.
3. Results and Discussion

Figure 1 shows the comparison between the photoluminescence spectra of a LiF crystal under c.w. UV excitation, acquired just after the UV illumination started and about one minute later. The \( \gamma \)-ray irradiation dose of that sample was estimated to be about \( 8 \times 10^4 \) Gy. Using the Smakula’s formula, the F centre concentration is determined to be \( \approx 1.33 \times 10^{18} \) cm\(^{-3}\). It is clear from the spectra in Figure 1 that the F\(_2\) centre emission is strongly reduced after the UV illumination, whereas the F\(_3^+\) photoemission shows a remarkable lower depletion. The effect is permanent (at least for a period of a few months), thus suggesting that the UV laser light at 244 nm really depletes the F\(_2\) centre population, due to an unknown non-radiative recombination mechanism.

The emission spectra can be fitted as a sum of Gaussian bands, whose main peaks are centred at 1.83 eV and 2.29 eV. Within the experimental errors, these values are compatible with previous measurements of F\(_3^+\) and F\(_2\) defects photoemission bands in LiF, respectively. They are generally observed under light excitation at around 450 nm, close to the absorption peak of the M-band, which consists of the superposition of F\(_3^+\) and F\(_2\) centres fundamental absorption bands [1]. However, the quality of the fitting can be improved when a third band, peaked at 1.96 eV, is included, as shown in the graph of Figure 2 (notice the X-axis in energy.
units). This band was reported by several authors and tentatively assigned to perturbed F₂ centres [13].

Figure 3. Fitting of the initial luminescence spectrum using two Gaussian functions with free peak energy parameter. Scattered line: experimental data, ——: resulting best fit, · · · · · ·: individual components of the fit.

Figures 3 and 4 show the spectra obtained in similar conditions for another LiF sample (X-axis in energy), irradiation dose ≈ 8.4 × 10⁴ Gy, together with the corresponding best fit by using two Gaussian bands. Even though the irradiation dose is similar to the previous sample, the F centre concentration, as calculated from Smakula’s formula, is lower for the second sample (≈ 5.01 × 10¹⁸ cm⁻³). The graph in Figure 3 is obtained with the peak energies as a free parameter in the fit, whereas the second fit, Figure 4, fixes the peak energy of each component to the known F⁺³ and F₂ emission bands. In both cases, the resulting best fits are of the same quality, so the usual F⁺³ and F₂ centre structure is assumed.

Figure 4. Fitting of the final luminescence spectrum using two fixed peak energy Gaussian functions. Scattered line: experimental data, ——: resulting best fit, · · · · · ·: individual components of the fit.

Figure 5. Time decay of the photoluminescence signals of a coloured LiF crystal under c.w. excitation at 244 nm, integration time 100 ms. The dotted lines show the best-fit of the experimental data with a single exponential decay.

From the spectra presented it is clear that the F⁺³ photoluminescence band intensity variation is much lower than that of the F₂ band, which is almost completely bleached after a short period of illumination, even by using low power c.w. light at 244 nm. This behaviour differs from the
known F$_2^+$ and F$_2$ emission intensity evolution when coloured LiF is illuminated by c.w. laser wavelengths at 458 nm, in the M-band absorption band [14].

Figures 5 and 6 show, respectively, the decay of the fluorescence signals obtained for the two previously mentioned samples. The general behaviour is the faster decay of the red component as compared to the green one. The decay data are fitted with a single exponential decay law to obtain the characteristics times.

![Figure 6. Time decay of the photoluminescence signals of the coloured LiF crystal (see text for details) under c.w. excitation at 244 nm, integration time 100 ms; notice that the monitored emission wavelengths are different from the previous figure. The dotted lines show the best-fit of the experimental data with a single exponential decay.](image)

For the first sample the resulting characteristic time constants are 9.9 s for the emission wavelength of 650 nm and 36.2 s for the 550 nm intensity; they are obtained with a fluence of about 0.12 W/cm$^2$. For the second sample, the corresponding time constants are 5.0 s and 27.1 s at the observed wavelengths of 670 nm and 540 nm, respectively.

4. Conclusion

From the measurements of the RT photoluminescence of coloured LiF crystals under c.w. laser illumination at 244 nm, it was derived that the emission bands associated to F$_2$ and F$_2^+$ centres possess different time behaviour. Their intensities decay are fitted with a single exponential law, with a faster decay rate for the F$_2$ emission band. The bleaching process is non-reversible, to the scale of several months. No other well-assigned emission bands were observed in the initial and final emission spectra, investigated in the 300 – 900 nm wavelength range.

The reported changes in the fluorescence spectra under c.w. laser illumination at 244 nm and the associated time constants are compatible with our previous work about UV laser illumination in the F-band absorption peak as an effective method to control the ratio of F$_2$ to F$_2^+$ centres in LiF [9, 10] due to permanent bleaching of the former defects. This characteristic can be useful for obtaining LiF laser action in the green region of the spectrum.

Both the time constants and the relative spectral intensities are strongly dependent on the initial F-centre concentration in the sample, as well as the UV laser power density. Further experiments are in progress to clarify these points.

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