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Colour centres induced in LiF by low-energy electrons

G Baldacchini[†], G d'Auria[†], R M Montereali[†] and A Scacco[‡]

[†] ENEA, Dipartimento Innovazione, Settore Fisica Applicata, CR Frascati CP 65, 00044 Frascati, Italy

[‡] Dipartimento di Fisica and Unità INFN, Università La Sapienza, P.le A Moro 2, 00185 Roma, Italy

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Abstract. A detailed study has been carried out on the optical properties of intrinsic colour centres, created in LiF crystals under irradiation with low-penetration 3 keV electrons. The kinetics of the production of F and M centres, determined from optical absorption measurements, exhibits a typical three-stage structure and an evident saturation at high doses. The quantitative evaluation of the kinetic parameters is in excellent agreement with the predictions of the most comprehensive theoretical model. A comparison of the effects of irradiation at different temperatures, determined from absorption and photoluminescence spectra, allows one to deduce the conditions for preferential formation of F₂ or F₃⁺ defects in LiF crystals.

1. Introduction

Due to its relevance to both the understanding of the fundamental properties of solid-state matter and the development of devices suitable for technological applications, the production of colour centres in ionic materials exposed to ionizing radiations has been studied in a number of experimental and theoretical investigations [1–3]. In particular, models of the mechanisms which lead to the formation of F and F₂ defects in the lattice of alkali halide crystals have been proposed and compared with the considerable amount of data collected in the measurements [4–6].

It is well known that the F-colouring process consists of three different stages, occurring in different dose regions. In the initial stage I, observed at low doses, a very efficient increase of the F-centre concentration with irradiation takes place. The fast saturation of this growth leads to an essentially constant number of defects typical of stage II. At high doses, a further steep increase in the growth corresponds to stage III, which in general ends when there is a final saturation at higher doses [5].

If the irradiation is carried out by using x-rays or γ -rays, then a uniform concentration of F centres throughout the sample (let us say 1–2 mm thick) is normally produced. Unfortunately, this favourable event is accompanied by such an intense optical absorption that the kinetics of the coloration process can hardly be measured up to the saturation. In contrast, irradiation with low-penetration radiations, such as low-energy electrons or ion beams, involves only thin surface layers (thicknesses of the order of a few micrometres) of the crystalline material, thus allowing for an easy determination of the defect concentration for any irradiation time and of its final saturation [7]. On the other hand, ion implantation gives rise along the particle tracks in the crystal to an energy transfer which is not uniform, being strongly dependent on the velocity of the incident ions [8]. As a consequence, low-energy electrons, whose dissipation is almost constant up to the end of the particle tracks

[9], seem to be the most suitable radiation for studying the optical properties of crystals containing high concentrations of F and F₂ centres, in order to investigate the mechanisms of the defect formation and to measure their saturation levels.

Another crucial problem concerning irradiated alkali halide crystals is the coexistence of several kinds of aggregate defect with often overlapping optical bands, which makes it difficult to measure the actual contributions due to the individual centres in the samples. This is for example the case for LiF of F₂ and F₃⁺ defects, which are both relevant to developments in colour-centre laser technology. Information on the parameters affecting the relative concentrations of such active centres, at the moment not available in detail for LiF, would allow for a selective generation of the desired kind of defect and therefore for an improvement of the light emission performances.

In this work, optical spectra are measured for single crystals of LiF irradiated in different conditions with 3 keV electrons, in order to obtain a detailed picture of some intrinsic colour centres in the system. From optical absorption measurements the kinetics of formation at room temperature (RT) and at liquid nitrogen temperature (LNT) of F and F₂ centres are determined. The results are compared with those obtained in the cases of other low-penetration radiations, and their agreement with the predictions of theoretical models is discussed. Photoluminescence experiments, which are able to discriminate between the emissions of F₂ and F₃⁺ defects, are used to evaluate their relative amounts and to test the experimental conditions of irradiation temperature and pumping light wavelength for optimizing selective light emission from one kind of centre.

2. Experimental procedure

Slabs of comparable thicknesses (about 1 mm), cleaved from a LiF single crystal, were used in this work as targets for electron bombardment. All of the samples were mounted on a brass holder kept under vacuum (about 10⁻⁶ mbar) during the irradiations. The sample holder was connected with a vessel containing liquid nitrogen in order to perform irradiations at temperatures between RT and LNT. Electrons with an energy of 3 keV were produced by a Varian electron gun, working with beam currents from 20 to 1000 μA (as measured by means of a Faraday cup), and impinging on an area of the sample surface of the order of 1 cm².

The concentrations of colour centres in the irradiated samples were calculated, by using Dexter's modification of Smakula's equation [2], from optical absorption spectra measured at RT with a Perkin-Elmer λ19 Spectrophotometer in the wavelength range 200–850 nm. All of the measurements were carried out within a few minutes from the end of the irradiations, and some of them were repeated after 24 hours of storage of the samples in the dark in order to check for fading phenomena. No significant differences were observed in the second series of spectra, confirming the stability of colour centres in LiF [10] (unlike their behaviour in other alkali halides). All of the spectra were corrected by subtraction of the absorption of an uncoloured LiF crystal, and the resulting curves were interpreted and computer fitted as the sums of Gaussian bands. Absorption coefficients were deduced from the optical density of the samples by taking into account that the penetration of 3 keV electrons in LiF is about 0.15 μm [11].

Photoluminescence of aggregate defects was excited by the 458 and 476 nm lines of an argon laser, which were appropriately filtered out before the detection system was reached; this system was formed by a SPEX Minimate monochromator (focal length 22 cm) and an S-20 photomultiplier. Emission spectra were measured at RT and LNT with the same pumping power for every curve.

3. Experimental results and discussion

A typical absorption spectrum, computer resolved into its various components, of colour centres created by irradiation with 3 keV electrons in a LiF crystal is shown in figure 1. The most conspicuous bands are found at about 243 nm (5.10 eV) and 445 nm (2.79 eV), which correspond to the peak positions of the absorptions of F and F₂ defects, respectively [12]. Several weaker bands, due to more complex aggregate centres, are observed: those at about 315 nm (3.94 eV) and 375 nm (3.31 eV) are caused by the R₁ and R₂ transitions, respectively, of F₃ centres, and those at about 515 nm (2.41 eV) and 545 nm (2.28 eV) are attributable to N₁ and N₂ transitions, respectively, of F₄ defects [8]. It should be noted that ionized defects are much more stable in LiF than in other alkali halides, so their absorptions give some minor contributions to the spectrum. The F₂⁺ absorption (not reported in figure 1) appears at about 630 nm (1.97 eV), and that of F₃⁺ centres at 458 nm (2.71 eV) is presumably overlapped by the F₂ band (giving rise to the band usually labelled M) [12]. The absorption at about 210 nm (5.90 eV) is commonly reported as due to unwanted impurities, such as oxygen or magnesium, but not reliably assigned [13]. The features of the whole spectrum, including the intensity ratios of its various components, reproduce well (with perhaps some more evident details) those observed for thin layers of LiF irradiated with 5 keV electrons [14] and, more recently, with secondary electrons emitted by a microwave discharge [15].

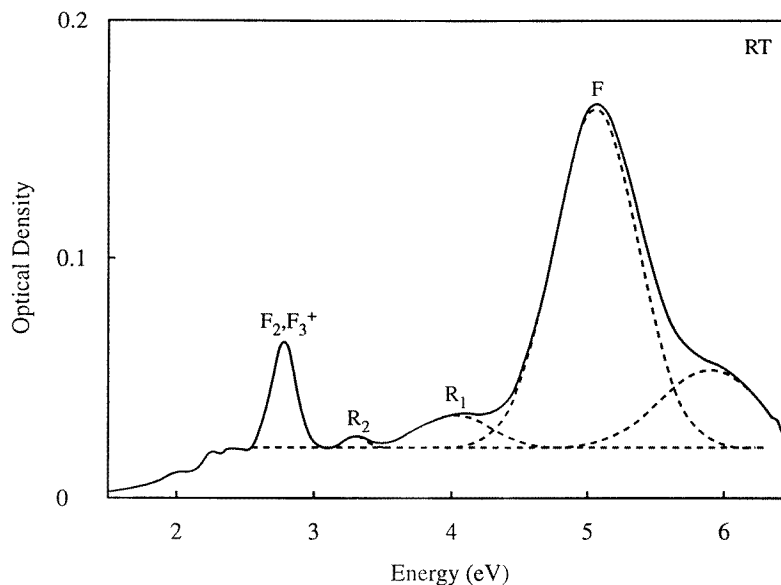


Figure 1. The absorption spectrum at room temperature, computer resolved into Gaussian bands (dashed lines), of a LiF crystal irradiated at room temperature with 3 keV electrons for 40 s at $1000 \mu\text{A cm}^{-2}$.

Crystalline samples of LiF, all suitably irradiated in their surface layers with 3 keV electrons and therefore showing the above-described absorption spectra, have been used to study: (A) the kinetics of the colouring process; (B) the photoluminescence of aggregate defects.

3.1. The kinetics of the colouring process

Due to the much higher intensities of the absorption bands of F and F₂ centres with respect to those caused by larger aggregates, the kinetic study of the colouring process has been restricted to the former two classes of defect.

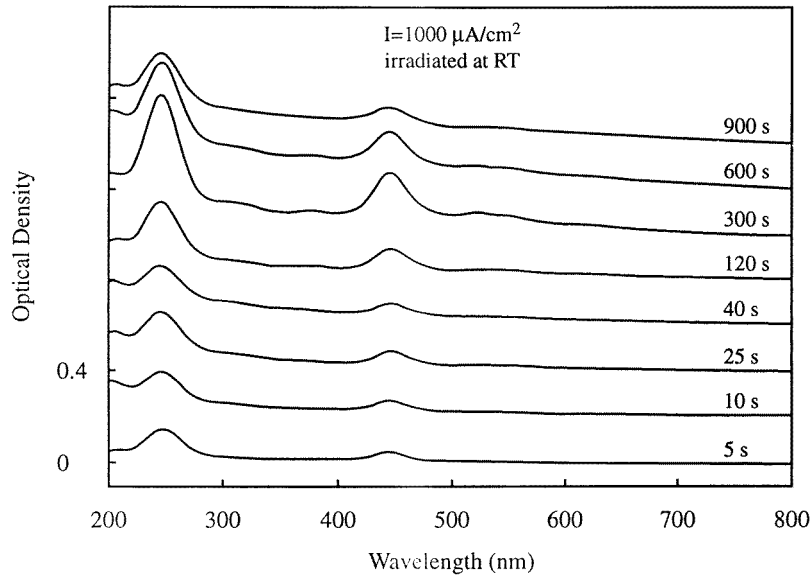


Figure 2. The dependence on irradiation time at room temperature of the absorption spectrum of LiF crystals coloured with 3 keV electrons at $1000 \mu\text{A cm}^{-2}$.

The dependence of the absorption spectrum on the time of irradiation at RT is displayed in figure 2. Every curve is shifted upwards by a constant value with respect to the previous one for the sake of clarity. Only the F and M bands are detected at first, while for longer irradiations the growth of the two main absorptions is accompanied by the appearance of the bands due to more complex defects. From such spectra the dose dependences of the concentrations of F and M centres are deduced, assuming for the oscillator strength the following values: 0.56 for F defects [16] and 0.28 for F₂ defects [1] (such a parameter being unknown for F₃⁺ centres). The results are represented in log–log plots for different values of the current density in figure 3. The F-colouring curves exhibit the three stages described above in a rather evident way at least for the cases of low current densities (20 and $50 \mu\text{A cm}^{-2}$), while stage I cannot be clearly observed in the other curves because of difficulties in achieving very short irradiation times and in evaluating very low absorption bands. The scattering in the experimental values is partly caused by the overlap of the F absorption with the unassigned band at 210 nm. It can be inferred, at least from the data of the two more detailed curves, that stage I is represented by a continuous increase up to about 2×10^{20} centres cm^{-3} (corresponding to a dose of about 2×10^{24} eV cm^{-3}), and is followed by the plateau of stage II (between 2×10^{24} and about 4×10^{25} eV cm^{-3}) and then by the new rise of stage III at higher doses. In general, the dose range in which the flat zone of stage II is observed decreases with increasing current density and is negligible at $1000 \mu\text{A cm}^{-2}$. Curves relating to the M absorption show analogous behaviours, with the exception of appreciable shifts towards higher doses of the separations between different

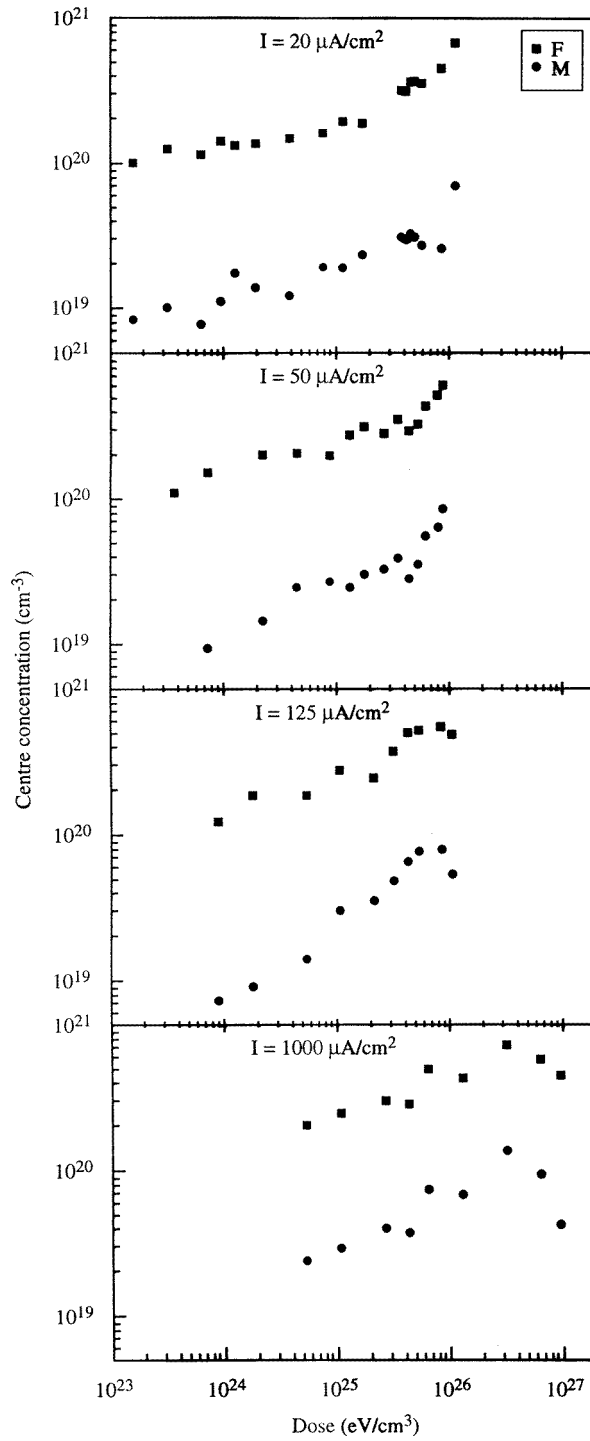


Figure 3. The kinetics of formation of F and F₂ centres in LiF under 3 keV electron irradiation at room temperature for different values of the current density.

stages, as expected for aggregate defects. In this case, the scattering of the data is less pronounced than that found for the F absorption because the M band is completely isolated in the spectrum. A striking feature, observed mostly in the cases of high values of the current density, is the evident saturation reached in the centre production: for doses higher than 10^{26} eV cm⁻³ the defect concentrations no longer increase and eventually begin to decrease. This effect is in agreement with the general behaviour of alkali halides, but is new in the case of LiF. Indeed previous experiments, carried out on crystals irradiated with 5 keV electrons [17] or with 0.2–2 keV electrons [18], were never able to reveal saturation in the LiF coloration process. As a consequence, the present results supply for the first time evidence of limiting values of the concentrations in LiF of F and M centres, which are about 7×10^{20} and 1×10^{20} centres cm⁻³, respectively.

The F-centre concentrations reached in this work at the end of stage I ($(2-3) \times 10^{20}$ centres cm⁻³) turn out to be comparable with those attained in LiF crystals bombarded by protons or positive ions [19], by He⁺ ions [7], or by electrons at temperatures between 77 and 250 K [20].

The slope evaluation for the two linear rises of the F-colouring curve during stages I and III allows for the determination of the coloration yield n in the equation

$$N_F = k(\text{dose})^n \quad (1)$$

where N_F represents the concentration of F centres and k is a proportionality constant. The values of n , ranging from 0.3 to 0.6 for stage I, are quite similar to those found for LiF for other low-penetration radiations, such as α -particles, protons and deuterons [8, 19]. As far as the slope of the linear zone of the F-colouring curve during stage III is concerned, its average value is 0.77.

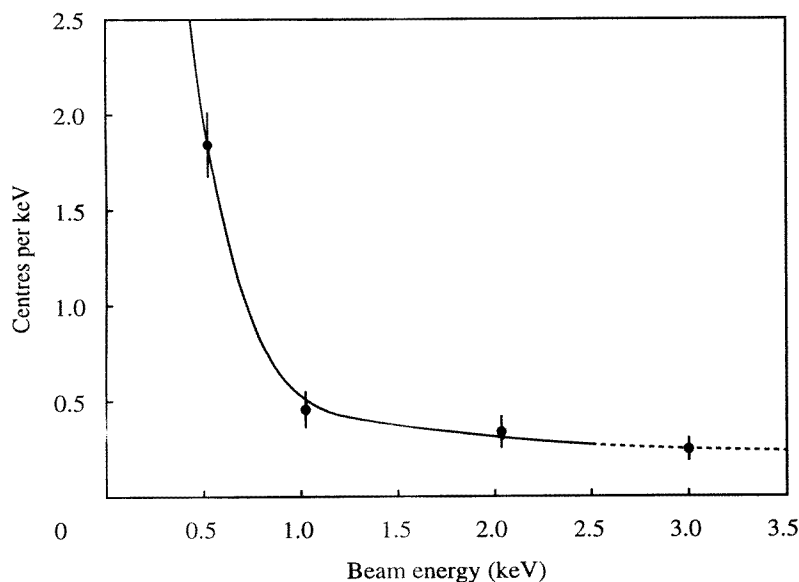


Figure 4. The dependence on the electron beam energy of the number of F centres formed per energy unit [16]. The value at 3 keV is from the present work.

The energy needed to produce an F centre, from which the coloration efficiency can be estimated, is calculated from stage I and found to be 3 keV irrespective of the current

density. Such a value is in very good agreement with previous data obtained for LiF colorations carried out with electrons of lower energies, as shown in figure 4.

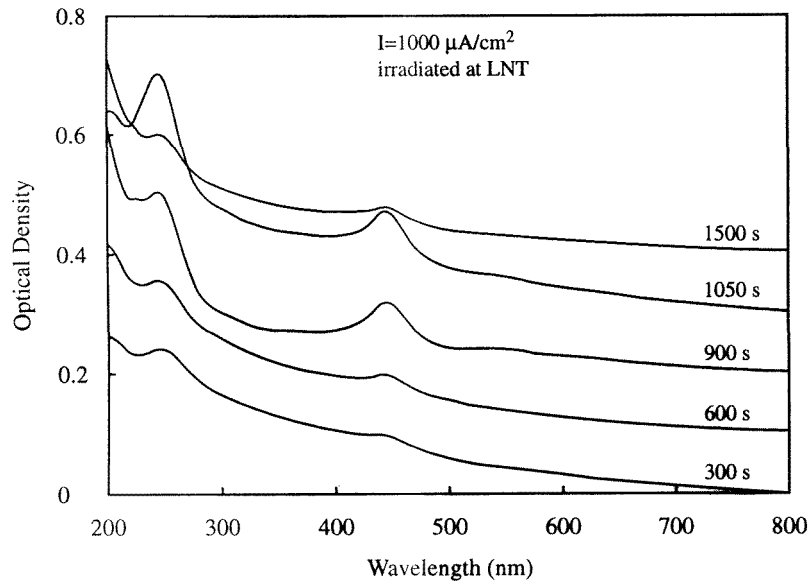


Figure 5. The dependence on irradiation time at liquid nitrogen temperature of the absorption spectrum of LiF crystals coloured with 3 keV electrons at $1000 \mu\text{A cm}^{-2}$.

In order to establish the influence of the sample temperature during the electron bombardment on the colouring process, a set of irradiations were performed at LNT. The absorption spectra of samples exposed for different times, displayed in figure 5, clearly show that the bands due to both F and M centres initially increase with the irradiation time, reach their maxima and then are dramatically bleached for longer exposures. This last feature, analogous to that observed in the case of RT irradiations (see figure 2), indicates that the decrease of concentration of F centres at high doses cannot be explained by their aggregation into F_2 defects. A tentative interpretation of such a result is linked to a possible local increase of temperature due to long irradiation times and therefore to thermal bleaching processes affecting all colour centres. A comparison of the LNT colouring curves, shown in figure 6, with those obtained for RT irradiations with the same current density (see figure 3) allows one to deduce that at LNT higher doses are required to obtain appreciable colouring of the samples, and saturation levels are noticeably lower. Both such findings point to the conclusion that the colouring efficiency, not directly measurable because stage I cannot be isolated at high current densities, is appreciably reduced for irradiations at low temperature.

All such results fully confirm previous knowledge about the kinetics of the colour centre production in alkali halides, and supply new information on such processes in the case of LiF crystals exposed to low-energy electrons.

A primary mechanism of creation of anionic Frenkel pairs via a non-radiative exciton decay [4] is generally accepted to explain the F-centre generation. After a very detailed study on the effects of x-rays on LiF [21], a model based on competitive recombinations of interstitial halogen ions with vacancies and traps (the latter formed by aggregates of interstitials) was proposed [22] to account for a few features of the F-colouring curve.

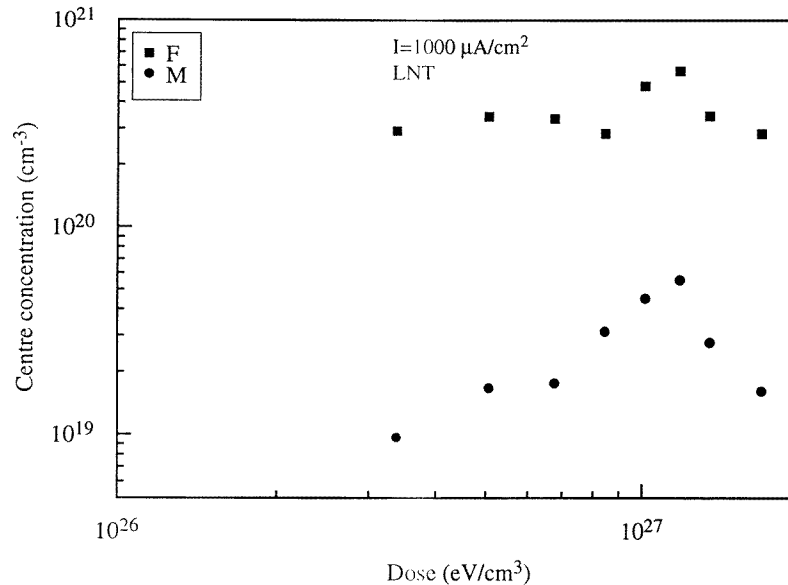


Figure 6. The kinetics of formation of F and F₂ centres in LiF under 3 keV electron irradiation at liquid nitrogen temperature for a current density of 1000 $\mu\text{A cm}^{-2}$.

A unified model describing all stages of the coloration kinetics has been presented [6] and later improved [23]. Competition between recombination with F centres and capture by empty traps and clusters is again postulated, but two new hypotheses are assumed: a heterogeneous nucleation of interstitial clusters and the peculiar instability of a short-lived aggregate (formed by two trapped interstitials). In this way, the experimental results found for NaCl and KCl are satisfactorily explained. In contrast, in the case of LiF an apparent discrepancy is found between the prediction of the theoretical model, which yields $n = 0.75$ in equation (1) at very high doses, and the experimental colouring curve supplying $n = 0.5$ at low doses. The results obtained in the present work confirm that n is very close to 0.5 in stage I and reaches the value 0.77 for stage III. Such an excellent agreement with calculations is evident support for the validity of the model, which can then be adopted for several (if not all) alkali halides.

The reduced defect formation efficiency at LNT is clearly associated with the reduced interstitial mobility at low temperature, which, by slowing the aggregation process, impedes the stabilization of F centres.

Another important result is the pronounced shortening of stage II with increasing dose rate (or current density). This effect is again predicted by the model, which describes stage II as the result of the equilibrium between the decay of the unstable aggregates and the increase of the number of stable traps caused by further aggregation of interstitials into larger clusters. At high dose rates the equilibrium is modified in favour of aggregate stability, so the interstitial traps are more efficient and cause an earlier occurrence of stage III with a higher F-colouring rate.

It is worthwhile to notice also the exceedingly high values of the F-centre density at the saturation in LiF: the colorations are so intense that presumably they could not be quantitatively measured in previous experiments. From the present data, an average distance of five lattice sites between two halogen vacancies can be deduced at the saturation level.

3.2. Photoluminescence of aggregate defects

Optical excitation of coloured LiF crystals into the spectral region where the absorption bands of F_2 and F_3^+ defects (at 445 and 458 nm, respectively) are overlapping induces photoluminescence of both kinds of centre. Since the typical F_2 emission is a band centred at about 650 nm, while that of F_3^+ centres is peaking at about 530 nm, their overlap is much less pronounced than that of the absorptions and, as a consequence, it allows for a reliable estimate of the individual band intensities and therefore of the relative concentrations of the two types of aggregate centres in the sample. Photoluminescence spectra measured under excitation at 476 nm exhibit in general weaker signals with respect to those excited at 458 nm with the same pumping power, as expected because of a reduced excitation efficiency due to a larger spectral displacement from the absorption peaks. For this reason, in the following only emission curves excited at 458 nm will be discussed in detail.

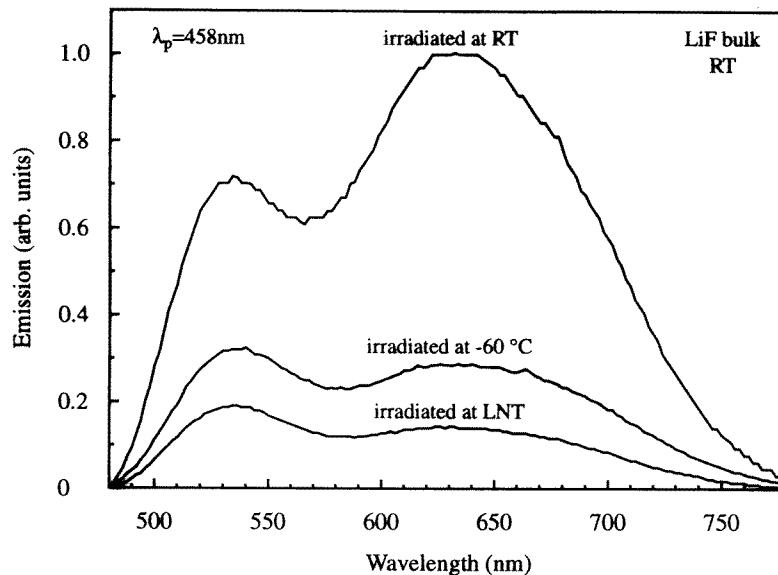


Figure 7. Emission spectra, measured at room temperature under 458 nm excitation, of LiF crystals irradiated with 3 keV electrons at room temperature (60 s at $160 \mu\text{A cm}^{-2}$), at -60°C (900 s at $160 \mu\text{A cm}^{-2}$) and at liquid nitrogen temperature (900 s at $1000 \mu\text{A cm}^{-2}$).

Emission spectra measured at RT for LiF samples irradiated with 3 keV electrons at three different temperatures are shown in figure 7. Their most evident feature (besides the poorer colouring efficiency at lower temperatures, which is consistent with the absorption results reported above) is the increase in the intensity ratio between the F_3^+ band at 530 nm and the F_2 band at 650 nm as the irradiation temperature decreases. This means that the main result of the LiF bombardment with 3 keV electrons at low temperature is the preferential formation of F_3^+ centres, whose green emission becomes, for LNT irradiations, dominant even over the red luminescence of the F_2 defects. Such a conclusion, which has been reached for the first time for low-energy electrons, is in agreement with previous findings concerning high-penetration ionizing radiations [24, 25]. By comparing spectra measured at different temperatures for the sample irradiated at -60°C , displayed in figure 8, a further huge enhancement of the above intensity ratio is observed at LNT, when only the F_3^+ emission intensity is considerably higher than at RT. Such a temperature-induced change can be

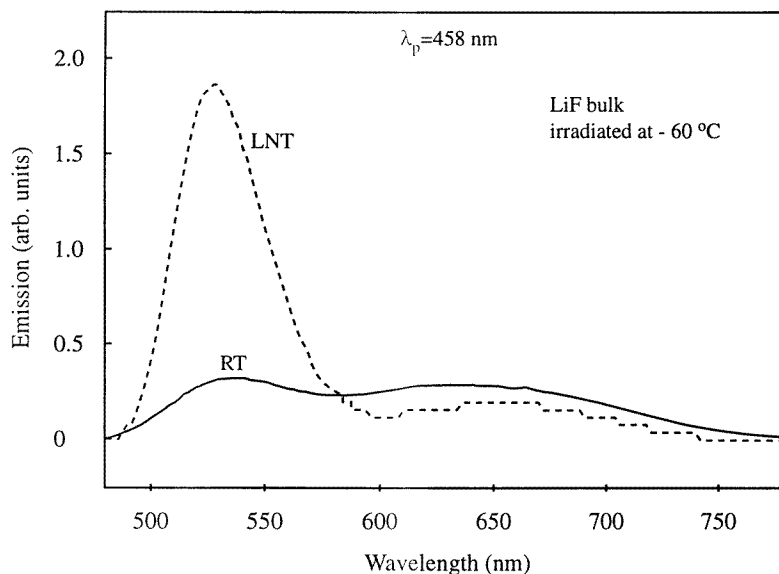


Figure 8. Emission spectra, measured at room and liquid nitrogen temperature under 458 nm excitation, of a LiF crystal irradiated with 3 keV electrons at $-60\text{ }^{\circ}\text{C}$ (900 s at $160\text{ }\mu\text{A cm}^{-2}$).

explained by considering that the absorption band of the F_2 centres becomes appreciably narrower and shifts to shorter wavelengths at low temperatures, so the excitation efficiency for such defects is strongly reduced with respect to that for F_3^+ centres. As a consequence, LiF crystals coloured with 3 keV electrons exhibit practically only the F_3^+ luminescence at 530 nm if their irradiation is performed at low temperature and their emission is optically excited at 458 nm at LNT.

4. Conclusions

The results reported above lead us to the following conclusions.

The production of colour centres in LiF by bombardment with 3 keV electrons exhibits a kinetics which, unlike the results of previous experiments (carried out with other kinds of ionizing radiation) and of other interpretations, is analogous to that observed for other alkali halides and can be successfully interpreted on the basis of the most comprehensive theoretical model. The quantitative agreement of the experimental kinetic parameters with the calculated predictions is valid support for the correctness of the present investigation and the validity of the model.

The concentration of F centres in surface layers of LiF crystals turns out to be so high that very careful measurements must be adopted for its determination. The saturation level of colour centres in LiF has probably been determined for the first time in this work because of unsolved difficulties in the previous absorption measurements.

The experimental conditions for selective production and preferential optical excitation of F_2 and F_3^+ centres have been determined. The optimization of the luminescence properties of these two kinds of defect can be relevant for the improvement of the performances of solid-state lasers based on coloured LiF crystals.

Acknowledgments

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