Eur. Phys. J. D **17**, 261–264 (2001)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences
© Società Italiana di Fisica
Springer-Verlag 2001

Energy transfer among color centers in LiF crystals

G. Baldacchini[1,a], R.M. Montereali[1], and T. Tsuboi[2]

[1] ENEA, Divisione Fisica Applicata, Centro Ricerche Frascati, C.P. 65, 00044 Frascati, Rome, Italy
[2] Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kyoto 603-8555, Japan

Received 25 June 2001 and Received in final form 16 July 2001

Abstract. In colored LiF crystals there are many absorption and emission bands which cover a wide region of the spectrum from 200 up to 1 300 nm without breaking the continuity. In the frame of these favourable conditions we have performed some experiments of energy transfer among various color centers. The results indicate the existence of efficient exchanges of radiative energy among several bands by using only one exciting wavelength. In particular, the emissions of the F_3^- and F_2^- color centers centered at 900 and 1 100 nm, respectively, have been observed by pumping at 672 nm completely outside their absorption bands.

PACS. 61.72.Ji Point defects (vacancies, interstitials, color centers, etc.) and defect clusters – 78.40.Ha Other nonmetallic inorganics – 78.55.Fv Solid alkali halides

1 Introduction

LiF occupies a special place among the alkali halide crystals because it is not hygroscopic, possesses good physical and optical qualities, and it can host a rich zoology of different species of color centers (CC) stable at room temperature (RT). Figure 1 shows the absorption spectrum at RT of a crystal of LiF irradiated with a beam of 5 MeV electrons, and the various bands correspond to different CCs as indicated. Although CCs in LiF have been studied since long time [1], they cannot be produced by using the usual additive coloration method but only by means of ionizing radiations, and the F center associated with an absorption band around 250 nm does not produce any emission under optical excitation [2]. However, just to compensate the previous drawbacks, many of the CCs displayed in Figure 1 possess efficient emissions which have been used in solid state lasers operating in pulsed regime at RT [3,4].

Figure 2 shows schematically the absorptions and the corresponding emissions of several of the above known CCs. They cover the visible and the near infrared region of the spectrum almost in a continuous way. However, it is not possible to control the concentration of the various CCs in the same crystal and at the same time. Indeed, the production of the various types of CCs proceeds essentially according to their complexity. So, initially the F centers, which are the simplest and often a model case among the other more complex CCs, are produced and successively the F_2, F_3, F_4 and the positive and negative ionized species of them follow up with decreasing concentration. In conclusion, while it is possible to produce a crystal with mainly F centers, a crystal with an appreciable amount of F_3^+ and F_2 centers will contain always orders of magnitude more of F centers. However, it has been well established that also in these inflationary conditions it is possible to study the properties of the single CCs, as it is the case for the well-known F_3^+ and F_2 CCs [5]. Indeed, although they possess their absorption bands almost overlapped and their optical properties are heavily tangled each other, it is still possible to sort them out.

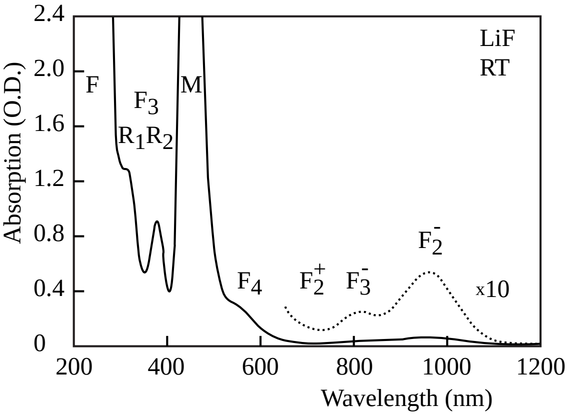

Fig. 1. Absorption spectrum at RT of a LiF crystal 0.5 mm thick colored at RT with 3 MeV electrons. The band M contains the F_3^+ and F_2 bands which overlap each other almost completely.

Analogous interactions exist among others CCs in LiF shown in Figures 1 and 2. In particular, in this work we would like to address the optical properties of the F_4-like, F_3^- and F_2^- CCs, which absorb just outside the visible

---

[a] e-mail: `baldacchini@frascati.enea.it`

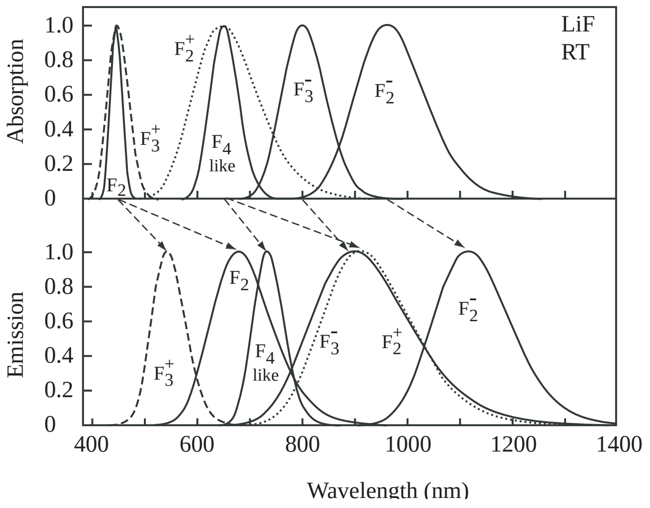

Fig. 2. Absorption and emission bands in a colored LiF crystal at RT, outlined as normalized Gaussian curves, of the known color centers which possess also emission.

region in the near infrared region of the spectrum, and are formed with four (?), four and three electrons trapped by four (?), three and two negative-ions vacancies in the nearest neighbor positions, respectively. The question mark for the F_4-like center indicates a tentative attribution for this CC absorbing around 648 nm and emitting at 735 nm [6]. Indeed, it could also be the F_3^- center absorbing at its second band at 660 nm [7]. Anyway, it will be shown that the F_4-like, F_3^- and F_2 CCs can be excited at the same time by using only one wavelength, and that the intensity of their emissions is strongly dependent on the absorption and the geometry of the crystal with respect to the optical pumping. In practice, an energy transfer process is going on among the various centers based on emission and absorption effects in the volume of the colored crystal. In particular, in this paper we investigate the energy transfer from the F_4-like center to the F_3^- center and from the F_3^- center to the F_2^- center.

2 Experimental procedure

A LiF crystal of dimensions 9.72 × 10.04 × 54.80 mm^3, purchased from the General Physics Institute of Moscow, has been heavily colored by irradiation with high energy electrons at RT. This crystal was originally produced for Q-switching a Nd-YAG laser by using the broad emission band of the F_2^- CCs between 800 and 1 000 nm, and for this purpose the two faces perpendicular to the long dimension were carefully polished.

A semiconductor diode laser, SDL 7470-P5, emitting in cw mode 2.5 W at 672 nm with a half width of 8 nm, has been used to excite the crystal at one of the polished surfaces, by means of an optical fiber of core diameter 0.05 mm at 0.2 mm from the surface of the crystal.

Another optical fiber of core diameter 0.1 mm has been positioned perpendicular to the first one along the long dimension at 0.2 mm from the surface of the crystal. The emission collected by the optical fiber has been revealed by an Advantest Q8381A optical spectrum analyzer working in the interval 400–1 750 nm. The absorption spectrum of the crystal has been measured with a Shimadzu UV-3100 spectrophotometer. All absorption and emission spectra have been measured at RT.

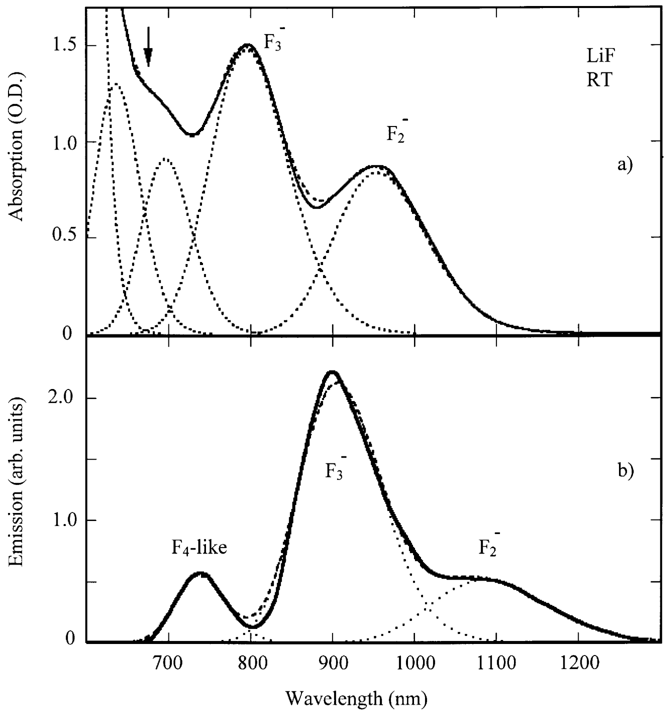

Fig. 3. Absorption (a) and emission (b) spectrum in the region 650–1 300 nm at RT of a LiF crystal colored with a high energy electron beam at RT, full lines. The absorption refers to the crystal thickness of 10.04 mm. The emission has been excited by a diode laser at 672 nm, as indicated by the arrow. The two spectra have been fitted with Gaussian curves, dotted lines, and their sums reported as dashed lines. See text for details.

3 Experimental results

Figure 3a shows the absorption spectrum of the LiF crystal well above 600 nm. Two absorption bands with peaks at 960 and 800 nm are observed in addition to an absorption structure appearing in the 640–730 nm region, which is not very well resolved because of the overlap with the long wavelength tails of the much stronger absorption bands due to F_4 (N_2 and N_1), F_2 and F_3^+ centers which peaks at about 530, 445 and 448 nm, respectively [4,8,9]. The 960 and 800 nm bands have been already attributed to the F_2^- and F_3^- CCs, respectively, while the 640–730 nm absorption structure could be due to the second band of the F_3^- center, also called R_1', centered at 660 nm according to reference [7] and at 680 nm according to reference [10], to an F_4-like center which possesses an absorption band peaked at about 648 nm and half width 1 500 cm^{-1} [4,6], or to both them.

In order to clarify better this matter we have resorted to a fitting procedure of the absorption spectrum with Gaussian curves, by using peak positions and half width values known from the literature as a starting set of parameters. The calculated total absorption spectrum and single absorption bands are reported in Figure 3 by dashed and dotted lines, respectively. In general the agreement is very good, in spite of the intrinsic difficulties to fit the experimental data below 730 nm, from where the strong F_4 ($N_2 + N_1$) band starts to dominate over all the other ones. Anyway, in order of decreasing wavelengths the F_2^- and F_3^- (R_2') bands have been well resolved, while the F_3^- (R_1') and F_4-like bands overlap each other and with the tail of the F_4 band. It is clear that at this stage of knowledge it is not yet possible to give a definitive assessment of this strongly entangled absorption region of the colored LiF crystal which requires more detailed studies, still in progress at moment. For this reason we have preferred not to label the bands below 730 nm. However, the band picture reported in Figure 3a agrees in a reasonable way with what is known up to now [11], and so it will be used with the necessary caution in the following of the present work.

Figure 3b shows the emission spectrum, full line, of the crystal 12 mm far away from the front surface where the crystal is excited with the diode laser. Three emission bands are observed, the more intense one at 900 nm, a less intense one at 735 nm and the weakest one at the low energy tail of the strong 900 nm band. As in the absorption, the emission spectrum has been fitted with Gaussian curves and the result of the best fit is reported in the same figure, dashed line for the whole spectrum and dotted lines for the three single bands which were required to accomplish the feat. The 900 nm band is attributed to the F_3^- centers, while the 1 100 nm band is due to the F_2^- CCs [3,4,10]. The 735 nm emission band has been already observed in various colored LiF crystals, and has been attributed to the F_4-like CCs just described in this section.

The 672 nm pumping radiation has been used to excite the LiF crystal in the absorption structure well below the F_3^- (R_2') band, as shown in Figure 3a by an arrow. It is evident that this wavelength can excite both F_3^- (R_1') and F_4-like bands but, however, it cannot explain both the high intensity of the emission at 900 nm and the 1 100 nm emission, for which we have to resort to other mechanisms. In order to clarify them, we have carefully measured the luminescence of the crystal along the long dimension, and the intensity of the various bands at their peaks has been reported in Figure 4. Also the intensity of the exciting light, measured by the weak scattering of the light in the crystal, has been reported for comparison. The experimental data follow an exponential behavior with different slopes up to a distance of 15 mm from the front surface of the crystal, after which they start to decrease faster, although it should be kept in mind that the last values at about 0.3 arb. units of the emission intensity may have errors up to 100%. Indeed, their intensity is barely observed above the noise.

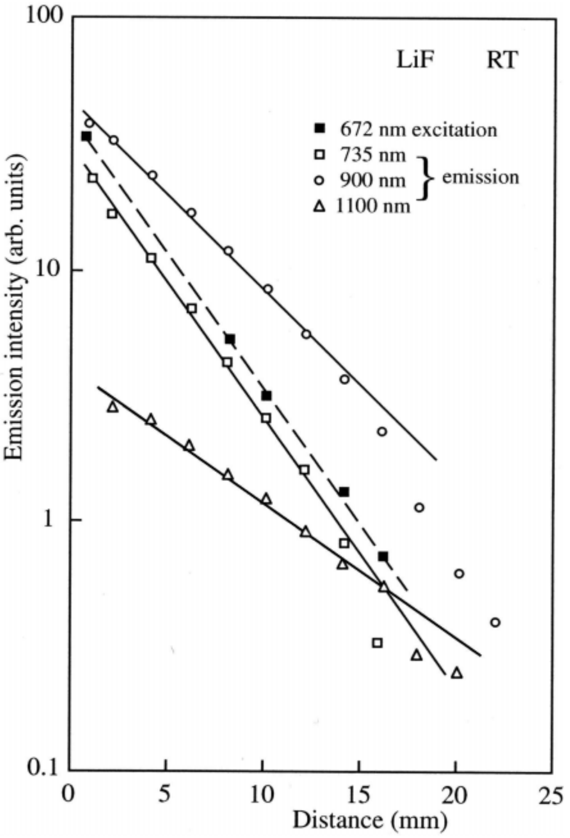

Fig. 4. The peak intensities of the three emissions of Figure 3b, full line, are reported as a function of the distance from the front surface of the excited crystal. Also the intensity of the exciting light, dashed line, has been reported for a direct comparison.

4 Discussion and conclusions

As we have shown in the previous section, the F_4-like, F_3^- and F_2^- emissions are observed under optical pumping with the 672 nm radiation, which excites the F_4-like band and also the F_3^- (R_1') band. In our opinion, the F_3^- and F_2^- luminescences are observed mainly because each of them is excited in cascade by the preceding luminescence. Indeed, we are in presence of an energy transfer process due to the simple mechanism of emission and absorption in the volume of the crystal, as it is demonstrated indirectly by the intensities of the various emissions along the long dimension of the crystal in Figure 4.

The emission of the F_4-like CCs follows the same slope as the intensity of the exciting light along the crystal measured through its scattering, *i.e.* the two exponential coefficients have the same value of 0.24 mm^{-1}. As a matter of fact, this slope also corresponds to the crystal absorption at 672 nm. At distances bigger than 15 mm the emission at 735 nm decreases more quickly than expected, which can be due both to geometrical factors (the diode laser has not been collimated and, so, it emits with the well-known directional lobe mode) and experimental errors (unavoidable at the present low signal intensities).

The light emitted at 735 nm is absorbed by the two F_3^- bands with successive emission at 900 nm. In this case, we do not expect the same slope as the exciting luminescence. Indeed, at a certain point along the crystal the emission at 900 nm depends on the integral emission at 735 nm produced in a volume of the crystal surrounding that point, and whose dimensions are a complex function of the geometry of the optical pumping with respect to the crystal and of its absorption coefficient at 735 nm. Qualitatively, at the beginning it is expected an higher intensity of luminescence with distance and so a smaller initial slope than that of the exciting light at 735 nm, as it has been found experimentally in Figure 4, where the exponential coefficient is 0.17 mm^{-1}. However, after a certain distance, which coincides approximately with the longitudinal dimension of the integral emission volume which contributes to the emission, the slope should be similar to that of the exciting light at 735 nm, as it is observed in the same Figure 4 above 15 mm.

Generally speaking, the intensity of the external pumping light entering into the crystal is expected to decay exponentially, since the transmitted light intensity I at the distance d from the incident surface is given by $I = I_0 \exp(-kd)$, where I_0 is the incident light intensity and k is the absorption coefficient. The observed exponential decay of the 672 nm excitation light indicates that the 672 nm light is indeed the transmitted light. Additionally, the same slope is observed for the intensity of the 735 nm emission. This result confirms that the 735 nm emission is generated directly by the 672 nm radiation propagating through the crystal.

The emission at 900 nm is absorbed by the F_2^- band with a new emission at 1 100 nm. Here the situation is similar to the previous one, with the difference that the slope of this new emission should be still smaller than that of the 900 nm emission, which is exactly what has been reported in Figure 4, *i.e.* the exponential coefficient is 0.12 mm^{-1}. Eventually, after about 15 mm the intensity starts decreasing faster as in the case of the 900 nm emission.

At the end, all the luminescences reported in Figure 4 should decay with the same slope as the initial exciting radiation at 672 nm. However, because of the very low intensity of the luminous signals at large distances from the front surface of the crystal, the measurements of Figure 4 hint at this hypothesis but do not support it with absolute certainty.

In conclusion, the measurements reported here are a good example of energy-transfer processes from one type to another type of CC. The intensities of the various emissions involved in the present cascade processes are interwound each other in a complex way. Their behaviors have been described by a simple phenomenological model, which most probably could be expressed in an analytical way in case of more simple experimental conditions.

Two of the present authors greatly appreciate the support of ENEA (T.T.) and KSU (G.B.) for visiting fellowships which have enabled them to work at the Frascati Research Center and at Kyoto Sangyo University, respectively. Many thanks are due to F. Bonfigli, and T. Marolo for their precious scientific contribution in the last stages of this work and to M. Cimino for her skillful assistance during the preparation of the manuscript.

References

1. *Physics of Color Centers*, edited by W.B. Fowler (Academic Press, New York, 1968).
2. G. Baldacchini, M. Cremona, R.M. Montereali, U.M. Grassano, V. Kalinov, in *Defects in Insulating Materials*, edited by O. Kanert, J.-M. Spaeth (World Scientific, Singapore, 1993), Vol. 2, p. 1103.
3. T.T. Basiev, S.B. Mirov, *Room Temperature Tunable Color Center Lasers* (Harwood, Academic Publ., Switzerland, 1994).
4. V.V. Ter-Mikirtychev, T. Tsuboi, Prog. Quant. Electr. **20**, 219 (1996).
5. G. Baldacchini, M. Cremona, G. D'Auria, R.M. Montereali, V. Kalinov, Phys. Rev. B **54**, 17508 (1996).
6. V.V. Ter-Mikirtychev, T. Tsuboi, Can. J. Phys. **75**, 813 (1997).
7. A. Perez, J. Davenas, C.H.S. Dupuy, Nucl. Instrum. Meth. **132**, 219 (1976).
8. N. Seifert, H. Ye, N. Tolk, W. Husinsky, G. Betz, Nucl. Instrum. Meth. Phys. Res. B **84**, 77 (1994).
9. G. Baldacchini, M. Cremona, R.M. Montereali, L.C. Scavarda do Carmo, R.A. Nunes, S. Paciornik, F. Somma, V. Kalinov, Opt. Commun. **94**, 139 (1992).
10. J. Nahum, Phys. Rev. **158**, 814 (1967); J. Nahum, D.A. Wiegand, Phys. Rev. **15**4, 817 (1967).
11. G. Baldacchini, F. Menchini, R.M. Montereali, T. Tsuboi, *The Bulletin of the Institute of Computer Sciences* (Kyoto Sangyo University, Vol. 16, n. 2, March 2000), p. 11; and references cited therein.