

SOLID-STATE SPECTROSCOPY

$F_L V_a^+$ and $F_L F$ Color Centers in Lithium Fluoride Crystals

L. I. Shchepina, S. S. Kolesnikov, V. M. Kalikhman, and I. V. Teryaeva

Research Institute of Applied Physics, Irkutsk State University, Irkutsk, 664003 Russia

Received June 20, 2000

Abstract—Using optical spectroscopy and X-ray diffraction analysis, the nature of defects in γ -irradiated lithium fluoride crystals is found, mechanisms of their formation are proposed, and the absorption bands at 385 ($F_L F$ centers) and 506 nm ($F_L V_a^+$ centers) are interpreted. © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

The exposure of γ -irradiated lithium fluoride crystals to the integrated emission of xenon lamps induces in their absorption spectra the band with $\lambda_m = 506$ nm and a half-width of 1130 cm^{-1} at $T = 78$ K through optical bleaching. The aim of this work was to study the conditions under which the defects responsible for this absorption band are formed and to determine their nature. Previously, F_5 centers were observed in this spectral region in γ -irradiated and annealed crystals [1]. However, this model is unsatisfactory. First, there takes place the interaction with H centers (interstitial halogen atoms) in addition to the ionization of color centers (CCs) during the exposure to optical emission. This causes a decrease in the degree of CC aggregation, and a crystal becomes bleached. It is natural to assume that the same is true for the F_5 centers. Second, as will be shown below, these defects are charged (they efficiently interact with electrons of F centers).

EXPERIMENTAL

We studied γ -irradiated ($D = 10^6$ – 10^8 R) LiF crystals grown by the Kyropoulos method in air and enriched with oxygen. The crystals were exposed to the integrated emission of xenon lamps in a “Kvantron” type laser head of a Kvant-17 laser (1 MW) for the purpose of inducing CCs with the absorption maximum at 506 nm (they will be referred to as 506-nm centers) and to the fourth harmonic of an Nd:YAG laser for the study of CC phototransformation. The isochronous annealing was carried out in a temperature range of 293–523 K. The temperature was changed with a step of 50 K, and a sample was held at each temperature for 15 min. The absorption spectra were measured on an MPS-50L spectrophotometer at 78 and 300 K. The emission and excitation spectra were measured on a standard setup. The X-ray diffraction analysis was carried out on a DRON 2.0 diffractometer using $\text{CuK}_{\alpha 1, \alpha 2}$ emission. We determined the interplanar spacing d_{hkl} and the broadening $\beta = S/I_{\max}$, where S is the area under the envelope

of a peak being studied, for all the reflections observed in the spectrum depending on the γ -irradiation dose.

RESULTS AND DISCUSSION

The fact that the accumulation of the defects under study linearly depends on the γ -irradiation dose up to 10^8 R (Fig. 1a) suggests that we deal with intrinsic defects of the crystal lattice (because impurity defects are saturated as early as at the first irradiation stage with a dose of 10^7 R). The efficiency of defect accumulation as a function of the number of emission pulses of xenon lamps tends to saturation at 200 pulses (Fig. 1b). This may be caused by the fact that a crystal is heated in the course of irradiation and its temperature is increased above 200°C . Thus, the defects are both produced and destroyed. Indeed, using isochronous annealing of γ -irradiated crystals, we determined the effective temperature ($T = 200^\circ\text{C}$) of production of 506-nm centers and observed the transformation of F_3^+ centers into 506-nm centers (Fig. 1c). We emphasize that a high defect concentration is induced only in the crystals with a predominant content of F_3^+ centers. The analysis of data on defect formation in γ -irradiated samples upon annealing and optical bleaching showed that the efficiency of their production in the samples exposed to the integrated emission of xenon lamps, all other conditions (γ -irradiation dose, temperature) being the same, was higher by a factor of 1.67. This may be caused by the fact that, when an F_3^+ center is exposed to optical emission, its electron is found in the excited state [2] and is involved in the optical transformation of color centers.

The optical bleaching by F light (the fourth harmonic of a Nd:YAG laser at 266 nm) at a low temperature (78 K) causes the destruction of the 506-nm band, as well as of the F band ($\lambda = 250$ nm), the strengthening of the M absorption band at 441 nm, and an increase in the concentration of defects responsible for absorption at $\lambda_m = 385$ nm (Fig. 2). In the case of excitation in the M band, we observed red emission with $\lambda_m = 650$ nm,

which is typical of F_2 centers. In the case of excitation in the 385-nm band, no luminescence was observed. The analysis of the curves suggests that the 506-nm centers are transformed into the 385-nm centers. An increase in the concentration of F_2 centers may be caused by the electron trapping by F_2^+ centers and the interaction of anionic vacancies with F' . However, no changes in the optical density in the absorption region of F_2^+ centers (600–640 nm) was observed. The $F' + V_a^+ \rightarrow F_2$ reaction is also excluded because, first, the crystal were optically bleached at a low temperature and, second, the 385-nm absorption, which was attributed to F' centers [3], was not weakened. It is likely that the appearance of F_2 centers is associated with the decay of F_4 centers whose zero-phonon lines at 523.4 and 512.5 nm were observed in the absorption spectrum [4]. However, these centers had an insignificant concentration and were unable to affect the transformation of 506-nm centers into 385-nm centers. Thus, in our opinion, the electrons of F centers interact with positively charged defects that are responsible for absorption at 506 nm. Knowing the nature of defects (385 nm), we can also interpret the absorption band under study. As for the absorption of lithium fluoride crystals, it is known that absorption in the 385-nm region may be caused by F' centers [3]. These defects are unstable because they have an excessive charge and will interact with positively charged defects. The centers observed in our experiments are stable (the absorption band is unchanged on storage). The absorption band at 385 nm may be caused by F_3^+ -like centers that produce 490-nm emission under excitation [5]. However, the crystals optically excited in the 385-nm absorption band produced no emission either in the blue or in the red region. Therefore, the defects observed by us are closer in properties to quasi-metallic W_k^2 centers, which were studied in detail in neutron-irradiated (10^{16} – 10^{18} neutron/cm²) lithium fluoride crystals [6]. Subsequent annealing forms from these centers atomic defects with an absorption band at 275 nm (F_L centers, where F_L is Li⁰ in an F center [7]). Therefore, F_L centers are required for the formation of both 385- and 506-nm centers.

The 506-nm absorption band is produced by thermally or optically induced transformations of F_3^+ centers. Previously we observed the transformation of F_3 centers into $F_L F_2^+$ [8]. Similarly, it is reasonable to assume that the electron density in an F_3^+ center can be displaced under the action of light and temperature to the nearest lithium cation, and this produces a lithium atom, which occupies a position in one of the F centers of the initial defect:

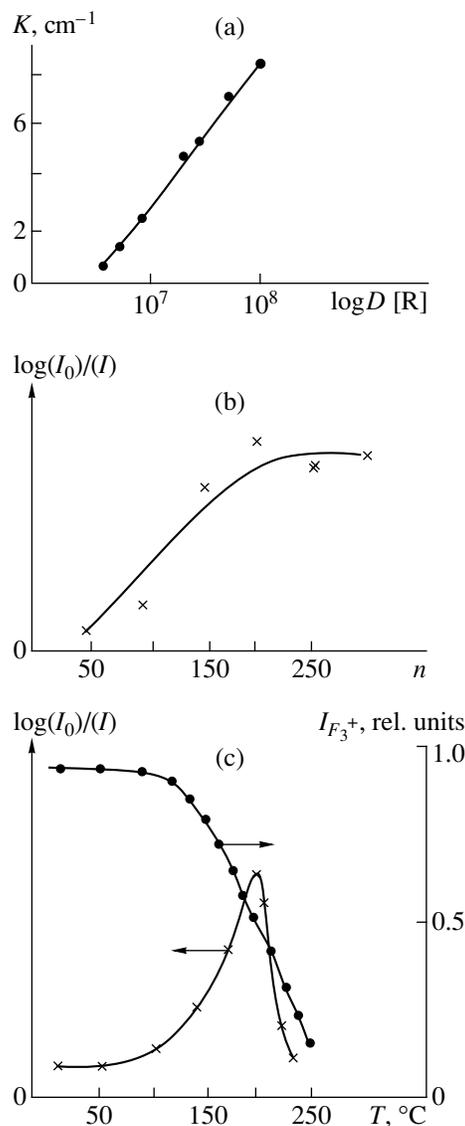


Fig. 1. (a) Efficiency of 506-nm center formation in γ -irradiated O, OH:LiF centers versus the γ -irradiation dose. (b) Accumulation of centers in γ -irradiated crystals ($D = 6 \times 10^7$ R) versus the number of pulses of integrated emission of a xenon lamp. (c) Isochronous annealing of F_3^+ centers (I_F is the 540-nm luminescence intensity) and 506-nm centers in γ -irradiated samples ($D = 6 \times 10^7$ R).

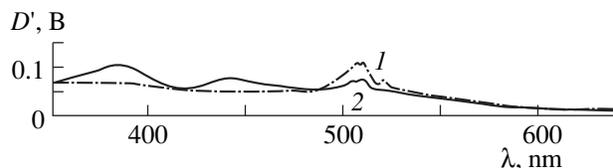
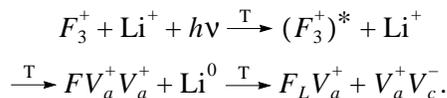


Fig. 2. Absorption spectra of the O, OH:LiF crystal ($D = 5 \times 10^7$ R) with induced 506-nm centers (1) before and (2) after optical bleaching by the fourth harmonic of a Nd:YAG laser at $T = 78$ K ($n = 10^4$ pulses, a crystal 300 μ m thick). D' is the optical density.



This produces an excessive concentration of vacancies in the crystal lattice, which should have an effect on d or β . Indeed, a decrease in the relative broadening of reflections is observed in the X-ray spectrum upon the exposure to the integrated emission of xenon lamps, which gives evidence of an elimination of local stress in the crystal lattice due to the appearance of vacancies because of the induction of 506-nm centers. The defects under study are positively charged because they interact with the electrons of F centers and are easily destroyed in the course of annealing at $T > 220^\circ\text{C}$. The optical bleaching by F light produces quasi-metallic centers with the 385-nm absorption band (F_LF centers):

$F_LV_a^+ + e \longrightarrow F_LF$. In summary, we determined the nature of defects, proposed the mechanisms of their formation, and interpreted the absorption bands at 385 (F_LF centers) and 506 nm ($F_LV_a^+$ centers).

REFERENCES

1. E. I. Shuraleva, P. S. Ivakhnenko, S. S. Kostenko, *et al.*, in *Proceedings of the V All-Union Conference on Radiation Physics and Chemistry of Ionic Crystals, Riga, 1983*, p. 275.
2. T. T. Basiev, I. V. Ermakov, and K. K. Pukhov, *Fiz. Tverd. Tela (St. Petersburg)* **39**, 1373 (1997) [*Phys. Solid State* **39**, 1218 (1997)].
3. S. V. Dorokhov, Author's Abstract of Candidate's Dissertation in Mathematical Physics (Irkutsk, 1999).
4. A. E. Hughes and W. A. Runciman, *Proc. Phys. Soc. London* **86** (6), 615 (1965).
5. A. G. Bazylev, V. S. Kalinov, and S. A. Mikhnov, *Zh. Prikl. Spektrosk.* **57**, 504 (1992).
6. L. F. Vorozheikina, Author's Abstract of Candidate's Dissertation in Mathematical Physics (Irkutsk, 1971).
7. B. D. Lobanov, V. M. Kostyukov, N. T. Maksimova, *et al.*, *Fiz. Tverd. Tela (St. Petersburg)* **37**, 2545 (1995) [*Phys. Solid State* **37**, 1397 (1995)].
8. L. I. Shchepina, S. S. Kolesnikov, V. M. Kalikhman, and I. V. Teryaeva, *Opt. Spektrosk.* **88**, 260 (2000) [*Opt. Spectrosc.* **88**, 222 (2000)].

Translated by A. Kirkin