## PHYSICAL AND QUANTUM OPTICS

# Nature of the $N_b$ Absorption Band in LiF Crystals

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**Abstract**—It was found by the methods of optical spectroscopy and X-ray diffraction analysis that the $N_b$ absorption band in LiF crystals is related to the reoriented $F_4$ center when all the $F$ centers lie in the (110) plane. These defects are decomposed into $F_2$ centers at annealing. © *2002 MAIK "Nauka/Interperiodica"*.

Recently, electron-beam lithography, simultaneously forming the waveguide structure and laser-active color centers (CC) with broad luminescence bands, is rapidly progressing [1, 2]. At the same time, the electron bombardment of crystals, as well as the γ-ray irradiation, efficiently forms optically active centers and simultaneously induces defects in the $N$ region of the spectrum. The study of defects absorbing in the $N$ region, in a γ-irradiated crystal, for example, will help one to improve the properties of waveguides by the optimization of irradiation conditions and by the proper selection of a CC type.

This study aims to study behavior of the $N_b$ absorption band under various photothermal impacts and to determine the nature and mechanism of formation of defects in γ-irradiated crystals. In the spectral region considered, there are known $N_a$, $N_b$, and $N_c$ centers absorbing at 500, 525, and 550 nm, respectively [3]. Unlike the origin of $N_a$ and $N_c$ bands, the $N_b$ band origin is still unknown. A band at $\lambda_{max} = 527$ nm was observed in [4] in the γ-irradiated LiF crystals with oxygen impurity. During the excitation of this band, a 890-nm luminescence was recorded. The model of a $F_2^+ O_2$ or $F_2^+ H_2$ center was suggested. The defects we considered do not emit under excitation in the 525-nm band. In [5], the formation of $F_4^+$ centers ($\lambda_{abs} = 525$ nm) was observed in the γ-irradiated LiF samples, additionally X-ray irradiated at low temperature, after heating the samples above the $V_k$ peak temperature, i.e. the temperature of the hole delocalization. As will be shown below, the defects we study are neutral. The $N_b$ band was at first observed in [3] in the irradiated and optically bleached samples. It was believed [3] that the high-energy transitions in the $R_N$ center were responsible for the $N_b^*$ absorption band at $\lambda_{max} = 365$ nm. The dichroism in the 525-nm absorption band, similar to that observed in the $R_N$ band of KCL crystals, made it possible to interpret these $N_b$ centers as $R_N$ defects. However, the behavior of these absorption bands in the photothermal transformations [6], especially the antibate changes of the 365-

and 525-nm bands under the second harmonic of a neodymium laser, contradicts this statement.

We studied lithium fluoride single crystals grown from commercial materials by the Stockbarger method in vacuum. For the experiments we used the γ-irradiated samples, the source of γ-radiation was $^{60}$Co with an activity of $3 \times 10^6$ R/h. A sample with $N_b$ centers was prepared by γ-ray irradiation with $D \sim 6 \times 10^7$ R, following bleaching by 700 pulses of xenon lamps and annealing at $T \sim 230°$C for 30 min. The sample was 220 μm thick, since the $F$ centers were to be selectively bleached by the fourth harmonic of a Nd:YAG laser at $T = 78$ K. Before this bleaching, the concentration of $F$ centers in the sample was $2 \times 10^{18}$ cm$^{-3}$. After $2.3 \times 10^4$ laser pulses with $\tau = 10$ ns, the concentration of destroyed $F$ centers reached approximately $\sim 10^{17}$ cm$^{-3}$. In the $N$ (or $R_N$) region of the spectrum, no changes were observed (Fig. 1, curves *1*, *2*). Hence, the defects we consider are neutral and do not interact with electrons of the $F$ centers. The spectrum measured within several hours after the experiment, shows an increase in the concentration of $F_2$ centers, approximately equal to $\sim 5 \times 10^{16}$ cm$^{-3}$ (Fig. 1, curve *3*). Thus, the defect transformation occurs as $F \longrightarrow Va^+ + e^-$; $F + Va^+ \longrightarrow F_2^+$; $F_2^+ + e^- \longrightarrow F_2$. To increase the concentration of $F_2$ centers by $\sim 5 \times 10^{16}$ cm$^{-3}$, a double amount of $F$ centers ($10^{17}$ cm$^{-3}$)is needed, which is confirmed by the experiment.

Dependences of the absorption coefficient of a γ-irradiated ($D \sim 6 \times 10^7$ $R$) LiF crystal on the number of xenon lamp pulses were measured for the bands at 450 nm ($M(F_2, F_3^+)$), 425 nm ($F_2 V_c^-$), 375 nm ($F_3$, $F_L F$, hole center), 525 nm ($N_b$ band of unknown nature), 550 nm ($N_2(F_4)$ or $F_2^+ F_L$), and 620 nm ($F_2^+$). The xenon lamp radiation heated the crystal approximately to $T \approx 200°$C, in spite of water cooling of the quantron. Under the effects of light and temperature, the 550-nm centers transform into 525-nm centers ($N_b$). The 550-nm centers may be either $F_4$ ($N_2$) or $F_2^+ F_L$ ($N_c$) centers. The
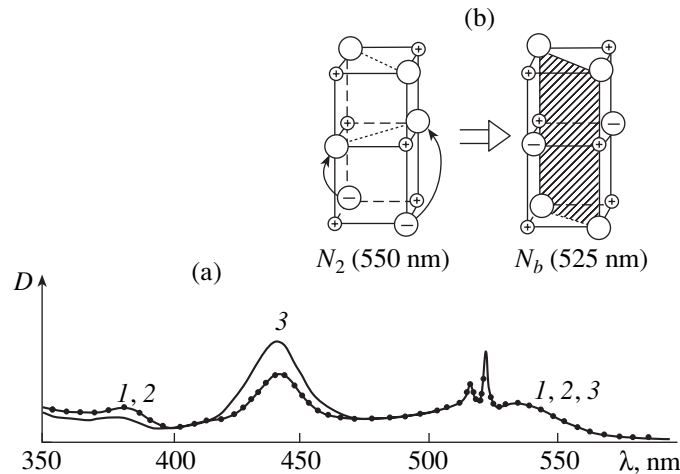
**Fig. 1.** (a) Absorption spectra of LiF crystals with the induced $N_b$ centers at $T = 78$ K (*1*) before and (*2*) after optical bleaching by the fourth harmonic of Nd:YAG laser at $T = 78$ K and (*3*) after the storage of the sample at room temperature for 6 h. (b) Schematic model of the $F_4$ center transformation, $N_2$ (550 nm) $\longrightarrow$ $N_b$ (525 nm).

energy spent on the formation of a reoriented $F_4$ center when all the $F$ centers lie in one (110) plane (Fig. 1b) is evaluated to be approximately 1.78 eV. Thus, the possible reactions occurring under exposure to light and temperature are $F_4 \longrightarrow N_b$ (reorientation of $F_4$ center) and $F_2^+ F_L + e \longrightarrow F_2 F_L$ (525 nm). The latter reaction should be accompanied by the transformation $F_2^+ + e \longrightarrow F_2$. However, analysis of the $F_2^+$ behavior shows that their concentration keeps increasing up to the maximum number of pulses, $n = 700$. Figure 2 shows the dependences of the absorption coefficients in the absorption peaks of various defects on the isochronous annealing temperature for the samples containing photoinduced $N_b$ centers (Fig. 2a) and for γ-irradiated crystals (Fig. 2b).

Analysis of these curves allows one to draw the following conclusions:

(1) $F_4$ centers ($N_1$ band) in the γ-irradiated crystals, having zero-phonon lines at 523.4 and 512.5 nm, contribute to the absorption at $\lambda = 525$ nm ($N_1$ band). This follows from the similar behavior of annealing curves for the bands at $\lambda_{max} = 550$ ($N_2$ band) and 525 nm ($N_1$ band), and is confirmed by the absence of the transformations presented by curves *4* and *6* in Fig. 2a for the samples with the photoinduced defects $F_2^+ F_L (N_c$, 550 nm) and $N_b$ (525 nm).

(2) The destruction of 550-nm centers and the $N_b$ band occurs in the temperature range from 125 to 250°C (Fig. 2a, curve *1*). The $F_2$ centers (Fig. 2a, curves *4, 6*) and $F_L$ defects (Fig. 2a, curve *2*) also grow in number in this temperature range. Taking into account the fact that the decrease in the concentration of 550-nm centers almost by one half (Fig. 2a, curve *3*)

is not followed by an appreciable increase in the $F_2$ center concentration (Fig. 2a, curve *6*), and considering curves *3* and *6* in Fig. 2b, which demonstrate a simultaneous destruction of $F_2$ and $F_4$ centers ($N_2$ band), we come to the conclusion that the main contribution to the $M$ band at the isochronous annealing is made by the $N_b$ centers. The $F_2^+$ centers also make no considerable contribution to the $M$ band because they begin to be destroyed at $T > 200$°C (curve *8*), while the luminescence of $F_2$ centers (Fig. 2a, curve *4*) increases at $T = 200$°C by an order of magnitude. The $F_L$ defects (274 nm) are the product of the decomposition of $F_2^+ F_L$ centers ($N_c$ band at $\lambda_{max} = 550$ nm). An anionic vacancy emerges at the annealing, $F V_a^+ F_L \longrightarrow F + V_a^+ + F_L$, and, hence, the concentrations of $F_L$ centers increase simultaneously with the concentration of $F$ centers (Fig. 2a, curve *9*). Thus, the $N_b$ band destruction gives rise to $F_2$ centers.

Taking into account that the appearance of $F_2$ centers at the annealing can result from the decomposition of both the $F_4$ centers ($F_4 \longrightarrow F_2 + F_2$) and the $F_2 F_L$ defects ($F_2 F_L \longrightarrow F_2 + F_L$), we attempted to study the photoinduced defects ($N_b$ band) by X-ray diffraction analysis. From this analysis, we estimated the lattice cell parameters, the internal stresses caused in the crystal lattice by various effects, and the electron densities at the lattice sites. If the $N_b$ band destruction gives rise to the $F_L$ defects, we would the observe an increase in the relative broadening β of X-ray reflection spots due to the appearance of local stresses (the dimensions of the Li and anion site are 1.56 and 1.36 Å, respectively). The analysis of changes in the broadening diagram of X-ray reflections in the γ-irradiated samples and the
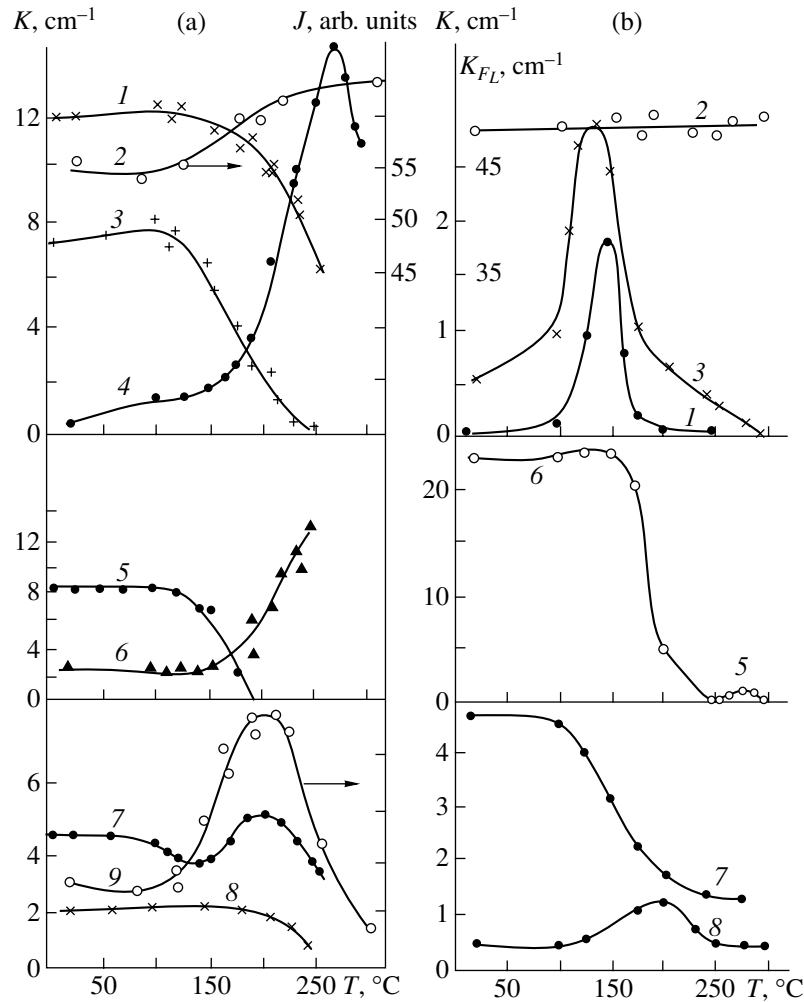
**Fig. 2.** Dependence of the absorption coefficients of peaks at $\lambda_{max}$ = (*1*) 525, (*2*) 274, (*3*) 550, (*5*) 425, (*6*) 450, (*7*) 375, (*8*) 620, and (*9*) 215 nm on the isochronous annealing temperature for the LiF samples (a) optically bleached after the γ irradiation and (b) γ-irradiated with a dose of $D = 6 \times 10^7$ R. Curve *4* was plotted using the emission spectra for $\lambda_{max} = 670$ nm ($\lambda_{exc} = 450$ nm).

samples with the photoinduced 525-nm centers shows no substantial increase in β in the latter samples. The slight changes in the broadening are evidently caused by the contribution made by the $F_L$ centers resulting from the decomposition of $F_2^+ F_L$ defects (550-nm $N_c$ band). The concentration of these defects was very low because, to study the 525-nm centers, the experimental conditions were made optimal for the formation of the $N_b$ absorption band.

Thus, under exposure to light and heating, the $F_4$ centers in the γ-irradiated crystals are reoriented, i.e., the $N_2$ band transforms into the $N_b$ band, and the formed defects are decomposed into $F_2$ centers at annealing.

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