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# The Nature of Optical Pumping Losses in Low-Threshold LiF($F_2$, $F_3^+$) Crystal Microlasers

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**Abstract**—The character of optical losses in Li($F_2$, $F_3^+$) crystals were studied for the first time by methods of optical absorption spectroscopy and X-ray diffraction. It is suggested that centers absorbing at 420 nm represent quasi-metallic defects of the $F_2F_L$ type. © *2004 MAIK "Nauka/Interperiodica".*

In recent years, LiF-based films colored by low-energy electron bombardment have found new applications [1] as active materials in vertical cavity devices (directed LEDs and low-threshold microlasers). These laser structures are pumped with argon lasers at $\lambda$ = 458 nm and, hence, it is important to know the nature of defects absorbing in this spectral region. After the external optical action (optical bleaching by exposure to the integral radiation of a xenon lamp), the room-temperature absorption spectra of $\gamma$-irradiated LiF–Me, O, OH crystals reveal the maximum density of defects absorbing at $\lambda_m$ = 420 nm. This study was aimed at elucidating the nature and the mechanism of formation of these defects (referred to below as 420-nm centers).

The optical absorption in the region of 415 nm in neutron-irradiated LiF crystals at low temperatures was originally observed by Kamikawa *et al.* [2] and assigned to the $F_2$ centers modified by crystal lattice defects. The same interpretation was used by Zhuravlev *et al.* [3]: the absorption band at $\lambda_m$ = 420 nm observed in the spectra of LiF–OH crystals upon electron irradiation and annealing at $T$ = 573 K was assigned to oxygen-modified $F_2$ centers. However, the defects under consideration are not emitting and, hence, cannot belong to the $F_2$-type centers. The colloidal nature of 420-nm centers is also excluded [4], because the spectral intensity distribution in this absorption band exhibits a change at $T$ = 78 K.

We used optical absorption spectroscopy and X-ray diffraction to determine the optimum conditions for the formation of 420-nm centers in LiF. We have studied the photo- and thermoinduced transformations of the radiation defects, evaluated the electron density $\rho(x, o, o)$ in the lattice sites, and determined the X-ray diffraction reflection broadening. The experiments were performed with LiF crystals grown by the Kyropoulos technique and $\gamma$-irradiated to a dose of $D = 6 \times 10^7$–$4 \times 10^8$ R. In order to induce the 420-nm centers, the crystals were exposed to the integral radiation of xenon lamps in the quantron of a 1-MW Kvant-17 laser. Selective optical bleaching was provided by exposure to the fourth harmonic of a YAG-Nd laser ($\lambda$ = 266 nm; $\nu$ = 12.5 Hz; $\tau$ = 10 ns, $n = 10^4$ pulses; $P$ = 0.03 W) at 78 K. The X-ray powder diffraction was studied in a DRON-3M diffractometer using Cu$K_{\alpha1, 2}$ radiation.

**Results and discussion.** Figure 1 shows the optical absorption spectrum measured at 78 K, which displays the absorption peaks at 413.0 and 420.12 nm (curve *2*). The position of a zero phonon line (ZPL) for the absorption band at $\lambda_m$ = 420 nm was determined by the formula $\nu_{00} = \nu_m^{\text{abs}} - (\Delta\nu_{\text{abs}})^2/16\ln2kT$, where $\Delta\nu_{\text{abs}}$ is the full width at half-maximum of the absorption band and $\nu_m^{\text{abs}}$ is the absorption peak position. The ZPL position (420.12 nm) calculated using this formula coincides with the experimental value. The peak at 413.0 and the ZPL at 420.12 nm exhibit analogous behavior in the course of isochronous annealing ($T$ = 573 K), which suggested that both signals belong to the same defect.

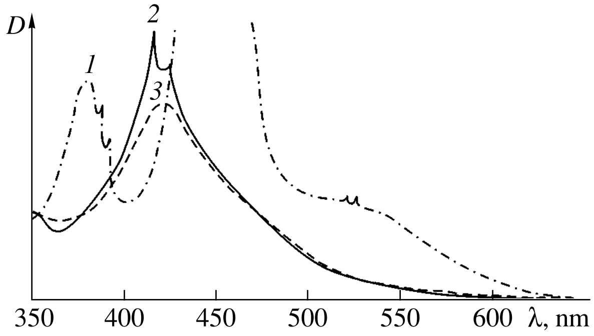

**Fig. 1.** The optical absorption spectra of a LiF–Me, O, OH crystal (*1*) after $\gamma$-irradiation to $D = 2 \times 10^8$ R and (*2*, *3*) after the subsequent optical discoloration by the integral light of a xenon lamp ($n$ = 3000 pulses); measured at $T$ = 78 K (*2*) and 300 K (*3*).

No redistribution of the intensity of these peaks was observed during various transformations of the defect centers.

The efficiency of formation of the defects under consideration was evaluated by studying the crystals γ-irradiated to various doses. The linear accumulation of 420-nm centers with the γ-irradiation dose $D$ increasing in the range from $6 \times 10^7$ to $4 \times 10^8$ R is evidence of the intrinsic nature of these defects in the crystal lattice, since the impurity defects exhibit saturation in the first stage of irradiation at a dose of $10^7$ R. This conclusion is also confirmed by the fact that the 420-nm band is present irrespective of the impurity composition: the ZPL at 420.12 nm was also observed in a vacuum-melted sample irradiated to $D = 4.2 \times 10^8$ R.

The curves of isochronous annealing showed that the optimum temperature for the formation of defects under consideration is ~573 K and confirmed that the 420-nm centers are induced in the course of annealing of γ-irradiated crystals. It should be noted that the efficiency of formation of these centers is higher in optically bleached samples.

The charge state of the 420-nm centers was determined using optical bleaching in the $F$ band at $T = 78$ K under the action of the fourth harmonic of a YAG-Nd laser. A sample with induced 420-nm centers was prepared by γ irradiation to $D \sim 1 \times 10^8$ R followed by the optical discoloration under the action of $n = 5700$ pulses of the integral radiation of a xenon lamp. In the sample with a thickness of ~1 mm, the $F$-center concentration prior to the optical discoloration amounted to $1.6 \times 10^{17}$ cm$^{-3}$. After the exposure to $2.3 \times 10^4$ nanosecond light pulses, the concentration of broken $F$ centers reached $\sim 1.72 \times 10^{16}$ cm$^{-3}$. At the same time, no changes were observed in the region of optical absorption studied. These results indicate that the 420-nm centers possess a neutral charge and do not interact with electrons of the $F$ centers. This explains the high optical stability of the defects under consideration, which are not broken by the light with a wavelength of 420 nm.

A phototransformation of the radiation defects was observed in the stage of induction of the 420-nm centers under the action of the integral radiation of a xenon lamp. It was found that defects with the ZPL at 520.0 nm and $\lambda_m = 508$ nm are converted into the centers with the ZPL at 413.0 nm (Fig. 2). Taking into account the analogous behavior of the absorption band with $\lambda_m = 508$ nm and the ZPL at 520.0 nm under the external optical action, it was suggested that the ZPL at 520.0 nm belongs to the centers absorbing at $\lambda_m = 508$ nm. As is known, these centers are formed as a result of breakage of the $F_3^+$ color centers.

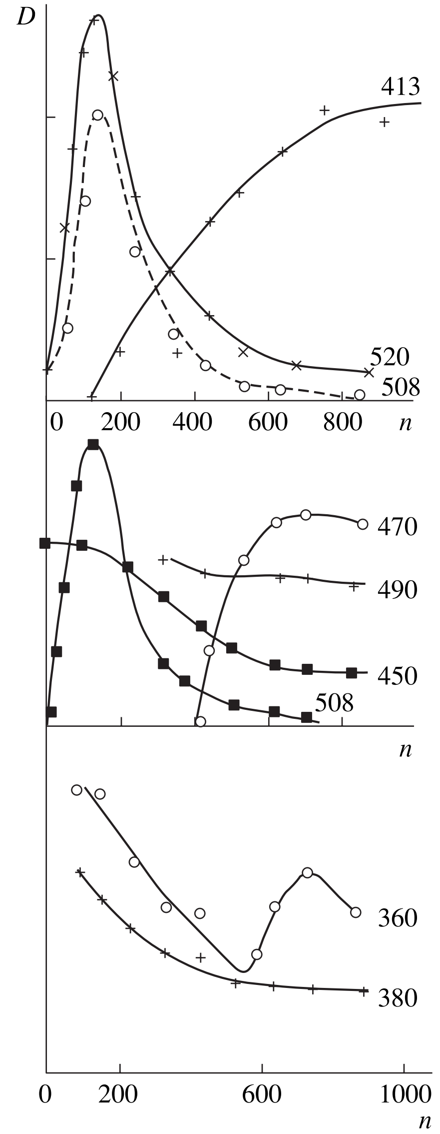

**Fig. 2.** Variation of the intensity of absorption peaks in the spectrum of a LiF–Me, O, OH crystal (γ-irradiated to $D = 8 \times 10^7$ R) in the course of the optical discoloration by the integral light of a xenon lamp ($n$ is the number of light pulses): 413.0 nm (ZPL of the defects under consideration); 520.0 (ZPL of the 508-nm centers); 508 nm ($F_L V_a^+ V_a^+ + V_c^-$); 470 and 490 nm (probably Li colloids); 450 nm ($F_2$, $F_3^+$); 360 nm ($V_k$ and Li colloids); 380 nm ($F_3$ and $F_LF$ centers).

Recently [5], we demonstrated that the action of light and temperature leads to displacement of the electron density from $F_3^+$ color centers in the excited state toward the nearest lithium cation. As a result, there appears an $F$ center containing lithium atom ($F_L$):

$$F_3^+ + Li^+ + h\nu \longrightarrow (F_3^+)^* + Li^+$$
$$\longrightarrow FV_a^+V_a^+ + Li^0 \longrightarrow F_LV_a^+V_a^+ + V_c^-.$$

The cation vacancy becomes free at a temperature of 573 K. This process is observed in the first stage of optical bleaching: beginning with $n = 150$ pulses ($D = 8 \times 10^7$ R), the centers absorbing at 508 nm are converted into 420-nm centers. A high-temperature peak of thermostimulated luminescence in LiF was observed at ~573 K in [6]. Taking into account the effective formation of defects under consideration and the release of electrons from traps at this temperature, we may suggest that the localization of electrons on the anion vacancies of the centers absorbing at 508 nm leads to the formation of a new defect: $F_LF_2$. The appearance of a lithium atom in the $F$ center will produce local stresses in the crystal lattice. This, in turn, must decrease the lattice parameter and cause broadening of the diffraction reflections, in agreement with what is observed in experiment.

It should be noted that an increase in the level of internal stresses might also be caused by an increase in the temperature. In this case, the electron density at the lattice sites must decrease: the greater the mean-square displacement of atoms from the equilibrium position, the weaker the interference peaks and the lower the $\rho(x, o, o)$ values obtained from the Fourier synthesis. However, an analysis of the electron density showed that this value increases at the lattice sites of both lithium and fluorine. Therefore, the increase in the internal stresses in the crystal lattice is due to the formation of a new defect.

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