Laser luminescent polarization microscopy of defects induced in lithium fluoride crystals by femtosecond pulses

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Abstract. We propose a spatial statistical model, based on the model of moving foci, of distribution of aggregate centers and other final products of reactions after the passage of a femtosecond laser pulse in a lithium fluoride crystal. Concentration of these defects grows higher on the way from the periphery to the center of filament trace. This model was confirmed experimentally with use of polarization confocal luminescence scanning microscopy method. The research results showed that the periphery of the filament trace is filled predominantly with stable F centers, the region closer to the filament trace center – with F₂ – color centers, F₃⁺ centers appear with the increasing concentration of anionic vacancies as the distance to the center of the filament trace decreases on the way to the filament trace center. Strongly damaged lattice area containing colloidal lithium particles and dislocation loops is located in the filament trace center itself.

1. Introduction
The effectiveness of the interaction of optical radiation with a condensed medium is largely determined by the type (multipolarity) and the orientation of elementary oscillators characterizing quantum systems that interact with radiation [1]. For example, in the case of electrodipole interaction, the interaction energy of optical radiation with the luminescence centers depends on the orientations of the electric field vector and the electric dipole moment vector of the elementary oscillator associated with the quantum transitions responsible for the absorption and emission of light in the luminescence centers. Polarized luminescence methods are used to study the nature and orientation of the absorbing and radiating oscillators modeling the transitions in the color centers [2, 3]. The theory of polarized luminescence of cubic crystals with anisotropic centers is based, on the one hand, on group theoretical representations of solid state spectroscopy about the energy states of active centers in fields of different symmetry and about the transitions between these states that are modeled by classical oscillators, and, on the other hand, on representations about the hidden anisotropy of cubic crystals – about the orientational degeneracy of individual equivalent groups of centers that differ in orientation [3].
The aim of this work is to use polarized luminescence methods in laser scanning confocal microscopy to investigate the spatial distribution of defects induced by intense femtosecond pulses in the self-focusing and filamentation mode of laser radiation.

2. Theoretical model

It is known that color centers characteristic of radiation-colored lithium fluoride crystals are effectively created in wide-band LiF crystals under the action of near IR femtosecond laser radiation. The formation of color centers in the investigated crystals takes place due to nonlinear absorption of the energy of laser radiation by the electron subsystem of matter with the formation of electron-hole pairs, as a result of self-focusing and filamentation of the exciting femtosecond laser radiation. The mechanism of formation of color centers under the influence of femtosecond laser radiation involves highly nonlinear generation of electron-hole pairs in the filament passage region, their recombination with formation of anionic excitons, decay of the excitons into Frenkel defects by the Luschik-Vitol-Hersh-Puli mechanism, their charge exchange, migration and aggregation [4, 5]. In contrast to irradiation with X-ray radiation, when relatively uniform radiation effect occurs over the whole surface (volume) of the sample (as evidenced by a homogeneous distribution of induced defects), the defect formation upon femtosecond irradiation is local in the places where self-focusing and multiple filamentation of laser radiation occur.

\[ P^{(m)} = J^{(m)} \cdot S^{(m)} \]

where \( P^{(m)} \) is the thickness of the time layer, and \( J^{(m)} \) is the light intensity in the \( m \)-th focus. Below to the right is the shape of the filament with a constant polarization of light, the largest cross-section of the focus at \( N \), corresponds to the focusing of the time layer \( P^{(N)} \).

Before proceeding to study of the spatial distribution of color centers formed in a LiF crystal after the passage of a femtosecond laser pulse, it is necessary to consider the mechanism of filamentation, self-focusing and defocusing of laser beam in a crystal. The authors have the opinion that in this case the model of moving foci is applicable. According to the model of moving foci [6], the beginning of filamentation is determined by focusing a temporal layer with the power \( P_{\text{peak}} \) (see figure 1, left), the
distance to the start (point 1 in figure 1, right) can be calculated using the Marburger formula [7]. Subsequent foci 2; 3; ... …N from temporal layers with higher power \( P^{(m)} \) to the maximum \( P^{(N)} \) go towards the pulse. Temporal layers decreasing in power from \( P^{(N)}; P^{(N+1)}; ... \) to \( P^{(2N)} = P_{\text{peak}} \) are focused at points \( N; N + 1; ... \); 2N arranged along the pulse propagation. Thus, the focus moves from the most distant (relative to the input point of the pulse) point 1 toward the pulse to the point \( N \), and then backward along the pulse from point \( N \) to point 2N (figure 1, right).

As shown in figure 2a, when the balance between self-focusing and defocusing is reached, most of the beams from the laser beam are reflected from the cylindrical surface, i.e. on this surface the density of electrons in the conduction band is sufficiently high and the surface behaves like a metallic mirror. Most of the radiation from the laser pulse does not enter the short cylinder. After passing of the pulse, electron-hole pairs are formed in this cylindrical layer near the surface with critical electron density, formation of excitons occurs. Excitons decay leads to generation of a number of primary defects mobile at room temperature, figure 2b. The concentration of these defects increases as you approach the center of the filament trace. Thus, it can be assumed that the periphery of the spur – region 1 (figure 2c) is mainly filled with the stable F centers. The region 2 closer to the center of the spur is mainly filled with \( F^3 \) – color centers. As the concentration of anion vacancies increases, \( F^{3+} \) – centers appear – region 3, etc. This assumption is confirmed by the results of experimental studies using the method of polarization confocal scanning luminescence microscopy realized with the Microscope MicroTime 200.

**Figure 2.** Model of the distribution of aggregate centers and other final products of reactions in the filament passage region: a) the surface of the moving focus; b) generation of mobile primary defects from the surface of the focus in the cross section; c) model of the distribution of stable defects in the cross section of the filament track.

**Figure 3.** Orientations of \( F^2 \) (a) and \( F^{3+} \) (b) – color centers in a cubic lattice: \( K^+ \) – cationic node; \( A^- \) – anionic node; \( E \) is the electric field vector and \( k \) is the wave vector.
The presence of a set of orientationally degenerate groups of centers in the crystals with anisotropic centers leads to the fact that in case of excitation of these crystals by light, with the corresponding mutual orientation of the acting electric vector of the incident light wave and the crystal symmetry axes, the light will be absorbed mainly by centers with certain orientation. As a result, the distribution of centers that have absorbed light and passed into excited state turns out to be anisotropic. The light emitted by these centers will be polarized in a certain way, and when summing over all possible orientations of the center the degree of polarization of the total luminescence of these centers will be different from zero and depends on the orientation of the crystal with respect to the direction and polarization of the exciting light and the direction of observation of the luminescence (see figure 3).

The measure of polarization of luminescence with linearly polarized exciting light is the degree of polarization:

\[ P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp}, \]

Here \( I_\parallel \) is the intensity of the polarization component of the luminescence, polarized in the same plane as the exciting light, and \( I_\perp \) – in the orthogonal to it.

Let’s calculate the degree of polarization of the luminescence of the \( F_2 \) centers in the LiF crystal under the conditions of their chaotic distribution. Let \( P_i^{\text{abs}} \) be the probability of absorption of the exciting light \( i \) by the oscillator per unit time, and \( P_i^{\text{em}} \) be the probability of emission of the photon of the luminescence in the direction of observation \( i \) by the oscillator per unit time. Then the radiation intensities \( i \) from the oscillator with polarization parallel and perpendicular to the vector \( E \) in the direction of observation \( I_\parallel^i \) and \( I_\perp^i \) are: \( I_\parallel^i = P_i^{\text{abs}} P_i^{\text{em}} \cos^2 \alpha_i \) and \( I_\perp^i = P_i^{\text{abs}} P_i^{\text{em}} \sin^2 \alpha_i \), respectively, where \( \alpha_i \) is the angle between the projection of the oscillator on the (100) plane and the vector \( E \) (figure 4).

\[ \text{Figure 4. The projections of linear oscillators on the (100) plane correspond to one of the six possible orientations of the F2 center, the exciting light fell along the normal to the plane of the pattern and had a polarization E. The luminescence was also observed in the direction perpendicular to the plane of the figure.} \]

The calculated values of the probabilities and intensities of the polarized luminescence components are given in the table 1.
Table 1. Calculated values of the probabilities and intensities of the polarized luminescence components.

| Term          | Expression                                                                 |
|---------------|-----------------------------------------------------------------------------|
| $P_{1}^{abs}$ | $C_1 \cos^2\left(\frac{\pi}{4} - \alpha\right)$                         |
| $P_{2,3}^{abs}$ | $C_1 \frac{1}{2} \cos^2 \alpha$                                               |
| $P_{4}^{abs}$ | $C_1 \cos^2\left(\frac{\pi}{4} + \alpha\right)$                         |
| $P_{5,6}^{abs}$ | $C_1 \frac{1}{2} \cos^2\left(\frac{\pi}{4} - \alpha\right)$             |
| $P_{1}^{em}$  | $C_2$                                                                      |
| $P_{2,3}^{em}$ | $C_2 \frac{1}{2}$                                                          |
| $P_{4}^{em}$  | $C_2$                                                                      |
| $P_{5,6}^{em}$ | $C_2 \frac{1}{2}$                                                          |
| $I_1^{II}$   | $C \cos^4\left(\frac{\pi}{4} - \alpha\right)$                           |
| $I_{2,3}^{II}$ | $C \frac{1}{4} \cos^4 \alpha$                                                |
| $I_2^{II}$   | $C \cos^4\left(\frac{\pi}{4} + \alpha\right)$                           |
| $I_{5,6}^{II}$ | $C \frac{1}{4} \cos^4\left(\frac{\pi}{4} - \alpha\right)$               |
| $I_1^\perp$  | $C \cos^2\left(\frac{\pi}{4} - \alpha\right) \times \sin^2\left(\frac{\pi}{4} - \alpha\right)$ |
| $I_{2,3}^\perp$ | $C \frac{1}{4} \cos^2 \alpha \sin^2 \alpha \times \sin^2\left(\frac{\pi}{4} + \alpha\right)$ |
| $I_4^\perp$  | $C \cos^2\left(\frac{\pi}{4} + \alpha\right) \times \sin^2\left(\frac{\pi}{4} + \alpha\right)$ |
| $I_{5,6}^\perp$ | $C \frac{1}{4} \cos^2\left(\frac{\pi}{4} - \alpha\right) \times \sin^2\left(\frac{\pi}{4} - \alpha\right)$ |

Where $C_1$; $C_3$ and $C=C_1C_2$ are constants.

Next, summing the contributions from the orientational ensembles of the centers, we obtain:

$$I_\parallel = \sum_{i=1}^{6} I_i^{II} = C \frac{1}{4} (4 + \sin^2 2\alpha) \quad I_\perp = \sum_{i=1}^{6} I_i^\perp = C \frac{1}{4} (1 + \cos^2 2\alpha)$$

and for the degree of polarization of the luminescence:

$$P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} = \frac{1 + \sin^2 2\alpha}{3}$$

Calculation of the polarization degree of the luminescence $P$ excited and observed under the given conditions with relation to the angle of rotation of the $\alpha$ crystal shows that the luminescence polarization degree changes from 0.33 to 0.66, and the obtained dependence is confirmed experimentally. For crystallographic sections other than (100), the value lies in the same interval 0.33-0.66 and depends on the orientation of the crystal [2].

3. Results of the experiment and their discussion

The experimental verification of the method was carried out with use of the Microscope MicroTime 200. We realized a two-channel luminescence detection circuit (receivers SPAD1 and SPAD2): radiation was divided by the polarizer into two components perpendicularly and parallelly polarized with respect to the exciting radiation. As a result, we get two images, process them, and construct the image corresponding to the distribution of the luminescence polarization degree.

We investigated a LiF crystal irradiated with a series of 1000 femtosecond pulses in the self-focusing and filamentation mode of laser radiation. In this experiment, the electric field intensity vector $E$ of the exciting radiation was directed along the diagonal of the face of the cube (the crystallographic $C_4$ axis), i.e. it made an angle ($45^\circ$) with the [100] axis. For a given luminescence observation geometry, the degree of polarization for each type of center under study will have a fixed value.

Images of the cross sections of the filaments tracks with selection of color centers over the decay time are shown. In figure 5 on the left the decay time of the luminescence is represented with rainbow pseudo colors. The centers of luminescence with the lowest decay time correspond to blue color and the centers with the largest decay time correspond to red color. In our case green color represents $F_3^\perp$ centers and red color represents $F_2$ centers.
In figure 5 the images of the cross section of the filaments traces are shown, to the right - the distribution of luminescence of color centers with selection over the polarization degree (scale values from 0 to 0.8). The green color corresponds to a value of the polarization degree of 0.33 – this is \( F^3_3 \) – color centers with decay time of 8 ns. Red corresponds to the value of the polarization degree of 0.66 – this is \( F^2_2 \) centers with a decay time constant of 16 ns.

We propose a spatial statistical model (based on the model of moving foci) for the distribution of aggregate centers and other final products of reactions after the passage of a femtosecond laser pulse in a lithium fluoride crystal. This model was confirmed experimentally by the method of polarization confocal luminescence scanning microscopy.

In contrast to the homogeneous distribution of defects characteristic of crystals irradiated with gamma radiation or X-rays, when irradiation of crystal is conducted with femtosecond laser pulses, the distribution of color centers and other stable defects is not homogeneous. The concentration of these defects increases as you approach the center of the filament trace. Thus, the periphery of the filament trace is filled predominantly with stable \( F \) centers, the region closer to the filament trace center - with \( F^2_2 \) – color centers, \( F^3_3 \) centers appear with the increasing concentration of anionic vacancies as the distance to the center of the filament trace decreases. In the center there is a strongly damaged lattice area containing colloidal lithium particles and dislocation loops.

**Figure 5.** Images of the cross section of filaments traces in a LiF crystal. To the left is the distribution of luminescence of color centers with selection over decay time, to the right is the distribution of luminescence of color centers with selection over the polarization degree.

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