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Formation of Defects in Lithium Fluoride Ceramics upon Irradiation with Femtosecond Laser Pulses

M. A. Moiseeva[a], S. V. Alekseev[b], V. P. Dresvyanskiy[a], V. F. Losev[b], and E. F. Martynovich[a]

[a] *Institute of Laser Physics (Irkutsk Branch), Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia*

[b] *Institute of High Current Electronics, Siberian Branch, Russian Academy of Sciences, Tomsk, 634055 Russia*

e-mail: sasha.moiseeva@mail.ru

Abstract—The interaction between femtosecond laser radiation in the filamentation mode and lithium fluoride optical ceramics is investigated experimentally. It is shown that irradiating optical ceramics based on lithium fluoride with femtosecond laser pulses in the near infrared spectral region effectively produces luminescence centers characteristic of radiation-colored single crystals.

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INTRODUCTION

The study of optical nanoceramics is of interest from the viewpoint of its possible applications. Extensive research is now under way for different optical materials that have a number of advantages over crystalline materials. For example, nanoceramics is a good material for producing bulk and layered highly nonlinear fluorescent media for information storage [1, 2].

Compared to single-crystalline media, the mechanisms of color center formation in nanoceramics based on alkali–halide crystals remain poorly understood. This is especially true of the formation of defects caused by irradiation with femtosecond laser pulses in the filamentation regime.

It is useful to consider the processes of defect formation in nanoceramics by comparing them to the similar processes that occur in single crystals of the same composition. Mechanisms of the creation and excitation of photoluminescence in color centers in LiF crystals using high power femtosecond laser pulses were considered in [3, 4], where it was shown that two conditions necessary for the formation of color centers upon irradiation with a titanium–sapphire laser (~800 nm, 1.5 eV) were self-focusing and the subsequent filamentation of the laser radiation, leading to a dramatic rise in its intensity, and to its highly nonlinear absorption.

EXPERIMENTAL

Our experimental setup for irradiating ceramics with femtosecond laser pulses contained a titanium-sapphire laser generating 50 fs pulses with energies of about 6 mJ and spectral emission line maxima at a wavelength of 950 nm. In our experiments, we used a configuration with narrow-aperture external focusing of light on a sample using a 425 mm focal length lens, with the sample at some distance before the lens's focal point.

The ceramics sample was free to move along and across the direction of the laser beam. Movement in transverse direction allowed us to discern the impact of laser radiation pulses in the space inside the sample. By moving the samples along the beam, the intensity of laser radiation inside a sample could by varied.

The ceramic samples were fabricated by mechanically pressing single crystals of lithium fluoride heated with a gas torch to a temperature close to the melting point. The resulting samples were wafers optically transparent in the visible range of 7 to 20 mm and up to 5 mm thick.

The topology of defect formation and the photoluminescence of the samples irradiated with the laser were studied on a highly sensitive MicroTime 200 confocal scanning luminescent microscope with picosecond time resolution manufactured by PicoQuant Gmbh with space-selective time-correlated single-photon counting. The microscope could register the longitudinal and transverse spatial distributions of defect concentrations produced by laser irradiation and plot images of microscopic objects inside the irradiated volume of the medium in luminescent emission with a scanning step of 10 nm and images selected according to the emission decay time. The photoluminescence spectra of LiF upon excitation with laser radiation at a wavelength of 450 nm were recorded on an Ocean Optics 65000 spectrometer.

RESULTS AND DISCUSSION

Microscopic studies show that in the studied ceramics samples, luminescent defects (color centers) quickly formed as a result of exposure to femtosecond radiation. These defects were distributed over thread-like channels produced in the regions where laser radi-

ation filaments formed as a result of multiple self-focusing.

Figure 1 shows the distribution of color centers in the channels induced by a series of 100 femtosecond laser pulses at different distances L (20 and 40 mm) from the lens's focal point to the sample surface.

The formation of filaments began at the distance from the crystal surface that corresponded to the effective length of self-focusing.

The density of the filaments that formed is worthy of note. From a comparison of the data obtained in this work and the results from studying the irradiation of lithium fluoride single crystals with femtosecond pulses [6], it was evident that the density of filament distribution was much higher in the ceramics, due to the lower homogeneity of the ceramics samples relative to single crystals.

It was also been that in the ceramics, the density of filaments grew as the sample moved closer to the focus; i.e., the density of filaments also depended on the intensity of the radiation. No such dependence was observed in single crystals.

It is known that the effective length of self-focusing is to a large degree determined by the intensity of laser radiation.

In our investigations, the laser radiation intensity was determined by the distance of the lens's focal point from the sample surface; i.e., the farther the sample was from focus, the longer the effective self-focusing length and the depth at which filamentation began.

This dependence was compared to the results from a computer simulation of filamentation based on the nonlinear Schrödinger equation.

Our simulation was performed for the formation of channels formed by color centers in LiF ceramics with 6 mJ pulses of laser energy 50 fs in duration. The initial pulse diameter was 0.1 mm. Our model allowed for preliminary focusing of the beam by a lens with a focal length of 425 mm.

Our mathematical model was based on the nonlinear Schrödinger equation (NSE) and allowed for diffraction, 9-photon absorption, and self-focusing. The NSE is a differential equation for the complex enveloping amplitude of electric field strength $E(x, y, z)$:

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + 2ik\frac{\partial E}{\partial z} + k^2\left(n_2|E|^2 + i\mu|E|^{2K-2}\right) = 0. \quad (1)$$

Here, $k = 2\pi/\lambda$ is the wavenumber; n_2 is the nonlinear refraction index; $K = 9$ is the multiplicity of photons corresponding to a wavelength of 950 nm.

The nonlinear refraction index we used was $n_2 \approx 4 \times 10^{-14}$ esu and was obtained from the known critical self-focusing power in lithium fluoride given by the formula $P_{cr} = \dfrac{cn_0}{2n_2k^2}$. Our value of the nonlinear

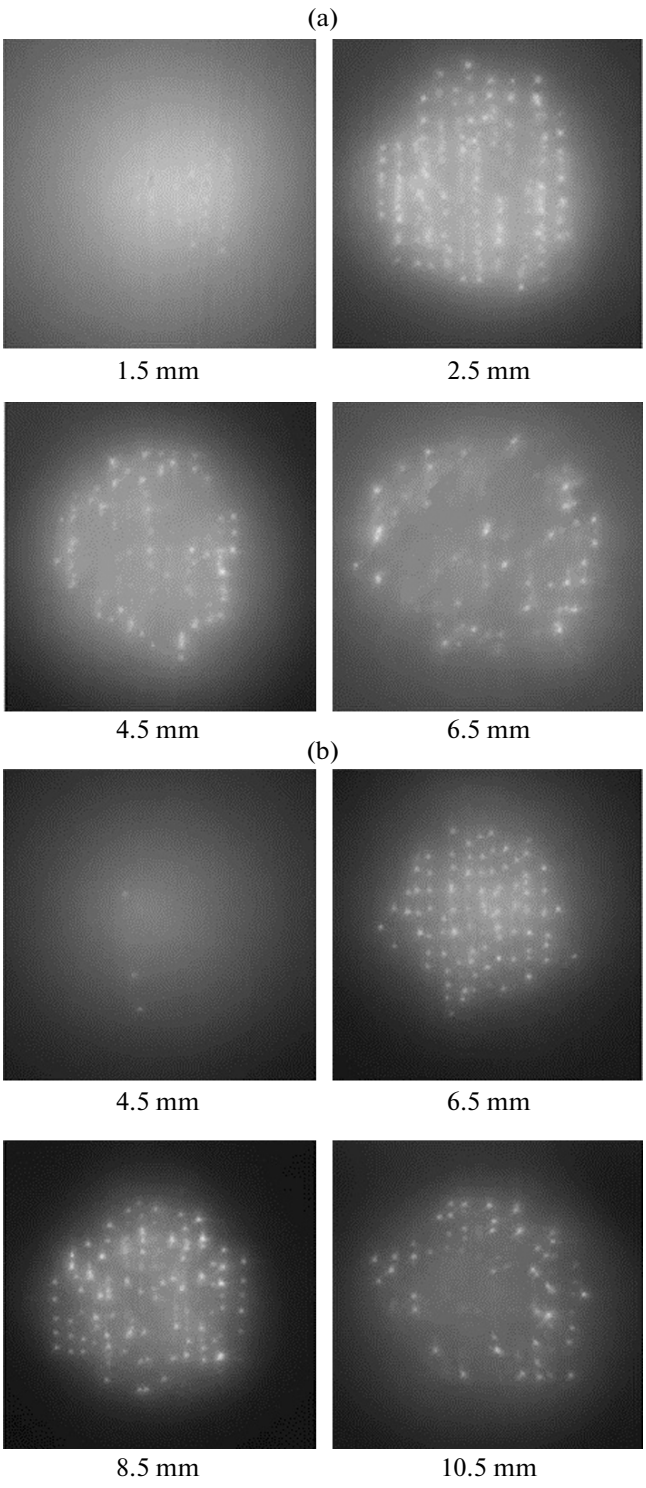

Fig. 1. Photographs of the longitudinal distribution of luminescence centers in channels at different depths from the output surface. The channels were produced by series of 100 femtosecond laser pulses (Olympus IX71 microscope): (a) distance L from the lens's focal point to sample surface, 20 mm; (b) distance L from the lens's focal point to the sample's surface, 40 mm.

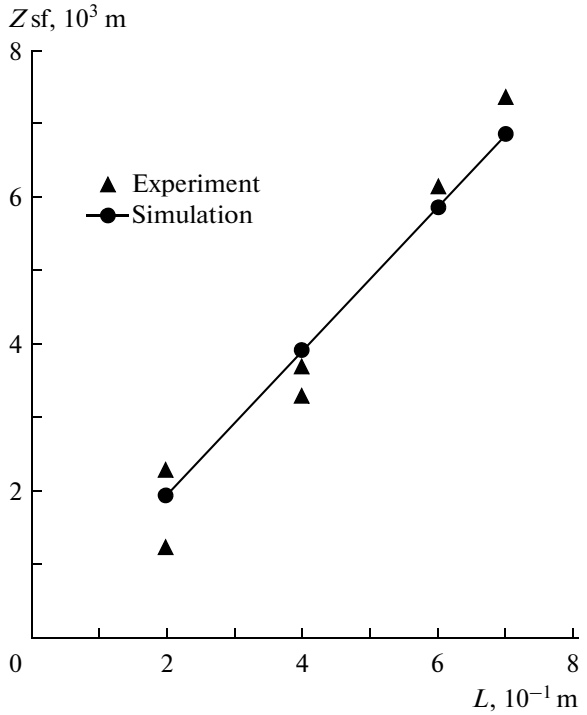

Fig. 2. Experimental and calculated dependences of the self-focusing length of femtosecond laser pulses in the studied ceramics samples on the distance from the sample's input surface to the lens's focus.

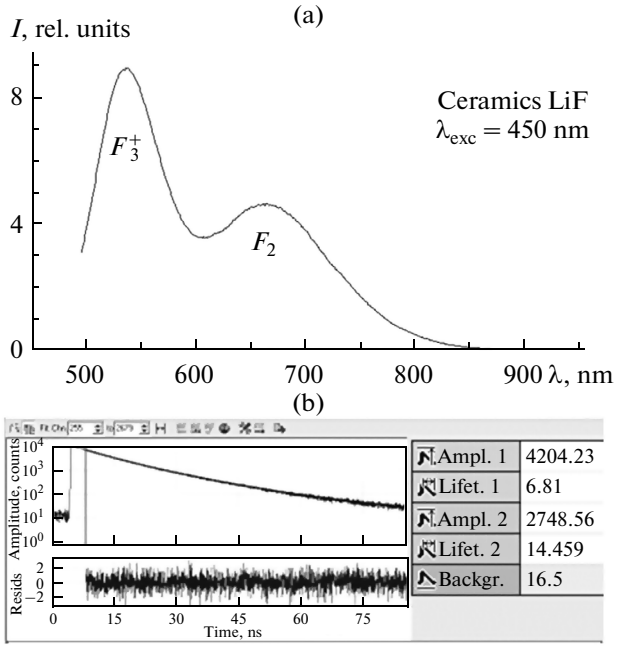

Fig. 3. Spectral–kinetic characteristics of luminescent defects: (a) luminescence spectra of the fluoride–lithium ceramics samples irradiated with femtosecond laser pulses; (b) curve of luminescence decay kinetics.

absorption coefficient was chosen to ensure conformity between the calculated diameter of small-scale channels formed by color centers and the observed diameter values (2–3 μm).

Ii was assumed that the transverse profile of the pulse at the sample input had a Gaussian shape:

$$E(x,y)\big|_{z=0} = E_0\left[1 + p(x,y)\right]\exp\left[-\frac{\left(x^2+y^2\right)}{2a^2}\right]. \quad (2)$$

Here, weighted parameter E_0 is the electric field amplitude along the laser beam's axis; a is the beam diameter; and function $p(x, y)$ describes small perturbations in the beam profile. Perturbations break down the initial pulse into many filaments. The longitudinal pulse profile was also assumed to be Gaussian.

NSE (1) was solved using a finite-difference scheme. From the calculated spatial–temporal distribution of the laser radiation intensity in the medium, we obtained the distributions of the electron-hole plasma density and the color centers formed after plasma relaxation.

Our simulation results gave a qualitative description of the experimental dependence of the self-focusing length on the position of the lens (Fig. 2). The experimental and theoretical dependences were both adequately approximated by linear function $l = 0.98L$.

The results from our investigation of the spectral–kinetic characteristics of luminescent defects formed in optical lithium fluoride ceramics as a result of small-aperture external focusing under the impact of a single femtosecond laser pulse are shown in Fig. 3. The photoluminescence spectrum excited by laser radiation with the wavelength $\lambda_{exc} = 450$ nm for fluoride ceramics samples irradiated with femtosecond laser radiation is presented in Fig. 3a. The photoluminescence kinetics of the centers induced by femtosecond laser radiation are shown in Fig. 3b.

Analysis of the these results shows that upon the excitation of luminescence by laser radiation with the wavelength $\lambda_{exc} = 450$ nm (the M-band of absorption) two luminescence bands characteristic of radiation-colored lithium fluoride single crystals were observed in the luminescence spectrum of the fluoride ceramics samples irradiated with femtosecond laser pulses. One of these was due to F_2 centers with the maximum emission wavelength $\lambda = 680$ nm; the other was due to F_3^+ centers with maxima at $\lambda = 540$ nm. The obtained values of luminescence decay time constants, 14.5 and 6.8 ns (Fig. 3b), were also close to the characteristic decay times of F_2 and F_3^+ centers in single crystals (16 and 8 ns, respectively) [5].

The above results show that color centers characteristic of radiation-colored single crystal are effectively created as a result of exposure to femtosecond laser radiation in the near-infrared spectral region in

optical ceramics based on wide bandgap LiF compounds.

It is known that the first stage in the formation of color centers is the generation of electron-hole pairs. The energy needed for their generation is greater than the bandgap width, which for lithium fluoride is around 13–14 eV. The photon energy corresponding to radiation from a femtosecond titanium–sapphire laser with $\lambda = 800$ nm is ~1.5 eV. The formation of color centers in the studied ceramics was thus a consequence of multiphoton absorption by the electronic subsystem of the laser radiation energy with the formation of electron–hole pairs as a result of self-focusing and the filamentation of the exciting femtosecond laser radiation. The multiphoton mechanism was confirmed by the study of lithium fluoride single crystals in [6].

CONCLUSIONS

It was shown that luminescence centers are effectively created upon exposure to femtosecond laser radiation in the near-infrared spectral region in optical ceramics based on lithium fluoride. The luminescence centers produced by laser radiation are the color centers characteristic of radiation-colored single crystals. These centers are distributed over threadlike channels produced in the regions where laser radiation filaments are formed as a result of multiple self-focusing.

The mechanism of color center formation includes the high-energy generation of electron-hole pairs in the region of filament transmission, or in the regions of radiation focusing, filament recombination with the formation of anionic excitons, the decay of excitons into Frenkel defects, and their recharging, migration and aggregation [7].

Our simulation of the filamentation process was performed using a solution to the nonlinear Schrödinger equation. The results were in good agreement with our experimental findings.

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