ISSN 1062-8738, Bulletin of the Russian Academy of Sciences. Physics, 2016, Vol. 80, No. 1, pp. 85–88. © Allerton Press, Inc., 2016.
Original Russian Text © V.P. Dresvyanskiy, M.A. Moiseeva, A.V. Kuznetsov, D.S. Glazunov, B. Chadraa, O. Bukhtsoozh, B. Zandan, N. Baasankhuu, E.F. Martynovich, 2016, published in Izvestiya Rossiiskoi Akademii Nauk. Seriya Fizicheskaya, 2016, Vol. 80, No. 1, pp. 93–96.

Storing Energy in Lithium Fluoride Crystals Irradiated with Femtosecond Laser Pulses

V. P. Dresvyanskiy[a], M. A. Moiseeva[a], A. V. Kuznetsov[a], D. S. Glazunov[a], B. Chadraa[b], O. Bukhtsoozh[b], B. Zandan[b], N. Baasankhuu[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 Physics and Technology, Mongolian Academy of Sciences, Ulaanbaatar, 210651 Mongolia*
e-mail: filial@ilph.irk.ru

Abstract—The release of energy in the form of the light sum of thermally stimulated luminescence (TSL), stored under conditions of self-focusing and the multiple filamentation of femtosecond laser radiation during the interaction between model wide-bandgap dielectric crystals of lithium fluoride is studied. It is shown that F_2 color centers are important centers of emission in the TSL process.

DOI: 10.3103/S106287381601007X

INTRODUCTION

It is known that luminescent defects are effectively created when dielectric crystals (preferably with an excitonic defect formation mechanism) are irradiated with intense femtosecond laser pulses [1, 2]. Simple and aggregate color centers, which are typical of radiation coloring, are induced by femtosecond laser pulses in such crystals [3, 4]. They are formed as a result of the multiphoton absorption of laser radiation energy by the electronic subsystem of the irradiated material with the production of electron-hole pairs upon an increase in intensity, due to the self-focusing and filamentation of the excitation femtosecond laser radiation [5]. The production of color centers in a material exposed to femtosecond laser radiation involves the highly nonlinear generation of electron–hole pairs in the region of filament propagation, their recombination with the production of anionic excitons, the decay of excitons into Frenkel defects, the charge exchange between them, and their migration and aggregation [6].

The aim of this work was to investigate the mechanisms of energy storage in lithium fluoride crystals irradiated with femtosecond laser pulses, the formation of structural defects that accumulate laser radiation energy, the transfer of this energy to recombination centers, and its release. The release of energy in the form of a light sum of thermally stimulated luminescence, stored under conditions of the self-focusing and multiple filamentation of femtosecond laser radiation was studied for the first time.

EXPERIMENTAL

Our experiments were conducted using model wide-bandgap crystals of lithium fluoride (LiF) grown by the Kyropoulos method in air. Samples in the shape of rectangular blocks with cross sections of around 10×10 mm^2 and lengths of 30–35 mm were fabricated. The surfaces of these samples were natural cleavage planes, and the crystals' end faces, which were subjected to laser irradiation, were polished. The samples were transparent and colorless prior to irradiation, and their IR absorption spectra revealed the presence of oxygen and hydroxyl impurities that were identified based on the literature data.

The experiments on irradiating these crystals with femtosecond laser radiation were conducted using a titanium–sapphire laser that generated pulses with a duration of 50 fs and an energy of about 6 mJ. The maximum of the emission spectrum of this laser was at the wavelength of 950 nm. The excitation radiation was focused with a lens having a focal length of 425 mm.

The mode of interaction between the light and the samples corresponded to the conditions of small-aperture external focusing (the excitation laser radiation pulses were focused with a lens having a long focal length). The sample could be moved along and transverse to the laser beam. The sample's transverse motion allowed us to resolve spatially the effects produced by isolated laser irradiation pulses, while its motion along the beam helped to vary the intensity of laser radiation within the crystal. The total energy of laser radiation propagating through the sample was determined from the number of pulses.

The topology of defect formation and the photoluminescence of the irradiated samples were studied using a MicroTime 200 (PicoQuant) high-sensitivity scanning confocal fluorescence microscope with picosecond time resolution and spatially selective time-correlated single photon counting. The spectra of photoluminescence produced by picosecond laser

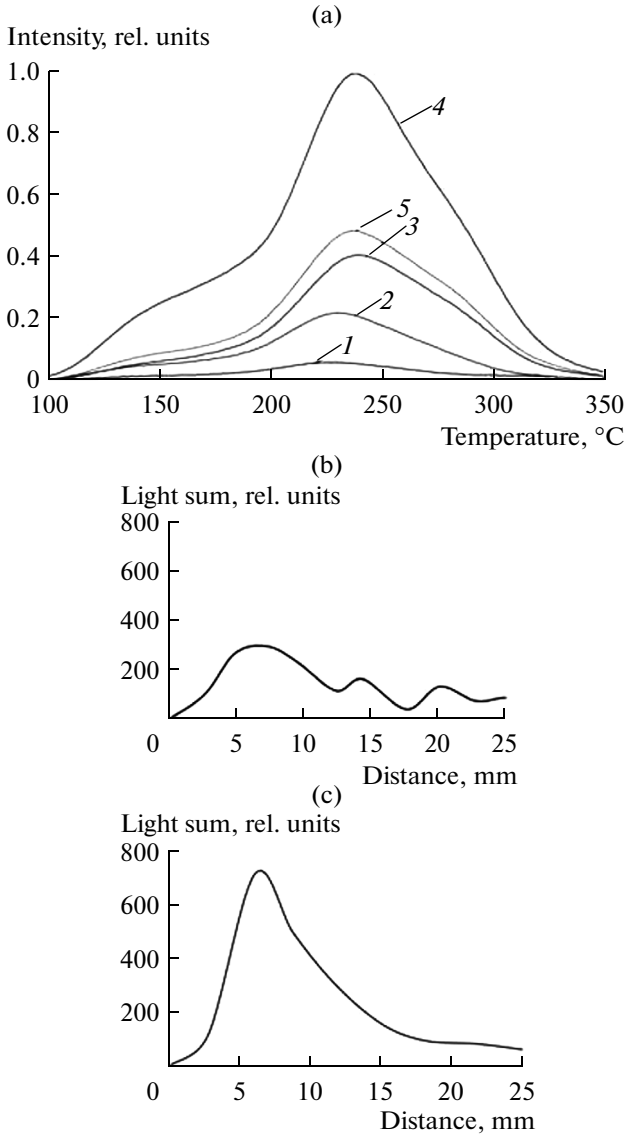

Fig. 1. (a) Curves of thermally stimulated luminescence of LiF crystal samples irradiated with (*1*) 25, (*2*) 125, (*3*) 625, (*4*) 3125, and (*5*) 15 625 pulses. (b, c) Axial distribution of TSL light sum along the length of LiF crystal samples irradiated with (b) 10 and (c) 1000 pulses of femtosecond laser radiation.

pulses in the spectral region of absorption of induced color centers (370–640 nm) were recorded with an Ocean Optics 65000 spectrofluorimeter.

The storage of energy in crystals irradiated with intense femtosecond laser pulses was characterized by thermally stimulated luminescence (TSL) at temperatures of 20 to 400°C at a constant rate of 0.25 deg/s. A proprietary specialized setup was used. Each sample was cut into slabs about 1 mm thick to investigate the axial (in the direction of laser radiation propagation) spatial distribution of stored energy. Thermoluminescence curves were recorded for each slab, and the stored light sum was determined as an integral under

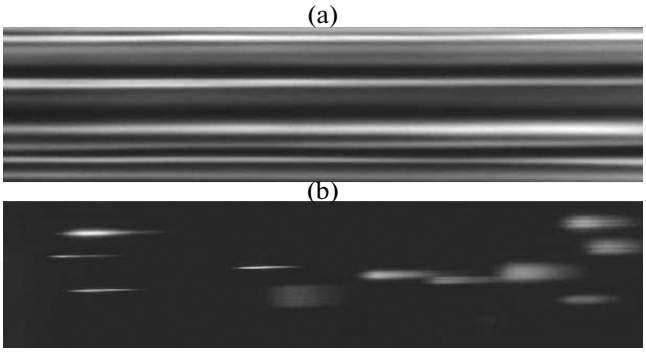

Fig. 2. Photographs of the spatial distribution of intensity of photoluminescence of centers produced in crystals by irradiating them with (a) a periodic series of pulses and (b) a single femtosecond pulse. The size is 80 × 300 μm.

the thermoluminescence curve. Having found the light sums stored in each slab, we plotted the dependences of the axial spatial distribution of energy stored in the studied samples.

RESULTS AND DISCUSSION

Our experiments showed that lithium fluoride crystals irradiated with intense femtosecond laser pulses stored energy that could be released in the form of thermally stimulated luminescence during subsequent heating (Fig. 1). The major TSL peaks were located at 200–300 K. The obtained data generally agreed with the results from studies of the TSL of nominally pure radiation-colored lithium fluoride crystals [7].

The presented axial dependences show that energy was not stored in the initial part of the crystal. The dependences corresponding to isolated femtosecond laser pulses or short series of such pulses were of a ragged, nonmonotonic nature. When the number of irradiating pulses was increased, the dependences of the stored light sum became smooth and turned into asymmetric curves with a single maximum (Figs. 1b and 1c). Microscopic studies of the topography of channels in the crystal irradiated with laser pulses were conducted to indentify the reasons for this behavior of the dependences. Since luminescent color centers were produced in the crystal by these pulses, time-resolved luminescence microscopy was used in our study.

The photographs of luminescent channels obtained with an Olympus IX 71 microscope after the samples were irradiated with femtosecond pulses of a titanium–sapphire laser are shown in Fig. 2. Spurs (the tracks left by filaments) and channels were visualized by inducing the photoluminescence of the products of chemical reactions occurring within the crystals during irradiation with femtosecond pulses and after such irradiation. The wavelength of radiation inducing the luminescence was 450 nm.

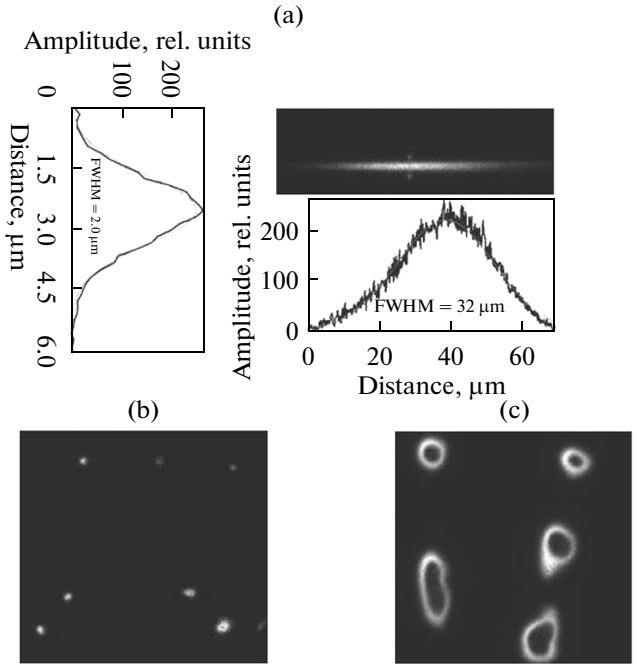

Fig. 3. (a) Results from scanning a single spur in longitudinal and transverse directions. (b, c) Transverse distribution of the intensity of luminescence of color centers in spurs (scanning region, 25 × 25 μm) induced in a crystal irradiated with (b) 25 and (c) 1000 laser pulses. The minimum spur length was 32 μm; the minimum diameter, 2.0 μm.

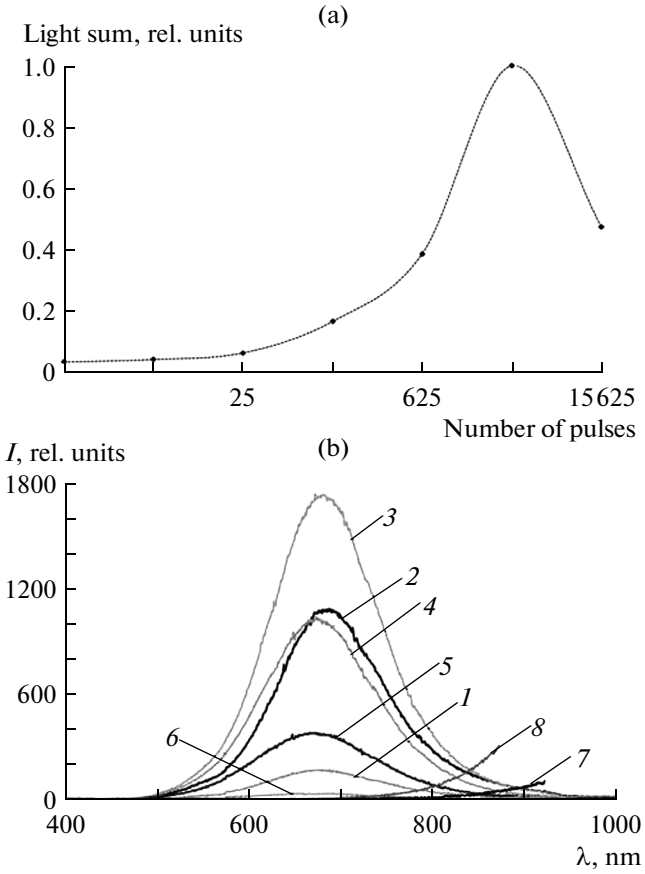

Fig. 4. (a) Dependence of the TSL light sum on the number of laser irradiation pulses. (b) Spectra of the thermally stimulated luminescence of a LiF crystal measured upon heating at temperatures of (*1*) 200, (*2*) 240, (*3*) 260, (*4*) 270, (*5*) 280, (*6*) 300, (*7*) 350, and (*8*) 400°C.

The topography of defect formation and the photoluminescence of samples irradiated with laser pulses were studied in more detail using a MicroTime 200 (PicoQuant) high-sensitivity scanning confocal fluorescence microscope with a picosecond time resolution and spatially selective time-correlated single photon counting. The results from scanning a spur formed by a single filament of a femtosecond pulse of near-threshold (for filamentation) intensity in the longitudinal and transverse directions are presented in Fig. 3a.

The data obtained in our microscopic study indicate that the ragged, nonmonotonic nature of the axial dependence of the stored light sum (Fig. 1a) resulted from the energy being stored in the regions of the self-focusing filaments of laser radiation. At the initial stage of irradiation, these regions were few and small (length, ~30 μm; diameter, ~2 μm). The length of spurs induced by filaments in the crystal and their diameters grew upon an increase in the number of laser pulses, and the axial dependence of the stored energy was smoothed (Figs. 1b, c). Since the energy was stored only under the conditions of filamentation due to self-focusing (and self-focusing in turn occurred at a certain distance), there was no such energy in the initial part of the crystal, and storage was characterized by a certain spatial offset (see Fig. 1).

The light sum of thermally stimulated luminescence emitted by irradiated crystals first grew superlinearly upon an increase in the number of pulses of laser irradiation, then reached its maximum and fell afterwards (Fig. 4a). The results from microtime spectral probing of luminescence over the cross sections of the spurs (Figs. 3b and 3c) induced by laser radiation showed that the observed effect of the saturation of the stored light sum was induced by the density, the degree of aggregation, and the variety of color centers in the central paraxial region of spurs being greater than the corresponding parameters in the peripheral region; the yield of luminescence of F_3^+ and F_2 centers, which play a critical part in the thermoluminescence process, was therefore higher in the peripheral region. At the same time, the spur diameters (and thus the volumes of their paraxial regions with low luminescence yields) grew upon an increase in the number of irradiation pulses. This led to a reduction in the intensity of thermally stimulated luminescence. The spectral sweep of TSL peaks showed that F_2 centers made the main contribution to luminescence. This follows from

the shape of the spectra in Fig. 4b. This was the primary emission center that emitted luminescence quanta at the final stage of thermoluminescence. The question of the nature of kinetic particles and the centers of their recombination that could yield excited F_2 centers now arises. It is important to understand which particles are kinetic (i.e., which particles are freed from their localization sites) and recombine with other particles, thus inducing the emission of TSL quanta (luminescence photons of F_2 centers). We may assume that interstitial fluorine ions (I centers) are kinetic particles. They are produced as a result of the thermal decomposition of X_3^- centers into I centers and X_2^0 molecules. I centers recombine with F_3^+ centers and turn the latter into excited F_2 centers (i.e., into excited emission centers that produce the characteristic spectrum of the thermally stimulated luminescence of F_2 centers).

ACKNOWLEDGMENTS

The authors wish to thank their colleagues V.F. Losev and S.V. Alekseev at the Institute of High Current Electronics (Tomsk) for providing them with the opportunity to irradiate the studied samples with femtosecond laser pulses and for helping in these experiments, respectively.

This work was supported by the Russian Foundation for Basic Research, project no. 13-02-92202; and by the state science academies' Program for Fundamental Scientific Research, project II.10.1.6.

REFERENCES

1. Martynovich, E.F., Glazunov, D.S., Grigorova, A.A., Starchenko, A.A., Kirpichnikov, A.V., Trunov, V.I., Merzlyakov, M.A., Petrov, V.V., and Pestryakov, E.V., *Opt. Spectrosc.*, 2008, vol. 105, p. 348.
2. Martynovich, E.F., Balyunov, D.V., Kuznetsov, A.V., Kirpichnikov, A.V., Trunov, V.I., Pestryakov, E.V., and Bagaev, S.N., *Izv. Vyssh. Uchebn. Zaved., Fiz.*, 2009, vol. 52, no. 12/3, p. 198.
3. Blunt, R.F. and Cohen, M.I., *Phys. Rev.,* 1967, vol. 153, no. 3, p. 1031.
4. Sibley, W.A. and Facey, O.E., *Phys. Rev.*, 1968, vol. 174, no. 3, p. 1076.
5. Martynovich, E.F., Kuznetsov, A.V., Kirpichnikov, A.V., Pestryakov, E.V., and Bagaev, S.N., *Quantum Electron.*, 2013, vol. 43, no. 5, p. 463.
6. Lushchik, Ch.B. and Lushchik, A.Ch., *Raspad elektronnykh vozbuzhdenii s obrazovaniem defektov v tverdykh telakh* (Decomposition of Electronic Excitations with Defects Formation in Solids), Moscow: Nauka, 1989.
7. Baldacchini, G., Montereali, R.M., Nichelatti, E., Kalinov, V.S., Voitovich, A.P., et al., *J. Appl. Phys.*, 2008, vol. 104, p. 063712.

Translated by D. Safin