

PACS numbers: 78.60.Lc; 42.65.Re; 42.65.Jx; 42.70.Gi; 52.50.Jm
DOI: 10.1070/QE2013v043n05ABEH015117

Formation of luminescent emitters by intense laser radiation in transparent media

E.F. Martynovich, A.V. Kuznetsov, A.V. Kirpichnikov, E.V. Pestryakov, S.N. Bagayev

Abstract. **The formation of luminescent colour centres in the LiF crystal under the action of femtosecond pulses of the first harmonic of a Ti:sapphire laser is experimentally studied. The experiments were carried out at low- and high-aperture focusing of radiation. The effect of both single pulses and multi-pulse trains on the crystals was studied. Channelling of laser radiation in the waveguides, induced by the filaments of the first pulses, is found. The multiphoton mechanism of interband absorption is confirmed. The optimal conditions of laser impact for designing luminescent emitters in the LiF crystal are determined.**

Keywords: *colour centres, LiF, femtosecond laser, filament.*

1. Introduction

Formation of luminescent regions (emitters) in the bulk of transparent materials using laser radiation has been extensively studied in recent time, because in the future they can be useful for developing novel methods of digital and visual information storage. The research in this field is carried out using different materials. Bellec et al. [1] used the zinc-phosphate glass, in which the photosensitivity to laser radiation was provided by adding the traditional for photochemistry compounds of silver. In Ref. [2] the laser structuring was based on the transformation of two types of luminescent colour centres in sapphire crystals. The role of photosensitive centres interacting with laser radiation was played by colour centres, the concentration of which cannot be significant. The same can be said about Ref. [3], where the glass with the addition of only a small fraction (0.5%) of samarium fluoride was used.

Based on our research [4–6] and the results of other authors [7, 8], we came to the conclusion that it is more promising to study other types of media, namely, the crystal materials that allow luminescent colour centres to be formed under the action of femtosecond laser pulses. An example of such materials is presented by alkali-halide crystals. In the present work we have chosen lithium fluoride (LiF) as an experimental medium. As shown by the studies, such media possess sufficient photosensitivity, which, in contrast to the majority of other materials that require a large number of pulses of the same energy, allows recording the result of action even for a single femtosecond pulse. Moreover, the resolution of the media with intrinsic (provided by each molecule of the medium) photosensitivity is essentially higher than that of media with photosensitivity, provided by the impurity molecules, the content of which is usually smaller than 1%. Significantly higher nonlinearity of the photosensitivity of our media than that of the media used in the referred papers provides smaller size of the emitters, induced by laser radiation, which allows the formation of nanoscale emitters (nanoemitters).

Moreover, formation of the colour centres in LiF under the action of femtosecond laser pulses allows the spatial pattern of their filamentation to be investigated. Particularly interesting is the study of filamentation of single pulses in comparison with the filamentation caused by a multi-pulse train, because in the majority of other works dealing with other materials, as a rule, the latter variant is used.

2. Experiment and its discussion

The studies were performed using two regimes of irradiation of the material with femtosecond pulses of the FemtoPower Compact PRO Ti:sapphire laser (0.8 mJ, 30 fs, 800 nm, 0–1000 Hz). In the first regime (the regime of low-aperture focusing of laser radiation), the properties of formation of the luminescent colour centres under the conditions of highly linear interaction of light with crystals were studied. In the second regime (high-aperture focusing), the formation of luminescent emitters and their properties were investigated.

In the low-aperture focusing regime the lens with the focal length 30 cm was used. The crystal was mounted so that the geometric focus of the lens was inside it and no plasma torch was observed at the entry surface. The irradiation was performed using a variable number of pulses, from one to a few hundred thousands. The spatial distribution of the luminescent centres (colour centres), induced in the crystal by the femtosecond laser radiation, the kinetics, and the spectra of their emission were investigated by means of a usual microscope, as well as the Micro Time 200 confocal scanning luminescence microscope with temporal resolution, operating in the regime of time-correlated photon counting.

Figure 1 presents the shape of the luminescent channels, induced by the radiation, focused by the lens into the bulk of the sample. The channel shape is similar if the crystal is mounted behind the geometric focus of the lens. The initial (non-coloured) zone corresponds to the region of self-focusing of the laser radiation with the growing intensity. When the

E.F. Martynovich, A.V. Kuznetsov Irkutsk Branch of the Institute of Laser Physics, Siberian Branch, Russian Academy of Sciences, ul. Lermontova 130a, 664033 Irkutsk, Russia; e-mail: femto@bk.ru, rubin@ilph.irk.ru;
A.V. Kirpichnikov, E.V. Pestryakov, S.N. Bagayev Institute of Laser Physics, Siberian Branch, Russian Academy of Sciences, prosp. Akad. Lavrent'eva 13/3, 630090 Novosibirsk, Russia; e-mail: kirp@laser.nsc.ru, pefvic@laser.nsc.ru, bagayev@laser.nsc.ru

Received 24 December 2012; revision received 9 March 2013
Kvantovaya Elektronika **43** (5) 463–466 (2013)
Translated by V.L. Derbov

intensity becomes sufficient for efficient interaction of light with matter, colour centres are formed. The length of the non-coloured zone is determined by the peak power of laser pulses and the nonlinear refractive index of LiF, as well as by the type of inhomogeneity in the initial profile of the beam, leading to multiple filamentation. The peak power of the pulses in the present experiment exceeds by three orders of magnitude the critical self-focusing power, which is about 8.8 MW for LiF [9].

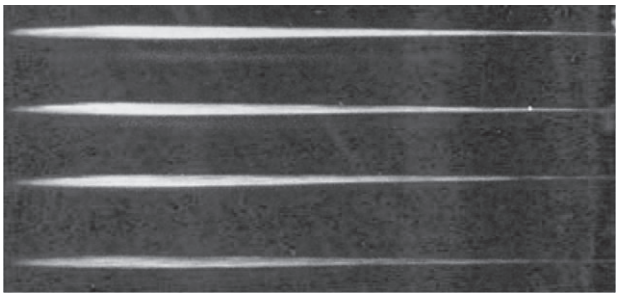

Figure 1. Shape of luminescent channels, induced by laser radiation in the crystal (propagation from left to right). The wavelength of the radiation, exciting the photoluminescence for the channel imaging is 470 nm, the sample length is 20 mm.

Higher spatial resolution shows that the channels (Figs 2 and 3) consist of a variety of individual thin traces, induced by the filaments of laser radiation under the conditions of its multiple filamentation in the course of self-focusing. The presented data show that in the fresh crystal directly after irradiation with a single pulse, the traces induced by filaments are thin and short. This means that the filaments themselves were thin and short. The fact that attracts attention is that with increasing number of laser pulses the number of traces does not essentially increase; however, they become longer (in the direction of laser radiation propagation) and thicker. We associate these phenomena with the effect of guiding the laser radiation by the traces, created by the earlier pulses.

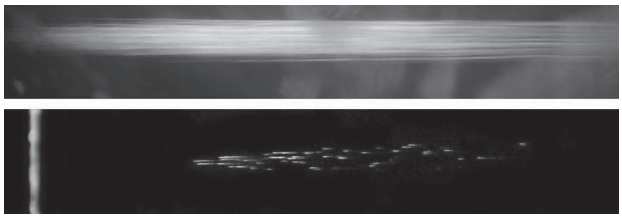

Figure 2. Longitudinal structure of the induced channel under magnification. The upper panel – after irradiation with 10 000 pulses, the lower panel – after a single pulse (the trace diameter, 1.3–2 μm; the length, ~30 μm). The traces grow in the direction of radiation propagation. Due to elongation of the channel, its image in the top photograph is shifted to the left. The vertical line in the bottom photograph is the entrance surface of the sample. The measurements were carried out using the Olimpus IX 71 luminescence microscope.

As seen from the spectral-kinetic studies, the induced traces consist of an ensemble of long-living electronic F-, F_2-, F_3^+- colour centres and the centres of interstitial void type, complementary to them. The change in refractive index within the traces, associated with these centres, provides the wave-

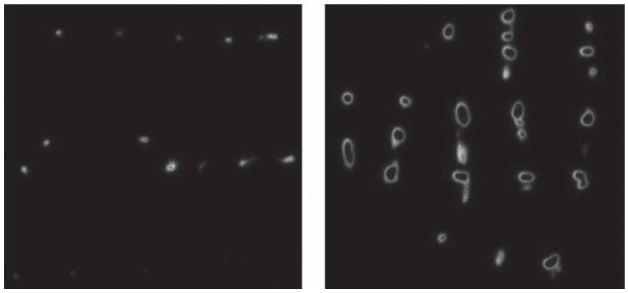

Figure 3. Transverse structure of the induced channel after 25 pulses (left) and 1000 pulses in a similar sample (right). The mean diameter of the traces is ~5 μm (right). The measurements were carried out using the MicroTime 200 microscope.

guide character of channelling of the femtosecond laser radiation that determines the elongation and thickening of the traces at the expense of creating additional centres on the way of the filaments passing. A similar effect was discussed in Ref. [10], where a photosensitive polymer was irradiated using trains of a large number of femtosecond laser pulses. In [10] the formation of prolonged tracks was observed, which was explained by the authors as a consequence of permanent modification of the polymer refractive index due to the cumulative effect of consequent pulses. However, in this paper no experimental evidence of the track length increase with growing number of pulses was presented, no images of the entrance surface of the sample and the beginning and end of the tracks were shown, which could make it possible to see the region of self-focusing.

Let us consider the results of the experiments on irradiating LiF in the second regime, the regime of high-aperture focusing of individual femtosecond pulses of the Ti : sapphire laser (800 nm). The combination of a large numerical aperture and a sufficiently small energy of femtosecond pulses makes it possible to create colour centres within a small vicinity of the geometric focus without self-focusing and filamentation. In LiF the most interesting from the practical point of view are the F_2- and F_3^+- colour centres that possess a high luminescence yield in the visible spectral region.

The laser pulses were focused into the crystal using the Olympus Plan N $40^{\times}$ microscope objective with the numerical aperture 0.65 through the polished crystal surface. The energy of individual pulses at the laser output in this series of experiments amounted to 0.55 mJ. For producing emitters such an energy is too high, which leads to the crystal damage in the focus region, including the formation of cracks. To reduce the energy of pulses to the acceptable level, we used two diffraction attenuators. The first attenuator had the transmission coefficient $T_1 = 0.11$. The transmission coefficient of the second attenuator was sequentially set to be 0.022, 0.078, 0.11, 0.18, 0.22, 0.32, 0.430, 0.720, and 0.95. Therefore, the mutual transmission coefficient of the two attenuators varied from 0.0024 to 0.1. The objective transmitted only about half the incident radiation because of a relatively small diameter of its aperture as compared to the diameter of the laser beam. The operation in the resulting interval of laser pulse energies allowed the study of the action of pulses on the crystal in the range of 'the absence of any detectable fingerprints of the material-destructive action'. The laser pulse repetition rate amounted to 10 Hz. To obtain the traces of individual pulse action the crystal was moved perpendicularly to the beam axis by means of an electric drive with the velocity 0.125 mm s^{-1}. For each of nine

values of the transmission coefficient T a series of 80 emitters, located along a straight line in the crystal, was obtained.

The emitters (Fig. 4) were investigated using the MicroTime 200 laser confocal scanning luminescence microscope. To excite the luminescence of F_2- and F_3^+- colour centres in the emitters the laser radiation with the wavelength 470 nm was used. The excitation of luminescence and its detection was implemented through the same Olympus Plan N 40$^\times$ objective as the formation of the emitters. The minimal energy of a femtosecond pulse, at which the colour centres were found, amounted to about 3 μJ (the transmission coefficient of two attenuators being 0.11). No traces were observed after the action of pulses with lower energy. It was established that the pulses with the energy about 5 μJ (the transmission coefficients being 0.11 and 0.18) create emitters with the luminescence intensity of the F_2- colour centres by three orders of magnitude greater than the pulses with lower energy. The ratio of pulse energies (and, therefore, their intensities) amounts to nearly 1.6 here. Therefore, the intensity of luminescence of the emitter is proportional to the 14th–16th power of the intensity of the femtosecond laser pulses. Improving the precision of this result requires conduction of an experiment with wider variation of the pulse energy.

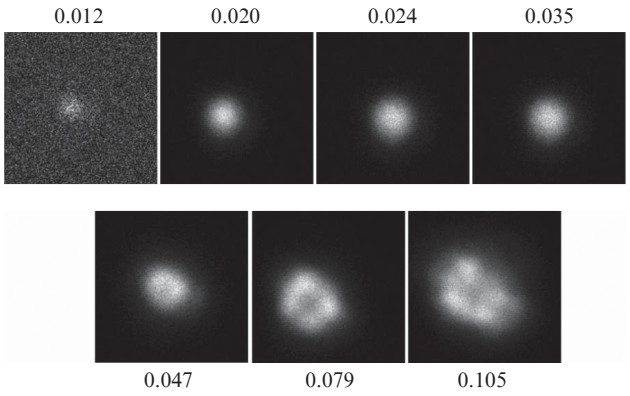

Figure 4. Shape variation of the cross section of the induced emitters with the growth of the laser radiation pulse energy (at each photo the transmission coefficients of the attenuator pair T is indicated). The images are obtained under the excitation at the wavelength $\lambda_{ex} = 470$ nm.

Since the concentration of F_2- colour centres is quadratically related to the concentration of F-centres [11], the concentration of the latter should be proportional to the 7th–8th power of the femtosecond pulse intensity. At the same time, the concentration of F-centres is proportional to the concentration of electron-hole pairs and excitons, produced by the laser pulse. Hence, we conclude that we obtained an experimental proof of the implementation of a high-nonlinear multiphoton intrinsic absorption of femtosecond laser pulses by the electronic subsystem of the LiF crystal, supposed earlier. Such absorption may be due to either the interband transitions, or the excitation of excitons. The width of the band gap in LiF, according to the data from different sources, amounts to 11.8 [9], 13.6 or 14.2 eV [12], while the energy of exciton creation is 12.9 eV [12]. The indicated values are approximately eight times greater than the energy of the laser radiation quanta, used by us (1.55 eV).

At the energy of femtosecond pulse from 7 μJ and greater in the vicinity of the objective focus the appearance of cracks in the crystal is observed. The greater the corresponding pulse energy, the larger the cracks. In this case, the integral luminescence intensity of the emitters (within the experimental error) is directly proportional to the energy of the emitter-forming pulses. This fact does not contradict the above conclusion about the high degree of nonlinearity of generating excitons and electron–hole pairs, but it indicates the necessity to consider additional channels of energy consumption, due to which the energy, absorbed by the electronic subsystem of the crystal, may be lost for creation of the colour centres.

The transverse size of the emitters increases with increasing energy of laser pulses that give them rise. Figure 5 presents the scanned luminescent image of the cross section of the emitter, produced in LiF by a femtosecond laser pulse with the energy 5 μJ. The observed half-maximum width of the transverse profile is about 700 nm.

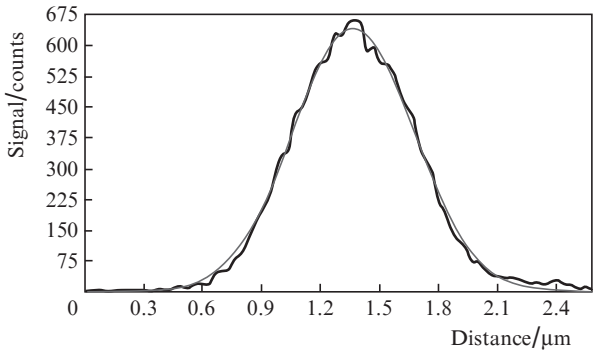

Figure 5. Measured transverse profile of the emitter luminescence intensity (thick line) and the fitting Gaussian curve. The data were obtained suing the confocal microscope, $\lambda_{ex} = 470$ nm.

The emitter size is smaller than the focal waist diameter of the laser radiation beam because of the nonlinearity of the medium photosensitivity. The beam waist diameter is calculated using the well-known formula $d = 1.22\lambda/\mathrm{NA}$. Therefore, for $\lambda = 800$ nm and NA = 0.65 we get $d = 1.5$ μm. According to the calculation, the 14th–16th power of nonlinearity for the formation of F_2 colour centres with respect to the intensity of laser radiation results in the reduction of the emitter width by 3.7–4 times as compared to the waist diameter in the objective focus (the transverse intensity profile in the waist being assumed Gaussian). In this case the calculated emitter width equals 370–400 nm for the used objective, which is smaller than the resolution of the objective. The use of objectives with greater numerical apertures for focusing the femtosecond laser radiation will allow significant reduction of the size of nanoemitters and the minimal pulse energy for their formation.

3. Conclusions

The studies carried out allow the following conclusions.

In the case of low-aperture focusing the filamentation of femtosecond laser radiation in LiF demonstrates elongation of the tracks (traces of filaments) and, therefore, of the filaments themselves, with the growth of the number of laser pulses. The number of filaments in this case grows insignificantly. These phenomena are due to the channelling of the laser radiation by the traces, created by the earlier pulses. The change in the refractive index due to the formation of colour centres

in the traces leads to waveguide propagation of laser radiation along them. This result can be generalised over other materials and should be taken into account when comparing theoretical models of filamentation with the experimental data for large number of pulses.

The existence of high-nonlinear multiphoton interband absorption of femtosecond laser pulses by the electronic subsystem of LiF, supposed earlier, is experimentally confirmed. The nonlinearity power, obtained in the experiment, is seven–eight. This result may be specified in subsequent papers.

It is experimentally established that the emitter size is significantly smaller than the diameter of the focal waist of the femtosecond laser radiation beam, producing the emitters. This is due to the high nonlinearity of the LiF material photosensitivity.

When using the objective with the numerical aperture 0.65, the optimal energy of a femtosecond laser pulse for emitter formation in LiF amounts to 3–5 μJ. Higher-energy pulses cause the material destruction, and the pulses having lower energies practically do not produce colour centres.

The additional (with respect to the formation of colour centres) channels of expenditure of the femtosecond laser pulse energy, absorbed by the electronic subsystem of the crystal, essentially decrease the efficiency of colour centre formation. The relation between the appearance of cracks in the crystal and the transition to linear dependence of the colour centres concentration increment with the growth of the femtosecond pulse energy was experimentally observed.

Acknowledgements. The authors are grateful to E.A. Khazanov for discussing the results of the work. The work was carried out under support of the programme 'Extreme Light Fields and Their Applications' of the Presidium of the Russian Academy of Sciences, and Programme No. II.8.1 of Fundamental Research of the Siberian Branch of the Russian Academy of Sciences 'Modern problems in physics of superstrong light fields, spectroscopy of super-high resolution. Frequency standards, high-precision optical measurements, problems of quantum and atom optics' (Project No. 6).

References

1. Bellec M., Royon A., Bourhis K., Choi J., Bousquet B., Treguer M., Cardinal T., Videau J.-J., Richardson M., Canioni L. *J. Phys. Chem. C*, **114**, 15584 (2010).
2. Akselrod M.S. *Jpn. J. Appl. Phys*. **46**, 3902 (2007).
3. Miura K., Qiu J.R., Fujiwara S., Sakaguchi S., Hirao K. *Appl. Phys. Lett*. **80**, 2263 (2002).
4. Martynovich E.F., Kirpichnikov A.V., Trunov V.I., Merzlyakov M.A., Petrov V.V., Glazunov D.C., Grigorova A.A., Starchenko A.A., Pestryakov E.V. *Mater. X Mezhd. shkoly-seminara* (Materials of X International School-Workshop) (Irkutsk: Izd-vo Irkut. Gos. Un-ta, 2007) pp 228–235.
5. Martynovich E.F., Glazunov D.C., Grigorova A.A., Starchenko A.A., Kirpichnikov A.V., Trunov V.I., Merzlyakov M.A., Petrov V.V., Pestryakov E.V. *Opt. Spektrosk*., **105**, 380 (2008) [*Opt. Spectrosc*., **105**, 348 (2008)].
6. Martynovich E.F., Balyunov D.V., Kuznetsov A.V., Kirpichnikov A.V., Trunov V.I., Pestryakov E.V., Bagayev S.N. *Izv. Vyssh. Uchebn. Zaved., Ser. Fiz.*, **52** (12/3) 198 (2009).
7. Courrol L.C., Samad R.E., Gomes L., Ranieri I.M., Baldochi S.L., Freitas A.Z., Morato S.P., Vieir N.D. *Laser Phys*., **16**, 331 (2006).
8. Kurobori T., Obayashi Y., Suzuki K., Hirose Y., Sakai T., Aoshima Sh. *Jpn. J. Appl. Phys*., **47**, 685 (2008).
9. Brodeur A., Chin S.L. *J. Opt. Sos. Am. B*, **16**, 637 (1999).
10. Korytin A.I., Bityurin N.M., Alexandrov A.P., Babina N.A., Smirnova L.A., Sergeev A.M. *Opt. Memory Neural Networks*, **7**, 11 (1998).
11. Abu-Hassen L.H., Townsend P.D. *J. Phys. C: Solid State Phys.*, **19**, 99 (1986).
12. Martynovich E.F. *Tsentry okraski v lazernykh kristallakh* (Colour Centres in Laser Crystals) (Irkutsk: Izd-vo Irkut. Gos. Un-ta, 2004).