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Highly sensitive nonlinear luminescent ceramics for volumetric and multilayer data carriers

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Abstract. **The interaction of optical ceramics based on wide-band-gap crystals with near-IR femtosecond laser radiation is studied experimentally. The formation of luminescent centres in LiF and MgF_2 ceramics under the action of single laser pulses is considered. Two interaction regimes are used. In the regime of low-aperture focusing of laser radiation (800 nm, 30 fs, 0.3 mJ), multiple self-focusing and filamentation in the samples are observed. The luminescent centres are formed in thin channels induced by light filaments. The average effective self-focusing length is $\sim$100 μm; the formation of luminescent centres begins at this length and ceases at a wavelength of about 380 μm. The luminescent trace (spur) induced by a single laser filament was $\sim$30 μm long and 1.3 μm in diameter. The second regime of light interaction with the sample was based on high-aperture focusing with a simultaneous decrease in the laser pulse energy. This led to the formation of single pits with a diameter smaller than the optical diffraction limit. The luminescent centres induced by the laser radiation were aggregated colour centres. The mechanism of their creation included the highly-nonlinear generation of electron–hole pairs in the filamentation region, their recombination with the formation of anion excitons and the decay of excitons into Fresnel defects by the Lushchik–Vitol–Hersh–Pooley mechanism, as well as their recharging, migration and aggregation.**

Keywords: *ceramics, luminescence, femtosecond pulse, filamentation, self-focusing, colour centres, information pit.*

1. Introduction

One of the directions of development of bulk optical data carriers is the use of fluorescent technologies in which a writing laser beam creates new luminescent quantum systems in a carrier. This makes it possible to read information using well-developed highly sensitive luminescent methods. It is known that modern data recording methods allow one to reliably determine the properties of even single quantum systems from the luminescence characteristics [1]. An example of the implementation of fluorescent technologies is the photoinduced transformation of Sm^{3+} ions into Sm^{2+} ions in fluoride glasses with 0.5 mol % of SmF_3 under the action of a recording laser beam [2]. In this work, information was read by a photoluminescence signal from Sm^{2+} ions. As data carriers, the authors of some studies used zinc phosphate glasses with addition of Ag_2O_3 (4 mol %), in which the recording femtosecond laser radiation caused the aggregation of single Ag^+ ions into clusters consisting of several silver atoms in different charge states Ag_m^{x+} [3, 4]. In addition to glasses, single crystals also can be used as data storage materials. For example, the authors of [5] used sapphire single crystals with colour centres as working quantum systems. Data recording occurred due to the two-photon ionisation of initial colour centres with the formation of other colour centres as a result of capture of detached electrons.

One of the drawbacks of all the above-listed methods is a limited spatial resolution of the optical medium because the concentration of initial quantum systems, which absorb recording laser radiation, cannot exceed a few percent or fractions of a percent. In addition, it is desirable to have a higher nonlinearity of the interaction of recording radiation with the optical carrier material, which will allow the information pit size to decrease due to nonlinear sharpening. This is achieved by using optical carriers based on wide-band-gap single crystals, for example, LiF, which demonstrate high nonlinearity of interaction with near-IR femtosecond laser radiation [6]. In these crystals, the recording laser radiation is absorbed not by the isolated quantum systems as in the above-described case, but by the crystal lattice itself, i.e., all 100 % of the material molecules can absorb the recording laser radiation, which ensures an extremely high spatial resolution of the photosensitive medium. The luminescent colour centres appearing in the medium due to the highly nonlinear interaction with femtosecond laser radiation allow creation of optical carriers for recording both visual and digital information [7, 8].

A drawback of these single crystalline carriers is their insufficient mechanical properties. Thin disks made of these single crystals can break along cleavage planes. In addition, the technology of their production, which includes crystal growth, mechanical treatment for fabrication of optical disks and their polishing, is a rather expensive and poorly automated. Therefore, we proposed fluorescent carriers based on optical ceramics in which laser radiation can create luminescent centres [9, 10]. It is known that optical ceramics have a higher strength and can be easily manufactured.

In the present work, we study optical ceramics based on lithium and magnesium fluorides. They are the most wide-band-gap crystalline compounds. The defect formation in ceramics is useful to consider in comparison with similar

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processes occurring in crystals of the same composition. The mechanisms of formation of colour centres and excitation of their photoluminescence in LiF crystals by intense femtosecond pulses are studied in [11, 12]. In these works, it is shown for the first time that a necessary condition for the formation of colour centres under irradiation by a Ti:sapphire laser (~800 nm, ~0.5 mJ) with low-aperture focusing (focusing with a small angular aperture) is self-focusing and subsequent laser beam filamentation accompanied by a sharp increase in the laser radiation intensity, which causes highly nonlinear absorption of laser radiation.

The mechanisms of the formation of colour centres in nanoceramics based on alkali-halide crystals are poorly studied compared to similar mechanisms in single crystals. The least studied process is the defect formation under the action of femtosecond laser pulses in the regime of their filamentation, which is investigated in this work apparently for the first time.

2. Experiment

The experimental setup for irradiation of LiF and MgF_2 ceramics by femtosecond laser pulses included a Ti:sapphire laser emitting 30-fs pulses with an energy below 0.3 mJ and a spectral maximum at a wavelength of 800 nm. The irradiation schemes are shown in Fig. 1. In experiments, we used two regimes of light interaction with the sample. The first regime corresponded to low-aperture focusing, when the pump laser pulses were focused using a long-focus lens with a focal length of 30 cm (Fig. 1a). In the second regime, we used high-aperture focusing by a short-focus objective ($20^{\times}$) with a simultaneous decrease in the laser pulse energy (Fig. 1b).

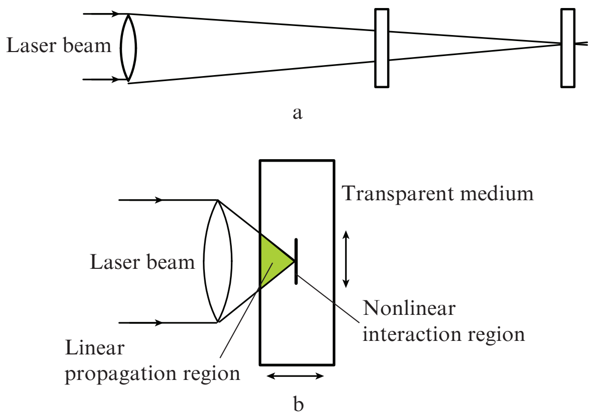


Figure 1. Scheme of experiments on irradiation of LiF and MgF_2 ceramics by femtosecond laser pulses in the regimes of (a) low-aperture and (b) high-aperture focusing.

The ceramic sample can be moved parallel and perpendicular to the laser beam axis. The transverse motion made it possible to spatially separate single laser pulses in the sample. Moving the crystal along the laser beam axis, it was possible to change the laser radiation intensity in the sample in the case of the scheme shown in Fig. 1a, or to choose layers inside the crystal to be exposed to focused radiation in the case of the scheme in Fig. 1b.

The defect formation topology and photoluminescence of irradiated samples were studied using a MicroTime 200 (PicoQuant Gmbh) highly sensitive luminescent scanning confocal microscope with a picosecond time resolution and spatially selective time-correlated single photon counting. The microscope allows one to record the longitudinal and transverse distributions of defects formed by laser radiation and reproduce the images of microobjects inside the irradiated volume of the medium in luminescent light with a scan step of 10 nm based on fluorescence lifetime imaging. The photoluminescence spectra excited at wavelengths of 450 nm for LiF and 405 and 450 nm for MgF_2 were recorded by an Ocean Optics QE65000 spectrometer.

3. Results and discussion

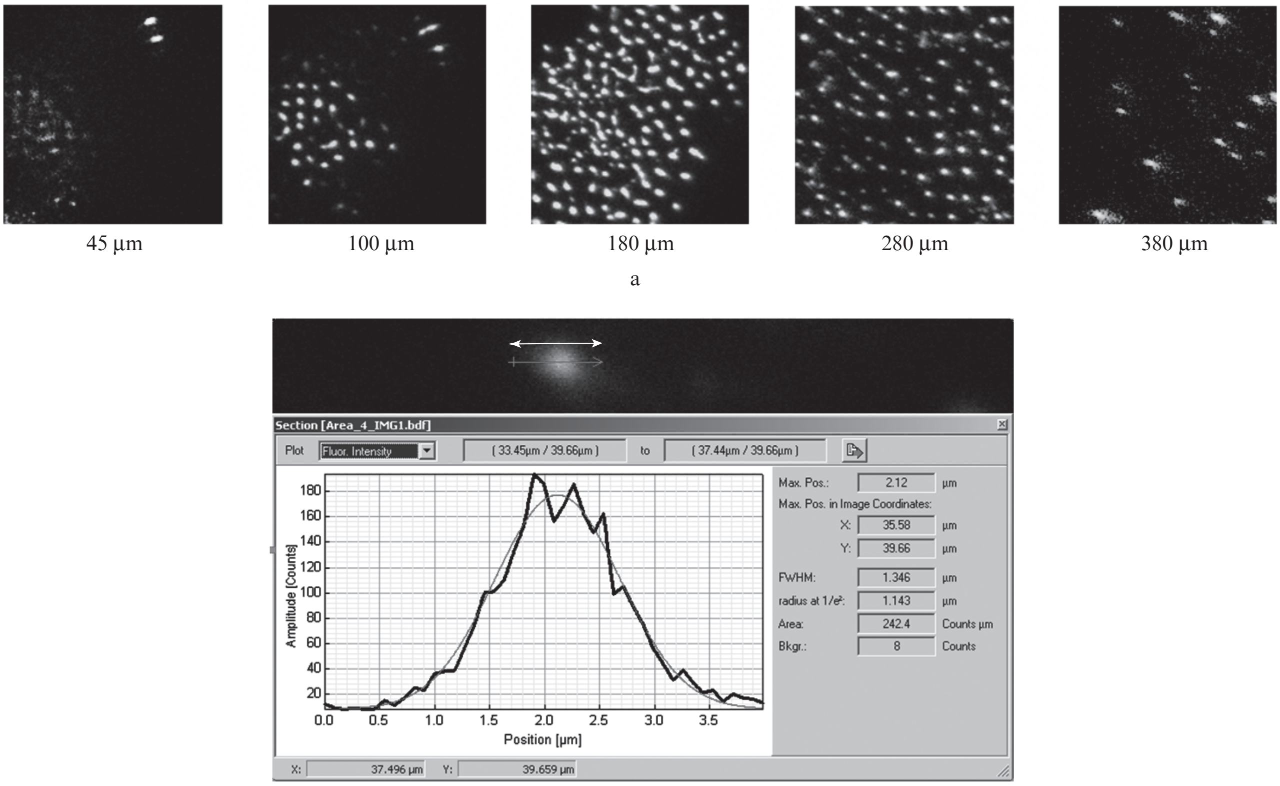
The investigations with the microscope show that femtosecond radiation efficiently forms luminescent defects (colour centres) in the ceramic samples. These defects are distributed over filamentary channels formed in the regions of laser radiation filaments appearing as a result of multiple self-focusing.

The observed spatial distributions of the concentration of luminescent defects are shown in Fig. 2. Figure 2a shows the fluorescent tomograms of the cross sections of spurs (filamentary traces) of colour centres formed in lithium fluoride optical ceramics under the conditions of low-aperture external focusing under the action of a single femtosecond laser pulse. The laser beam diameter on the sample surface was ~150 μm. The values under the images correspond to their depths from the sample surface. Figure 2b shows the luminescence intensity distribution in the cross section of a spur induced by a single laser filament of a single pulse.

These results show that irradiation under the conditions of low-aperture focusing leads to multiple self-focusing and filamentation of laser radiation. The luminescent centres are formed in thin channels in the regions of light filaments. The luminescent channel induced by a single laser filament has a diameter of 1.3 μm and a length of ~30 μm. The formation of luminescent centres begins at a depth of ~45 μm and is terminated at a depth of ~380 μm from the entrance face. The presented data testify that the mean effective self-focusing length is ~100 μm.

Attention is drawn to a high density of filaments formed by a single femtosecond laser pulse compared to their density in single crystals [11]. It is known that the position of filaments upon multiple self-focusing is determined by the existence of inhomogeneities either in the initial laser beam or in the medium. The studied ceramic samples had higher light scattering than single crystals, which points to the existence of optical inhomogeneities in the sample. Therefore, a higher inhomogeneity of the studied ceramic samples than that of single crystal is responsible for the higher density of femtosecond filaments of a femtosecond laser pulse in optical ceramics. We can expect that spurs in ceramics of a higher quality will be formed deeper in the sample and their density will be lower.

Figure 3 presents the results of investigations of the spectral and kinetic characteristics of luminescent defects formed in lithium fluoride optical ceramics under the action of a single femtosecond laser pulse under the conditions of low-aperture external focusing. The photoluminescence spectrum of the samples of lithium fluoride ceramics excited by laser radiation with the wavelength $\lambda_{ex} = 450$ nm after their irradiation by femtosecond laser pulses is given in Fig. 3a, while Fig. 3b



Section [Area_4_IMG1.bdf]

Plot: Fluor. Intensity (33.45μm / 39.66μm) to (37.44μm / 39.66μm)

Max. Pos.: 2.12 μm

Max. Pos. in Image Coordinates:

X: 35.58 μm

Y: 39.66 μm

FWHM: 1.346 μm

radius at 1/e²: 1.143 μm

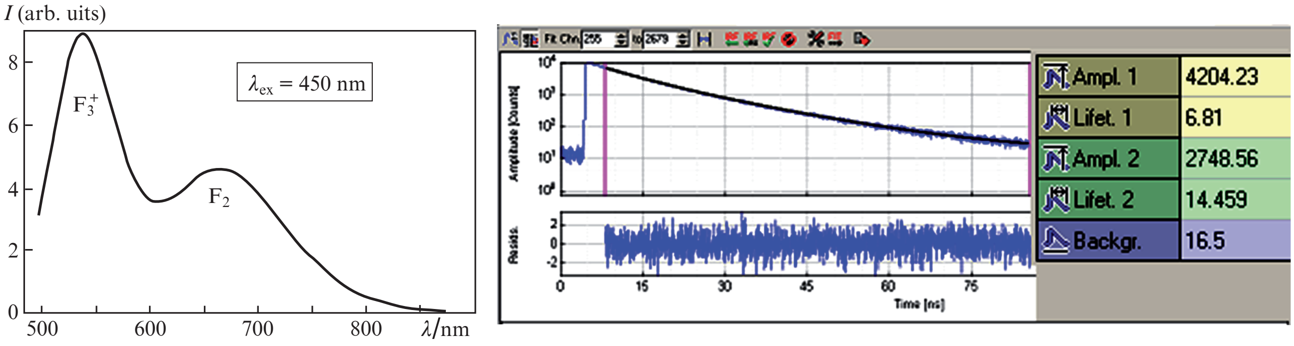
Area: 242.4 Counts μm

Bkgr.: 8 Counts

X: 37.496 μm Y: 39.659 μm

b

Figure 2. Transverse spatial distribution of luminescent defects (MicroTime 200 microscope): (a) fluorescent tomograms of cross sections of spurs at different depths from the studied sample surface (after 80 × 80 μm scanning); (b) luminescence intensity distribution in the cross section of a spur (diameter 1.3 μm).



Ampl. 1	4204.23
Lifet. 1	6.81
Ampl. 2	2748.56
Lifet. 2	14.459
Backgr.	16.5

a b

Figure 3. Spectral and kinetic characteristics of luminescent defects: (a) luminescence spectra of lithium fluoride ceramic samples irradiated by femtosecond laser pulses; (b) luminescence decay kinetics (shown on the right are the decay time constants and the intensities of two luminescence components determined by programme analysis of the luminescence kinetics).

shows the photoluminescence kinetics of centres induced by femtosecond radiation.

Analysis of the presented results shows that the laser radiation with λ_{ex} = 450 nm (M absorption band) excites in the lithium fluoride samples irradiated by femtosecond laser pulses two luminescence lines belonging to F_2 (peaking at λ = 680 nm) and F_3^+ centres (peaking at λ = 540 nm), which are typical for radiation-coloured lithium fluoride single crystals. The measured luminescence decay times of 14.5 (F_2 centres) and 6.8 ns (F_3^+ centres) (Fig. 3b) are also close to the typical luminescence decay times of these centres in the single crystal (16 and 8 ns, respectively) [13].

The luminescence spectra of magnesium fluoride ceramic samples irradiated by femtosecond laser pulses and then excited by laser radiation with wavelengths of 405 and 450 nm, which were measured through optical filters transparent for radiation with $\lambda > 430$ and 500 nm, respectively, are presented in Figs 4a and 4b. One can see that the luminescence spectra of irradiated magnesium fluoride ceramic samples have two emission bands of F_2 centres with maxima at λ = 420 and 560 nm, which are characteristic for radiation-coloured magnesium fluoride single crystals [14, 15]. The observed narrow spectral lines at λ = 405 and 450 nm correspond to the pump laser radiation passed through the optical filters.

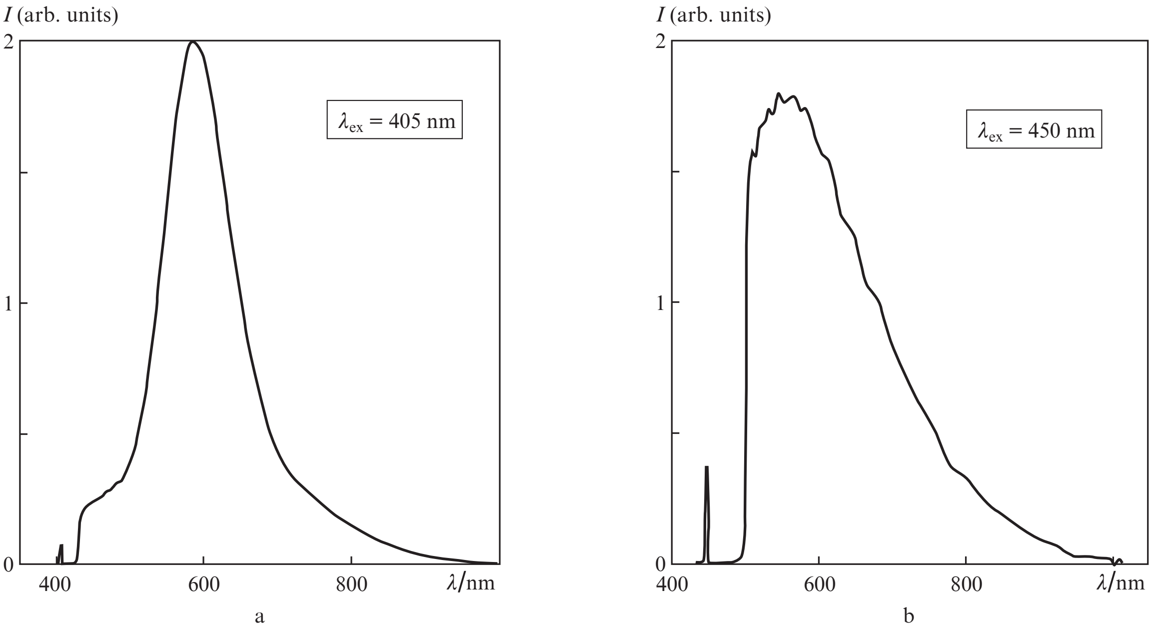
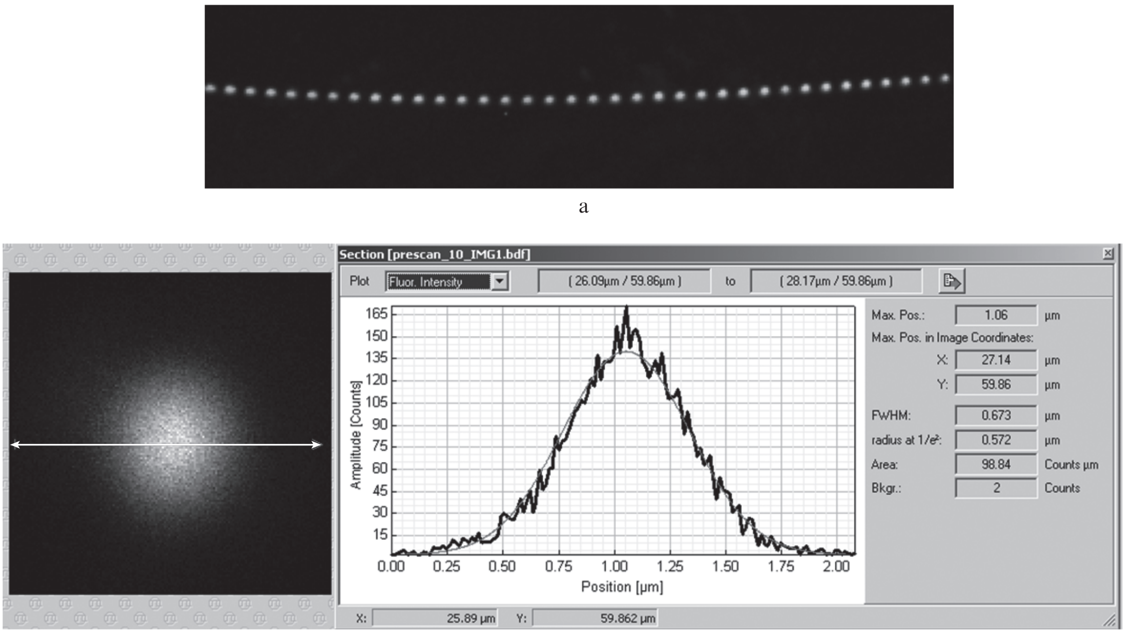


Figure 4. Luminescence spectra of magnesium fluoride ceramics irradiated by femtosecond laser pulses, which were (a) excited by laser radiation with λ_{ex} = 405 nm and observed through a filter transmitting radiation with $\lambda > 430$ nm and (b) excited at λ_{ex} = 450 nm and observed through a filter transparent at $\lambda > 500$ nm (b).

These results unambiguously indicate that the irradiation of optical ceramics based on LiF and MgF_2 wide-band-gap crystals by near-IR femtosecond laser pulses efficiently forms colour centres characteristic for radiation-coloured single crystals. It is known that the first stage in the formation of colour centres is the creation of electron–hole pairs and that the energy needed for this process must exceed the forbidden gap width, which, for lithium fluoride, is 13–14 eV. The photon energy of the femtosecond Ti:sapphire laser radiation with λ = 880 nm is about 1.5 eV. Hence, the formation of colour centres in the studied ceramics occurs due to the multiphonon absorption of laser radiation energy by the electronic subsystem of the material with the formation of electron–hole pairs as a result of self-focusing and filamentation of the exciting femtosecond laser radiation. This mechanism was proved by experiments with lithium fluoride single crystals [6]. Next, similar to the case of single crystals, the electron–hole recombination leads to the formation of anion excitons, which rapidly decay into anion Frenkel defects according to the Lushchik–Vitol–Hersh–Pooley mechanism [16]. Then, as a result of transition processes, these defects recharge, migrate and aggregate with the formation of stable aggregated colour centres, which can exhibit photoluminescence with a high quantum yield [12, 17].

The second regime of interaction of femtosecond laser pulses with a sample of lithium fluoride ceramics was realised by using high-aperture focusing with a simultaneous decrease in the laser pulse energy. This regime is usually used for data recording in optical carriers. The luminescent images of the transverse cross sections of pits formed from colour centres in optical lithium fluoride ceramics under the conditions of high-aperture external focusing are shown in Fig. 5a. Under these irradiation conditions, self-focusing of the femtosecond laser radiation does not occur and, as a result, multiple filamentation is absent. The colour centres are formed at the points of laser beam focusing, where the radiation efficiency is sufficient for multiphonon ionisation of the material.

The image of the transverse cross section of an individual pit induced by a single laser pulse and the luminescence intensity distribution in this cross section are presented in Figs 5b and 5c, respectively. The diameter of the cross section of an individual pit is 0.67 μm and corresponds to the diffraction resolution limit of the MicroTime200 luminescent microscope (with a $20^{\times}$ objective). The real pit diameter is smaller than this value. The highly nonlinear interaction of wide-band-gap crystalline and ceramic optical materials with laser radiation makes it possible to sharpen the profile of the transverse distribution of colour centres to a width several times smaller than the diffraction limit. The diffraction limit of microscope objectives with large numerical apertures determined by the Helmholtz formula is equal approximately to the half-wavelength of the optical radiation, and, in the case of a Ti:sapphire laser, can be 400 nm. If the degree of nonlinearity of the laser beam interaction with the optical carrier material is known, one can determine the shortening of this limit due to the nonlinear sharpening. As was shown above, the luminescence spectra and decay times of colour centres induced by laser radiation in lithium fluoride ceramics are close to the corresponding parameters of colour centres formed by femtosecond laser radiation in single crystals of the same composition. This means that the laser-induced defect formation processes occur almost only inside crystallites forming the ceramics, while inter-grain boundaries only slightly affect these processes. Hence, some properties of single crystals can be translated to ceramics. In particular, we assume that the internal photoeffect under the action of femtosecond laser radiation, as well as the subsequent aggregation of primary defects into luminescent colour centres in ceramics, have the same nonlinearity degree as in single crystals because all the processes occur inside crystallites whose composition and structure are the same as those of the single



a

b

c

Section [prescan_10_IMG1.bdf]

Plot: Fluor. Intensity

(26.09µm / 59.86µm) to (28.17µm / 59.86µm)

Max. Pos.: 1.06 µm

Max. Pos. in Image Coordinates:

X: 27.14 µm

Y: 59.86 µm

FWHM: 0.673 µm

radius at 1/e²: 0.572 µm

Area: 98.84 Counts µm

Bkgr.: 2 Counts

X: 25.89 µm Y: 59.862 µm

Figure 5. Luminescent images of (a) the transverse cross sections of pits formed by single pulses in lithium fluoride ceramics under the conditions of high-aperture external focusing and (b) the transverse cross section of a single pit induced by a single laser pulse, as well as (c) luminescence intensity distribution in the pit cross section. The pit diameter is 0.67 µm.

crystal. Based on this, we used the experimental results obtained previously in [6] on the nonlinearity degree for the complete process of creation of aggregated F_2 colour centres. In this work, it is shown that the yield of F_2 centres is proportional to the 16th power of the laser radiation intensity. At such a high nonlinearity, the width of the transverse spatial profile decreases approximately twofold and, hence, is ~100 nm. This allows one to use ceramic materials for creating highly nonlinear photosensitive media for optical 3D carriers with a high recording density.

4. Conclusions

Thus, we showed that irradiation of optical ceramics based on wide-band-gap LiF and MgF_2 crystals by near-IR femtosecond laser pulses efficiently creates luminescent colour centres characteristic for radiation-coloured single crystals. The mechanism of their formation includes the highly nonlinear generation of electron–hole pairs in the region of filaments or in the region of high-aperture focusing of radiation, their recombination with the formation of anion excitons, and the decay of the excitons into Frenkel defects according to the Lushchik–Vitol–Hersh–Pooley mechanism, as well as their recharging, migration, and aggregation.

Optical ceramics based on wide-band-gap crystals with the exciton mechanism of defect formation are efficient highly nonlinear photosensitive storage media for multilayer luminescent carriers of visual and digital information with a high recording density. The ability of the laser-induced defects to luminesce with a high yield ensures highly sensitive luminescent reading of information. The mechanical properties of the ceramic media based on the studied materials surpass the corresponding properties of single crystals due to the absence of cleavage planes. Therefore, the ceramic materials are preferable for manufacturing optical carriers, and the development of these media with a higher optical homogeneity is also topical.

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