Formation of aggregate color centers under the action of femtosecond laser pulses

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Abstract. A complex study of primary and aggregate defects formation in LiF crystals under the action of femtosecond laser pulses is carried out. These processes were compared for nominally pure and dosimetric LiF crystals (LiF:Mg,Ti). Taking into account high concentration of generated electron-hole pairs, it is proposed that the formation of primary Frenkel defects as a result of direct electron-hole recombination is possible along with the excitonic mechanism. Subsequent processes of aggregation of primary defects with stable defects formation are similar to LiF coloration with X-rays and other types of radiation.

1. Introduction

Usually color centers in dielectric crystals are created with high-energy radiation: X-rays, γ-radiation, accelerated electrons, neutrons or other particles. All crystals can be divided into two large groups. In the first group crystals only impact mechanism of primary defects creation is possible. Impact mechanism consists in displacement of atoms of a crystal lattice with accelerated particles. The displacement should be large enough for stability of displaced atom and created vacancy at given temperature. In the second group crystals low-energy excitonic mechanism of primary defects creation is possible as well. In these crystals excitons are able to decay with creation of Frenkel defects. Interaction between primary defects and their interaction with electrons and holes leads to formation of stable aggregate color centers. Generation of defects after direct creation of excitons or due to recombination of electron-hole pairs after interband photoexcitation is well studied [1].

Nevertheless, for applied coloration of wide bandgap crystals (for example for production of laser media with color centers), when it was necessary to color sufficiently thick crystals, in fact only γ-radiation or accelerated electrons were used [2]. This is due to the fact that in the vacuum ultraviolet region, where exciton excitation spectra and photogeneration spectra of electron-hole pairs are located in wide-gap crystals, there are no simple effective radiation sources. In addition, when optical radiation is used in this spectral region, only a thin surface layer of the crystal can be colored because of the high intrinsic absorption coefficient. At present, femtosecond laser sources of intense radiation are widely used. They make it possible to realize highly nonlinear generation of excitons and electron-hole pairs. With a nonlinear mechanism, the light absorption coefficient is a function of the intensity and can vary over a wide range. This makes it possible to color crystals of larger thickness.
One of the most common and reliable lasers that generate femtosecond pulses is a sapphire crystal with an admixture of titanium. The first harmonic of its radiation has a photon energy of about 1.4 eV. LiF crystals have the bandgap of about 14 eV. This is the biggest value among applied crystals. Energy of low-energy anionic excitons creation in LiF is 13.08 eV [2]. Thus, for one act of multiphoton ionization takes an energy of 8-10 photons of laser radiation. The probability of such a process is very low, nevertheless, the authors of [3-8] observed the coloration of LiF crystals with this radiation. The formation of both single F centers and aggregate color centers was observed: F_2^+, F_3^+, and the others. The authors of these works believe that the coloration is based on multiphoton interband ionization under the influence of laser radiation.

An attempt to analyze the role of self-focusing of exciting laser radiation in the coloration mechanism was made in [6, 7]. The authors concluded that the measured threshold of generation of color centers is 20 percent lower than the calculated self-focusing threshold. Therefore, they considered that self-focusing was not significant. The authors of [9, 10], on the contrary, concluded that self-focusing and filamentation have important role in the coloration.

It should be noted that these works are devoted to applied problems only. The mechanisms of formation of aggregate color centers under the action of femtosecond laser pulses are not studied in details.

The aim of this work is to investigate the generation of anionic Frenkel defects, their subsequent interaction, aggregation, and the achievement of the final stage of processes with the formation of stable aggregate color centers in LiF crystals under the action of femtosecond pulses in the self-focusing and filamentation mode of laser radiation.

2. Experiment

The investigations were carried out on LiF crystals grown by the Kyropoulos method in an air atmosphere. The width of the bandgap of LiF is about 14 eV. The surfaces of the samples were natural cleavages. Before irradiation the samples were transparent and colorless. IR absorption spectra of nominally pure crystals indicated the presence of impurities, identified by literature data as oxygen and hydroxyl impurities.

![Figure 1. Experimental setup.](image-url)
Type of crystal, recorded with heating at a constant rate, the band with a maximum at 480 K dominates. The light sum $S$ of this peak linearly corresponds to the absorbed dose of $D$ up to ~10 Gy. For higher doses the dependence $S(D)$ is superlinear with subsequent saturation and attenuation of the dosimetric band.

The crystals were irradiated with titanium-sapphire femtosecond laser generating pulses of 50 fs duration with a repetition rate of 10 Hz and a maximum energy of about 6 mJ (figure 1). The central wavelength of laser pulses was 950 nm (corresponding photon energy was about 1.3 eV). Low-aperture external focusing of laser beam (the focal length of the lens was 500 mm) was used to realize filamentation of laser pulses. In this mode nonlinear absorption of light and excitation of the electronic subsystem of the crystals occur without substantial heating, evaporation, optical breakdown or other destructive processes. The energy of single laser pulses passed through the sample was measured with laser energy detector STANDA-11QE50LP-H-MB. The total energy of the laser radiation transmitted through the sample was determined by the number of pulses.

Investigation of the spatial distribution of induced color centers in irradiated samples was carried out with a highly sensitive scanning confocal fluorescence microscope with a picosecond time resolution PicoQuant MicroTime 200. Photoluminescence spectra of induced color centers were recorded with the Ocean Optics 65000 spectrometer under the excitation light with wavelengths of 375, 405, 532 and 640 nm.

3. Experimental results

Photographs of luminescent channels in the samples irradiated with femtosecond laser pulses are shown in figure 2 (the photographs were obtained with the Olympus IX microscope 71). The excitation wavelength was 450 nm. One can see that luminescent defects (color centers) are efficiently created in the investigated samples irradiated with femtosecond radiation. The spatial distribution of these defects is filamentary due to filamentation of laser pulses. The traces of a single pulse are relatively thin and short. As the number of pulses increases, the thickness and length of the luminescent channels increase.

![Figure 2](image)

In figure 3 the absorption spectrum of samples irradiated by the series of 3125 femtosecond pulses of titanium-sapphire laser are shown. The spectra were registered with a spectrophotometer SF-56. To isolate the irradiated channel we used an aperture with a diameter of 1 mm. The same aperture was installed in the reference measuring channel of the spectrophotometer.

The obtained absorption spectra are typical for radiation-colored LiF crystals. Several bands are presented in the studied samples: absorption band of F centers with a maximum at a wavelength of 250 nm; R-absorption band of F$_3$-centers consisting of two bands R$_1$ and R$_2$ with maxima at wavelength of 320 and 380 nm, respectively; M-absorption band of F$_3^+$ and F$_2$-color centers with a
maximum at wavelength of 441 nm; N-absorption band in the region of 520-540 nm; absorption band of F$_{2}^{+}$ color centers with a maximum at wavelength of 640 nm.

![Absorption spectrum of LiF crystals](image)

**Figure 3.** Absorption spectrum of LiF crystals irradiated with a series of 3125 femtosecond pulses of titanium-sapphire laser.

Luminescence of all types of color centers induced with femtosecond laser pulses was observed under the excitation with wavelength of 375 nm (figure 4).

![Spectra of photoluminescence of color centers](image)

**Figure 4.** Spectra of photoluminescence of color centers induced by a series of 5 (curve 1), 625 (curve 2) and 3125 (curve 3) femtosecond laser pulses under excitation with laser pulses of with wavelength of 375 nm.

Generalized results of investigations of the spectral-kinetic luminescence characteristics of defects induced with series of 5 to 3125 femtosecond laser pulses with excitation of luminescence with lasers with emission wavelengths of 375, 405, 532 and 640 nm are represented in table 1.
Table 1. Luminescence characteristics of the samples.

| Number of pulses | Maximum of luminescence band, nm | Decay time, ns | Maximum of luminescence band, nm | Decay time, ns | Maximum of luminescence band, nm | Decay time, ns | Luminescence band, nm | Decay time, ns |
|------------------|---------------------------------|---------------|---------------------------------|---------------|---------------------------------|---------------|---------------------|---------------|
| 5                | 660                             | 15            | 540                             | 7             | 860                             | 20            | absent              | -             |
| 625              | 660                             | 15            | 540                             | 7             | 860                             | 20            | 820                 | 7-8           |
| 3125             | 660                             | 15            | 540                             | 6             | 680                             | 20            | 820                 | 7-8           |

One can see from the presented data that for the sample irradiated with the series of 5 pulses the luminescence spectrum has typical for colored LiF crystals bands of $F_2$ and $F_3^+$ color centers with a maximum wavelengths of 680 and 540 nm respectively. The measured values of the luminescence decay time of 15 and 6.8 ns of irradiated samples also coincide within experimental error to known values for $F_2$ and $F_3^+$ centers in LiF crystals (16 and 8 ns respectively). In the luminescence spectra, when excited with picosecond laser pulses with wavelength of 640 nm, a luminescence band of stabilized $F_2^+$ centers is observed with decay time of 17 ns typical for a this centers. As a number of pulses in series increases from 625 to 3125, the residual concentration of $F_2^+$ color centers increases, and more complex aggregate $F_3$ (R), $F_3$ and $F_4$ (N) centers appear.

Our experiments on the evaluation of the absorbed dose (the energy of femtosecond laser radiation) in dosimetric LiF:Mg,Ti crystals show that when the sample is irradiated in a low-aperture external focusing mode with a single pulse, the absorbed dose $D$ is 11.3 Gy. The obtained value of the femtosecond laser pulse energy $(E=D\cdot\Delta m=0.3\ \mu\text{J})$ absorbed by crystal corresponds to the absorption of $10^{13}$ photons with energy of 1.4 eV (excitation wavelength is 950 nm, pulse energy is 6 mJ, total number of photons in a pulse is of the order of magnitude of $10^{16}$). Upon exposure of a sample to series of 5 femtosecond pulses, the absorbed dose of $D$ is 55.7 Gy, with increase in the number of pulses to 10 the super-linear growth of the absorbed dose to 925 Gy occurs. As mentioned above, for doses more than 10 Gy the superlinear dependence of $S (D)$ observed, followed by saturation and the weakening of the dosimetric peak. The saturation of the stored light sum and its subsequent attenuation is described in more detail in [11]. In addition, investigations of the TSL of dosimetric LiF:Mg,Ti crystals irradiated with laser have shown that when a sample is exposed to a pair of femtosecond pulses with an energy of 1.1 mJ, high-temperature peaks are effectively stored. It indicates a high concentration of $(X_3)_\text{aca}$ centers. Effective storage of high-temperature peaks was observed by the authors in [12] when a crystal of this type was irradiated by high-energy particles ($\alpha$-particles and uranium ions). It is known that, in addition to exciton mechanisms of defect formation, impact mechanisms and mechanisms of electronic excitation multiplication with the production of secondary excitons due to the action of primary "hot electrons" play an important role in such types of radiation influence. With this, it is impossible to exclude the formation of primary defects by means of direct electron-hole recombination.

4. Discussion of results
The presented results definitely indicate that color centers typical for radiation-colored LiF crystals are effectively created in wide bandgap LiF crystals under the action of near IR femtosecond laser
radiation. However, the crystals irradiated with intense femtosecond laser pulses have a number of special features in comparison to crystals irradiated with X-rays and other types of radiation. First, the energy supplied to the crystal by laser radiation with single pulses is absorbed during 50 fs, while the irradiation of the crystals with X-rays can last several hours. Secondly: the energy spectrum of X-ray photons is much wider than spectrum of femtosecond laser radiation. Thirdly, in case of irradiation with X-rays, a relatively uniform radiation effect occurs in the volume of a sample (as evidenced by a homogeneous distribution of induced defects), whereas defect formation under the action of femtosecond laser pulses if highly non-uniform due to filamentation.

For media with an exciton mechanism of primary defects formation (with the subsequent formation of stable color centers) under the action of a femtosecond laser pulse, it is possible to distinguish three stages of the interaction process after self-focusing [13]:
1. Photoionization of the material via multiphoton or tunneling absorption.
2. The primary electrons are accelerated in the field of femtosecond pulse and generate an avalanche of secondary electrons in conduction band and holes in valence band.
3. As energy of the electron-hole gas decays, short-lived bound states of an electron and a hole (an exciton) are formed. Then self-trapping and decay of excitons occur with the formation of primary defects and subsequent formation of stable color centers due to diffusion of primary defects.

The first two stages occur in the electronic subsystem of the medium during the action of femtosecond laser pulse. In this paper we consider the third stage in details. The mechanism of the formation of primary Frenkel defects after the decay of self-trapped excitons in alkali halide crystals does not depend on way of formation of the excitons ($\gamma$-irradiation, X-ray, VUV, two-photon excitation with an excimer laser or with a femtosecond laser in our case). This mechanism is well studied and is described in a number of works, for example [1].

It is believed that the exciton mechanism is dominant in the formation of primary defects in alkali-halide crystals. However, in a number of works [14] an attempt was made to detect the formation of $F_2$ centers in LiF crystals with a maximum energy of anionic excitons (13 eV) upon irradiation of LiF with synchrotron radiation ($T=290$ K), i.e. an attempt to register the formation of $F_2$ centers in the decay of single excitons. Even a very sensitive luminescent method for detecting $F_2$ centers has not allowed authors to confidently register their formation in the decay of single excitons. The decay of excitons leads to the formation of $F$, $H$ pairs, and the formation of $F_2$ centers requires the possibility of hopping diffusion of anion vacancies $V_a^-$ over the crystal and the presence of electron flux. In subsequent works of this team, the authors also point to this circumstance [15].

In general, it should be noted that, to date, the conclusion about the predominance of this or that mechanism of defect formation in the alkaline earth metal has not been reached yet. In many respects this depends on the conditions of irradiation and the type of radiation. So until now the discussion is under way, in which cases the electron-hole mechanism predominates, and in which the exciton defect formation mechanism is dominant [16, 17].

The above data on the value of the energy that’ve been absorbed by a dosimetric crystal make it possible to estimate the number of electron-hole pairs induced during duration of a single femtosecond pulse (50 fs) as $N=\frac{E}{E_g}$, it equals to $10^{12}$. The fraction of primary defects formed during decay of excitons is only very few percents of the total number of excitons formed, and the concentration of $F_2$ centers is proportional to the square of the $F$ centers [6]. Thus, it can be assumed that when irradiating lithium fluoride crystals with intense femtosecond pulses, along with the exciton mechanism of defect formation, primary defects formation can take place due to direct electron-hole recombination with the reaction [16]:

$$e^- + e^+ + e^- + e^+ \rightarrow F + H + e^- + V_k \rightarrow F + I + V_k$$

The formation of the $(X_3)^{\text{aca}}$ centers responsible for the high-temperature peaks in the TSL curves occurs due to the reaction:

$$v_a^+ + i_a^0 + i_a^0 \rightarrow V_c^- i_c^{0+} + i_c^+$$
When the crystals are irradiated for a long time by series of large numbers of femtosecond pulses, the processes become more complex, the boundary between the electron-hole and exciton mechanisms is vanished, the processes of defect formation can be accompanied by the formation of an "avalanche" of electrons in the conduction band. When the concentration of primary defects increases, the concentration of their aggregates $F_2$, $F_3$, $F_4$ increases. The processes of further association of $F$ centers lead to the phenomenon of the formation of colloidal metal particles with the size of hundreds angstroms (in our case, Li), which has been well studied. The growth of associations of $H$ centers, as shown in a number of works, leads to the formation of dislocation loops.

5. Conclusions

Thus, the primary process of defect formation is the formation of a Frenkel pair: $F$ and $H$ centers. Recharging of these centers during irradiation leads to formation of an interstitial fluorine ion (I-center) and an anion vacancy. At room temperature, these defects, apart from the $F$ center, are mobile and, therefore, are kinetic particles that ensure the transport of matter and charge along with electrons and holes. In addition, it is known that holes and interstitial atoms form molecules and molecular ions consisting of two or three fluorine atoms located in one, two or three vacancies of different sign. Out of such centers $V_K$, $V_f$ and $V_t$-centers are mobile at room temperature. Consequently, they are also kinetic particles capable of participating in the processes of defects transformation during irradiation. $(X_3)_{ac}$ – centers are stable up to 570 K. $F_2^+$ centers are formed primarily from aggregation of electronic centers due to the attachment of mobile anion vacancies (lifetime 1–10 min) to the $F$ centers. The $F_2^+$ centers themselves are also kinetic particles (the lifetime is ~6 hours), their hopping diffusion ensures the creation of $F_3^+$ and more complex electron color centers. It is known that there is an increase in the $F_2^+$ absorption band for ~1 min. in crystals irradiated at room temperature after the end of irradiation. The mechanism of this process in the literature is treated unambiguously - an association of accumulated anion vacancies mobile at room temperature with $F$ centers takes place. As a result, there are $F_2^+$-centers:

$$v_u^+ + F \rightarrow F_2^+.$$

This is the first elementary aggregation process. The results obtained by us are associated with a slower process of the transformation of the centers, proceeding with a characteristic duration time of 3-6 hours, as a result of which the $F_2^+$ band falls, and the M band, which is a composition of the bands of the $F_2$ and $F_3^+$ centers, grows. During the approach of $F_2^+$ to other electron centers, they associate with formation of $F_3^+$ centers, diffusion-controlled tunnel recombination occurs, which leads to an increase in the number of $F_2$ color centers with a simultaneous decrease in the $F_2^+$ band:

$$F_2^+ \uparrow + F \rightarrow F_3^+$$

$$F_2^+ \uparrow + e \rightarrow F_2.$$

The experimental data obtained for the sample irradiated with 5 femtosecond pulses show that for the utilized irradiation mode (the entire absorbed dose of energy was introduced in a time shorter than the lifetime of the anion vacancies $\tau_v < \tau_a^+$) the nomenclature of formed centers is the simplest. This is due to the fact that the processes of aggregation do not occur during the irradiation. Consequently, electrons and holes arising under the action of exciting laser radiation cannot be captured by aggregate centers. Aggregation occurs after the end of irradiation, and therefore the processes of electron-hole charge exchange are practically eliminated. Under these conditions, $F_2^+$ centers are formed after irradiation, and their subsequent association with the $F$ centers results in $F_3^+$ color centers. $F_3^+$-centers cannot be formed. Indeed, there are no bands of $F_3$ in the luminescence spectra (see figure 4, curve 1). Moreover, $F_3$-color centers, as well as more complex aggregate and colloid centers, cannot be formed. The $F_2$ centers formed during the relaxation have lower concentrations than the $F_3^+$ color centers. Under the influence of prolonged laser irradiation, i.e. when $F_2^+$ centers have time to form during irradiation, and processes of their charge exchange are enabled, and created color centers can be
transformed into other types of centers. Therefore, the ratio of different types of color centers in a crystal depends on the intensity and duration of irradiation, which is confirmed by our studies.

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