Luminescence of $F_2$ and $F_3^+$ centres in LiF crystals irradiated with 12 MeV $^{12}$C ions

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Luminescence of F$_2$ and F$_3^+$ centres in LiF crystals irradiated with 12 MeV $^{12}$C ions

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Abstract. Dependences of the nanohardness and photoluminescence of F$_2$ and F$_3^+$ centers on the depth in LiF crystals irradiated with 12 MeV $^{12}$C ions to fluences $10^{10}$-$10^{15}$ ions/cm$^2$ were studied using laser scanning confocal microscopy, luminescent spectroscopy, and the nanoindentation method. The nanohardness measurements showed a significant hardening effect at the end of the ion run with the dominant contribution of defects formed by the mechanism of elastic collisions. The observed attenuation of the luminescence intensity at high fluences is associated with the intense nucleation of dislocations as traps for aggregate color centers.

1. Introduction
Ion modification of materials has proved to be an effective tool for the formation and modification of electrical, optical, mechanical and chemical properties of a wide range of materials. Investigation of the change in the properties of materials in the relationship is a complex task and LiF crystals play a role in solving such problems, due to the simple structure and good study of radiation damage.

In this paper, we present results on the study of the bulk luminescence of F$_2$ and F$_3^+$ centers, the luminescence of these centers along the ion path, nanohardness on the frontal surface, and the surface of the transverse cleavage in LiF crystals irradiated with 12 MeV carbon ions.

2. Experimental equipment
Irradiation of samples of LiF crystals (SOI, St. Petersburg and ISU, Irkutsk) was carried out on a DC-60 cyclotron at a beam current density of 10 nA/cm$^2$, for which the sample heating during irradiation can be neglected [1, 2]. The fluence varied from $10^{12}$ to $10^{15}$ ion/cm$^2$. Photoluminescence of the F$_2$ and F$_3^+$ centers along the ion pathway was measured with a confocal scanning microscope (LCSM). Agilent Nano G200 (USA) – the system for indenting was used to study nanohardness along the
profile depth, characterizing the evolution of nanoscale defects along the ion path, it makes it possible to make standard measurements of CSM (Continuous Stiffness Measurement) in the regime of constant recording of the applied force and displacement of the point of the indenter.

3. Results and discussion
Absorption spectra for LiF crystals irradiated with 12 MeV $^{12}$C ions are shown in figure 1. Analysis of the spectra shows that for large values of the fluences, the absorption in the F and F$_n$ regions of the centers decreases. The concentration of F centers was determined by the Smakul-Dexter formula $n_F = 9.48 \times 10^{15} D_{opt}(F)$, where $D_{opt}(F)$ – optical density at the maximum of the absorption band of F centers. and volume concentration $N_F (\text{cm}^{-3}) = n_F / R$. To compare the relative concentrations of F$_n$ and F centers, we used integral absorption ($A_{F_n}$ and $A_F$), which were determined by formulas

$$A_F = \int D(\varepsilon) \, d\varepsilon \quad \text{and} \quad A_{F_n} = \int D(\varepsilon) \, d\varepsilon$$

Figure 2 shows the dependences of $N_F$, $A_F$ and $A_{F_n}$ for LiF crystals irradiated by $^{12}$C ions with energy of 12 MeV. The decay of $N_F$, $A_F$ and $A_{F_n}$ can be explained by the creation of larger aggregates with increasing absorbed energy. We note that the $N_F$ decay occurs at an absorption energy several times lower than for $A_F$. This is explained by the fact that at large absorbed energies the area under the F-center curve widens due to the formation of defects from trace elements (mainly associated with magnesium).

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Absorption spectra of LiF crystals irradiated by $^{12}$C ions with energy of 12 MeV to various fluences.

![Figure 2](https://via.placeholder.com/150)

**Figure 2.** Dependence of concentration of F centers $N_F (\text{cm}^{-3})$ and integral absorption of $A_F$ and $A_{F_n}$ for F and F$_n$ centers as a function of the absorbed energy density $E_{abs} (\text{eV/cm}^3)$ in LiF crystals irradiated with 12 MeV $^{12}$C ions.

The absorption bands of F$_2$ and F$_3^+$ centers (the main F$_n$ centers) overlap greatly, making it difficult to study. For the first time detailed studies of F$_2$ and F$_3^+$ centers were carried out by the scientist Nahum [2]. In the future, studies (Skuratov, [4, 5]) established that these colour centres are formed by the reactions: $F + V_a^+ \rightarrow F_2^+$, $F_2^+ + e \rightarrow F_2^+$, $F_2^++V_a^+ \rightarrow F_3^+$. The presence of F$_2$ and F$_3^+$ centers can be observed by their luminescence (figure 3). It should be noted that at low optical densities, the concentration of F$_2$ and F$_3^+$ centers is proportional to the luminescence intensity. However, this is impeded by a
decrease in the luminescence of both $F_2$ and $F_3^+$ centers with increasing fluence, as shown in figures 3 and 4. Quenching of the luminescence of these color centers was observed by Montereali upon irradiation with electrons [6] and Skuratov under irradiation with fast ions [4, 5]. Quenching of luminescence [4, 5] in LiF crystals is associated with radiation-induced mechanical stress, which changes the potential and activation energy of $F_2$ and $F_3^+$ centers.

Figure 3. Photoluminescence spectra for $F_2$ (670 nm) and $F_3^+$ centers (530 nm) under excitation with 473 nm light for LiF crystals irradiated with 12 MeV $^{12}$C ions with different fluences.

Figure 4. The luminescence intensity for LiF crystals irradiated with ions of $^{12}$C with energy of 12 MeV depending on fluence (density of absorbed energy).

The growth of the luminescence of $F_2$ and $F_3^+$ centers begins with a fluence of $3 \times 10^{10}$ ion/cm$^2$ for 12 MeV $^{12}$C ions, reaches a maximum at $6 \times 10^{12}$ ion/cm$^2$ for $F_2$ centers, and a maximum for $F_3^+$ centers is shifted toward lower fluences. At low fluences, $F_3^+$ centers dominate, but since the fluence is $3 \times 10^{12}$ ion/cm$^2$, $F_2$ centers dominate. If in the stage of small fluences the processes associated with the capture of anion vacancies that are components of charged Frenkel pairs dominate, then the overlap of tracks contributes to the increase in the fluence, leading to the creation of $F_2$ centers by the reaction: $F+F\rightarrow F_2$. Starting with fluences $\Phi>6 \times 10^{11}$ ion/cm$^2$, when tracks start overlapping, detectable hardening and the appearance of dislocations are observed (figure 5). The luminescence of the $F_2$ and $F_3^+$ centers is sensitive to disturbances in the surrounding structure, and the $F_3^+$ centers, being charged, are more sensitive, which explains the shift of the intensity maximum towards lower fluences. A general decrease in the complex $F_n$ centers also contributes to this effect.

Nanoindentation tests on the frontal surface oriented normally to the ion beam show a significant hardening effect in LiF crystals when irradiated with 12 MeV carbon ions. The effect of hardening the frontal surface is present with fluence above $6 \times 10^{10}$ ion/cm$^2$, increasing with the fluence and reaching saturation at fluences above $6 \times 10^{13}$ ion/cm$^2$. Nanohardness measurements were made on the surface profile in order to characterize the damage along the ion path. The results presented in figure 5 show the evolution of hardness on the transverse cleavage of samples irradiated with 12 MeV $^{12}$C ions to various fluences. Calculated depth profiles for electron energy losses (dotted line) and for nuclear losses (solid line) are presented for comparison. At fluences $5 \times 10^{10}$ and $10^{11}$ ion/cm$^2$, hardening was not detected. At fluences of $3 \times 10^{11}$ and $6 \times 10^{11}$ ion/cm$^2$, hardening on the profile surface appeared only in the Bragg maximum region. At high fluences, the hardening effect increases, and its variations along the ion range follow the changes in electron energy losses of the ion, calculated using the SRIM code. This trend is clearly visible in figure 5.
In general, the results of nanoindentation characterize the evolution of lesions on the frontal and profile surfaces. The results show a significant hardening at the end of the ion range, despite the fact that the value of the calculated electron losses decreases to the lowest values. At high fluences, the area of maximum hardening expands to the end of the ion range, where the nuclear energy losses shift to the maximum (figure 5) [7]. We can conclude that irradiation with light ions $^{12}$C is capable of creating severe damage and hardening by means of the elastic collision mechanism. The effect is manifested in a narrow zone close to the end of the ion run.

The luminescence of $F_2$ and $F_3^+$ (figures 6 and 7) centers along the ion range grows at the surface from a fluence of $3 \times 10^{10}$ ion/cm$^2$ to $3 \times 10^{12}$ ion/cm$^2$, with a decrease in intensity as ions move inward, that is, these centers are created as a result of the mechanism of electronic energy losses.
observed attenuation of the luminescence intensity at high fluences is associated with the intense nucleation of dislocations as traps for aggregate color centers. This is also associated with the process of hardening. The luminescence quenching begins at $3 \times 10^{13}$ ion/cm$^2$, and a luminescence burst of both centers is observed at a depth of 6 nm, which corresponds to a sharp decrease in the electron energy losses and to an increase in losses due to elastic collisions, creating strong lesions creating a large number of anion vacancies. The creation of anion vacancies is more preferable than cation vacancies due to the more probable interaction of a positively charged carbon ion. Quenching of the luminescence of aggregate electron color centers occurs as a negative fluorine ion.

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