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Kr and Xe ion induced aggregation processes in LiF crystals during irradiation and thermal annealing

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Abstract. The efficiency of F and F_n center creation in LiF crystals irradiated with 147 MeV Kr and 195 MeV ions was studied via ion fluence and flux. In the case of Kr ions with flux of 8.9×10^9 ions/(cm$^2\times$s) saturation of F centers (~ 10^{19}cm^{-3}) was observed at a fluence of 10^{12} ions/cm^2. Further irradiation decrease the F center concentration. In LiF irradiated with both ions an enhancement of electron color centers (F and F_n) via flux was observed. In LiF crystals irradiated with Kr ions an enhancement of F_n centers was observed after thermal annealing up to 600 K. The mechanisms of the processes are discussed.

1. Introduction

A large scope of ion induced damage studies in dielectric materials is published in the last decades (see reviews [1] and [2] and references within). In papers [3, 4] an enhancement of electron color centers (F and F_n) in LiF crystals irradiated with 5 and 10 MeV Au ions at high flux and high fluence was observed. The effect depends both on the absorbed energy (fluence) and flux. The detailed mechanism of the enhancement of electron color centers is not clear. In paper [4] it was demonstrated that interaction of primary H centers leads to fluorine molecule (X_2) formation ($H + H \rightarrow X_2$) which play an essential role in the enhancement. The fluorine molecule formation leads to a decrease of H center recombination with electron color centers (e.g. $F + H \rightarrow 0$). Our preliminary studies [5, 6] confirmed these results.

The paper is aimed to analyze the efficiency of F and F_n center formation in LiF crystals irradiated with Kr and Xe ions during irradiation with various beam current densities (flux) as well as the transformation of these color centers by following thermal annealing.

2. Experiment

High quality LiF crystals grown from the melt in vacuum (Optical Institute (GOI) St. Petersburg, Russia) were used for the experiments. Platelets of 10×10 mm^2 and with the thickness of about 1 mm were irradiated at room temperature (RT) normal to one of the cleaving plane (001) with 147 MeV Kr^{+14} (range R = 17.8 μm, dE/dx = 12 keV/nm) and 195 MeV Xe^{+20}(R = 17.3 μm, dE/dx = 18.5

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keV/nm) ions at the DC-60 cyclotron accelerator (Astana, Kazakhstan). The fluence was varied in the range from 8×10^{10} to 10^{13} ions/cm^2 with the beam current density from 20 to 200nA/cm^2. The corresponding ion flux (φ) is equal to $\varphi = 6.24\times10^9 \times i_{ion}/q$ [ions/(cm^2×s)], where i_{ion} is the beam current density [nA/cm^2] and q is the charge of the ion.

Optical measurements were carried out with the spectrometer CΦ-103 in the spectral range of 1.8 eV (700 nm) – 6.2 eV (200 nm) corresponding to the absorption of the main electronic color centers (F, F_2, F_3, F_4). In the absorption spectra the peaks of F and F_2 centers were dominating. The concentration of F and F_2 centers (cm^{-2}) was estimated using the Smakula-Dexter formula [7]:

$$n_F = 9.48\times10^{15}\times D(F) \quad (1)$$

$$n_{F2} = 4.42\times10^{15}\times D(F_2) \quad (2)$$

where $D(F)$ and $D(F_2)$ are the optical density at the absorption maxima of F and F_2 centers, respectively. The average volume concentration can be estimated dividing n_F and n_{F2} with the ion range, i.e. $N_F = n_F/R$ and $N_{F2} = n_{F2}/R$. Unfortunately the complementary to electron color centers hole center V_3 has the absorption in the vacuum UV spectral region (maximum at 10.8 eV (114 nm)) and could be not analyzed with our technique [8].

3. Results and discussion

We studied the color center creation in irradiated LiF crystals via fluence at a constant flux as well via flux at constant fluence.

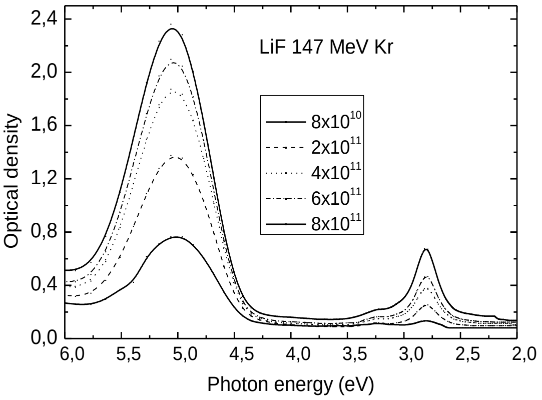

Figure 1. Absorption spectra of LiF crystals irradiated with 147 MeV Kr ions at flux of 8.9×10^9 ions/ (cm^2×s).

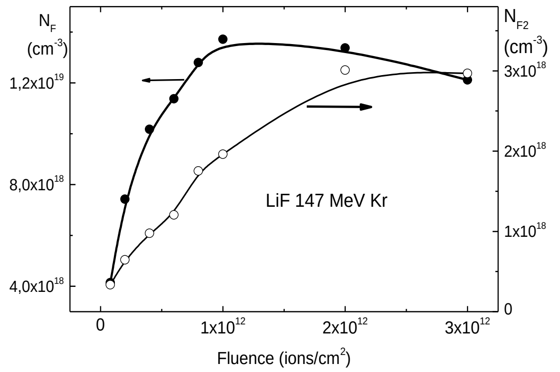

Figure 2. The dependence of the volume concentration (cm^{-3}) of F and F_2 centers via fluence in LiF crystals irradiated with Kr ions (see figure 1).

3.1. Dependence on the fluence

The dependence of the absorption spectra and the concentration of color centers on the fluence at a constant flux of $\varphi = 8.9\times10^9$ ions/ (cm^2×s) for LiF crystals irradiated with Kr ions are presented in figure 1 and figure 2. A special experiment demonstrate, that the ion induced temperature increase (heating) at the flux 8.9×10^9 ions/(cm^2×s) did not exceeds 30°C.

The efficiency to create an F center can be estimated by the average energy (ΔE_F) to create an F center according to [8]:

$$\Delta E_F = E_{ion} \times \Phi/n_F, \quad (3)$$

where E_{ion} [eV] is the ion energy, Φ [ions/cm^2] is the fluence, and n_F is the number of created *F* centers. The value of ΔE_F increases from 1.6 keV for $\Phi = 8\times10^{10}$ions/cm^2 to 6.1 keV for $\Phi = 10^{12}$ions/cm^2 (*F* center concentration maximum). In the absorption spectra at photon energies less than 4 eV the absorption of F_2 centers (maximum at 2.79 eV) is dominating. Therefore we used the concentration of F_2 centers for the characteristic of the formation of F_n centers. The concentration of F_2 centers increases with the fluence (figure 2) from $N_{F2} = 3.4\times10^{17}$ cm^{-3} (at $\Phi = 8\times10^{10}$) to $N_{F2} = 3\times10^{18}$ cm^{-3} (at $\Phi = 3\times10^{12}$). This can be explained by neighbour track overlapping which determined the higher recombination losses (increase of ΔE_F) and higher concentration of F_2 centers.

3.2. Dependence on the ion flux

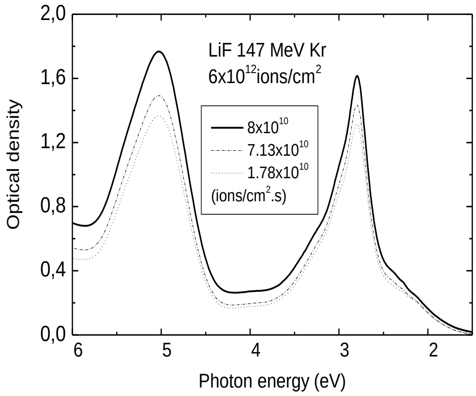

Figure 3. Absorption spectra of LiF crystals irradiated with Kr ions at various flux at a constant fluence of $\Phi = 6\times10^{12}$ ions/cm^2.

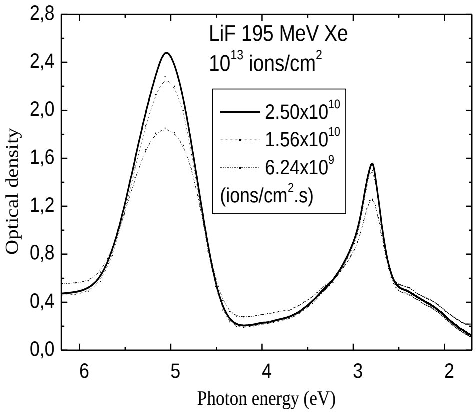

Figure 4. Absorption spectra of LiF crystals irradiated with Xe ions at various flux at a constant fluence of $\Phi = 10^{13}$ ions/cm^2.

The dependence on ion flux φ is determined mainly by the interaction of primary Frenkel pairs during irradiation [3, 4]. In paper [4] the role of primary *H* centers at high flux values was demonstrated. The interaction of *H* centers at RT leads to formation of V_3 centers ($X^0X^-X^0 = X_3^-$ – a three-halide molecule in the lattice) or di-halide molecules (X_2) by the reaction $H + H \rightarrow X_2$. The di-halide molecules can form halogen bubbles, which play a crucial role at high fluence and high flux preventing the recombination of hole centers with *F* and F_n centers.

The results on the dependence on the ion flux for LiF irradiated with Kr and Xe ions is presented in figure 3 and figure 4. To compare the ratio of single *F* centers and F_n centers we use the integral absorptions according to [7]:

$$A_F = \int_{4.2}^{5.8} D(E)dE \tag{4}$$

for *F* centers and

$$A_{Fn} = \int_{1.8}^{4.2} D(E)dE \tag{5}$$

for F_n, where *D* is the optical density and *E* is the photon energy.

For LiF crystals irradiated with Kr ions the ratio $\xi = A_{Fn}/A_F$ is constant for all used flux values and equal to $\xi = 0.8\pm0.2$. This demonstrates the saturation of the enhancement for *F* and F_n centers by irradiation with the used flux values (figure 3). Additional experiments are necessary to examine both the influence of the absorbed energy (fluence) and flux (beam current) on the enhancement.

Analyzing the average energy to create an F center ΔE_F (figure 3), we found that ΔE_F decreases from 67 keV for $\varphi = 1.78\times10^{10}$ to 50 keV for $\varphi = 8\times10^{10}$ (ions/cm^2×s). This demonstrates the increase of the mutual interaction between H centers leading to the enhancement of F and F_n centers.

Similar phenomena we observed for LiF crystals irradiated with Xe ions at a fluence of 10^{13} ions/cm^2 (figure 4). The value of ΔE_F for the lowest flux is 111 keV and it decreases for the highest flux of $\varphi = 2.5\times10^{10}$ ions/(cm^2×s) up to ΔE_F = 82 keV. The higher values of ΔE_F for LiF irradiated with Xe ions is determined by the higher absorbed energy $E_{abs} = E_{ion}\times\Phi$ (about 2×10^{21} eV/cm^2 for Xe) than that for Kr ions (9×10^{20} eV/cm^2). At higher absorbed energy the energy to create an F center ΔE_F decreases due to the higher recombination losses [7]. The ration A_{Fn}/A_F for LiF crystals irradiated with 195 MeV Xe ions was smaller ($\xi = 0.58$) than that for LiF irradiated with Kr ions. This demonstrates that by irradiation with Xe ions the saturation of the enhancement was not reached.

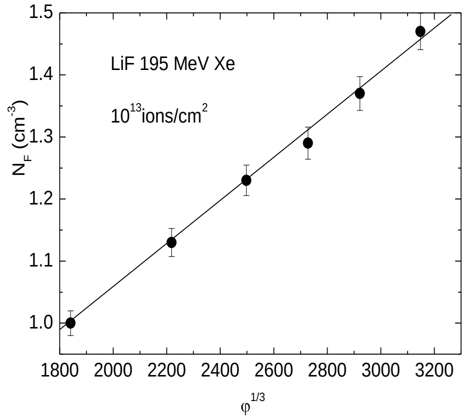

Figure 5. The concentration of F centers (N_F, cm^{-3}) via flux (φ). The dependence $N_F \sim \varphi^{1/3}$ indicate the formation of fluorine molecules [4].

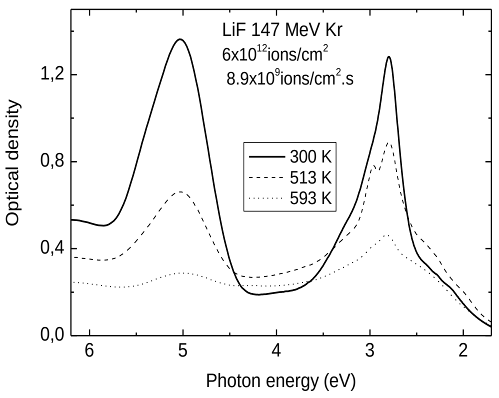

Figure 6. Absorption spectra of LiF crystals irradiated with 147 MeV Kr ions at a fluence of 6×10^{12} ions/cm^2 at room temperature and after thermal annealing.

In figure 5 the dependence of the F center concentration N_F via the flux is presented. The linear dependence $N_F \sim \varphi^{1/3}$ according to [4] is determined by the formation of halogen molecules ($H + H \rightarrow X_2$).

3.3. *Thermal annealing*

Thermal annealing of LiF crystals irradiated with heavy ions depends on the energy loss of the ions as well on the fluence [7, 10]. During thermal annealing two various processes takes place: (1) the decomposition of V_3 centers with H center production ($V_3 \rightarrow H + H$); (2) diffusion of single F centers with following complex electron color center formation according to the reactions $F + F_n \rightarrow F_{n+1}$, e. g. $F+F \rightarrow F_2$, $F + F_2 \rightarrow F_3$ etc. [9, 10]. The annealing process depends on the initial defect structure in the irradiated LiF crystal at RT and the annealing temperature. At T < 500 K F centers are not mobile and the decomposition of V_3 centers leads to recombination with electron centers according to $F + H \rightarrow 0$ and the absorption of F centers decreases. At higher temperature besides the recombination of H centers with electron color centers also coagulation of electron and hole centers are possible ($F + F_n \rightarrow F_{n+1}$ or $H + H \rightarrow X_2$). It was demonstrated, that in LiF crystals irradiated with heavy ions even at high fluences (high absorbed energies) no metallic Li colloids were observed [7,8]. Metallic colloids (Li, Mg) in irradiated with heavy ions LiF crystals are observed only after thermal annealing of irradiated LiF crystals at high temperatures [3].

Thermal annealing we studied in LiF crystals irradiated with 147 MeV Kr ions at a fluence of 6×10^{12} ions/cm^2 (Fig.6). Annealing up to 513 K and 593 K leads to a decrease of the absorption both for single F centers and F_n centers. A strong F center concentration decrease was observed (about two times at 513 K and more than 10 times at 593 K). Nevertheless, the ratio of F_n to F centers estimated by the integral absorption A_{Fn}/A_F increases with the annealing temperature from 0.66 at 300 K to 1.36 at 513 K and about 3 at 593 K (figure 6). This demonstrates that during thermal annealing up to about 600 K in heavily irradiated LiF (high fluence) the coagulation reactions ($F_n \rightarrow F_{n+1}$) are dominating.

The results of our study examine two phenomena on color center interaction during irradiation (dependence on fluence and on flux) as well as in the thermal annealing process of heavily irradiated LiF crystals.

Dependence on the fluence can be easy understood by neighbor track overlapping, i.e. by irradiation of a former irradiated area of the crystal. As a result more complex color centers (F_n) are crated (figure 1 and figure 2). The enhancement of F_n centers takes place when the volume concentration of single F centers reaches the value of about 10^{19} cm^{-3} [10, 11]. After the saturation of F centers, additional irradiation leads to a decrease of single F centers with a further increase of F_2 centers.

The ratio of the concentration of F_n centers to F centers at a comparable fluence increases with the flux value (figures 2 - 4).

Dependence on the flux is determined by processes during irradiation. The enhancement of color centers (F and F_n) depends both on the fluence (i.e. absorbed energy) and the flux [3]. It was demonstrated, that the enhancement is more effective for high fluence and high flux. In LiF crystals we observed a high ratio of the integral absorption A_{Fn}/A_F which is close to the saturation (figs. 3 and 6). For a better understanding more detailed investigations are necessary varying the fluence and flux.

Unfortunately, we have no direct measurements on the presence and the quantity of fluorine molecules in the irradiated crystals. Nevertheless, in many investigations the halogen molecules are one of the final products of radiolysis in ionic crystals (see [9, 11, 12, 13] and references within). Therefore, our indirect conclusion on the role of fluorine molecule production during irradiation with high fluxes (enhancement of F and F_n centers figure 3 and figure 4) as well as the dependence of $N_F \sim \varphi^{1/3}$ (figure 5) is justified.

The results of the increase of the ratio of the integral absorption during thermal annealing up to about 600 K demonstrates, that formation of fluorine molecules (interaction of H centers) occurs also by thermal decomposition of the V_3 centers. Probably, the enhancement of F_n centers during annealing occurs only at high initial concentration of F_n centers.

4. Conclusions

Color centre creation in LiF crystals by irradiation with Kr and Xe ions via fluence and flux was studied.

In LiF crystals irradiated with 147 MeV ions at a flux of 9×10^9 ions/(cm$^2\times$s) the saturation occurs at a fluence of 10^{12} ions/cm^2 where the volume concentration of F centers reaches about 10^{19} cm^{-3}. Irradiation at higher fluence leads to a decrease of the concentration of single F centers due to a coagulation to F_n centers.

An enhancement of electron color centers (F and F_n) in LiF crystals irradiated with Kr and Xe ions with high flux was observed. The enhancement increases with the flux value.

We observed also an enhancement of F_n centers during thermal annealing of heavily irradiated LiF crystals with Kr ions.

We suppose that the enhancement of F and F_n centers during irradiation and the enhancement of F_n centers during thermal annealing is determined by interaction of H centers with X_2 molecule formation.

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