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Effect of irradiation parameters on defect aggregation during thermal annealing of LiF irradiated with swift ions and electrons

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Absorption spectroscopy were performed to study the effects of thermal annealing on the aggregation of color centers in LiF crystals irradiated with different ions between carbon and uranium of megaelectron volt-gigaelectron volt energy. The beam parameters such as energy, energy loss, and fluence have a pronounced influence on the initial defect composition and concentration as well as their evolution upon thermal annealing. A distinct phenomenon was observed, viz., the enhancement of F_n centers for annealing temperatures between 500 and 700 K, followed by Li colloid formation above 700 K. The phenomenon requires specific irradiation conditions whereas the formation of Mg colloids from Mg impurities occurs in all irradiated crystals. The mechanisms of annealing and colloid formation are discussed.

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I. INTRODUCTION

When swift ions of specific energy above about 1 MeV per nucleon (MeV/u) penetrate into solids, they predominantly lose their energy by electronic excitation and ionization. In alkali halides these excitations produce lattice defects including neutral (F-H) as well as charged (v_a^+-X_{int}^-) Frenkel pairs [F centers are anion vacancies with a trapped electron ($v_a^+e^-$), H centers are negatively charged halogen molecules (X_2^-) replacing regular anions, and X_{int}^- centers are anions on interstitial positions].[1,2] Charged Frenkel pairs (v_a^+-X_{int}^-) are usually transformed into neutral (F-H) pairs by electron tunneling.

In this study, we investigate how ion-beam-induced defects in LiF respond to thermal annealing. The irradiation experiments were performed at room temperature (RT) where F centers are stable. F centers become mobile only above 500 K whereas H centers are mobile already around 100 K. Above this temperature, they are transformed into more complex hole centers, in particularly V_3 centers, which are stable at RT with the absorption maximum at 114 nm in the vacuum UV spectral region.[3,4] Thermal decomposition of V_3 centers results in the appearance of mobile H centers that considerably influence the annealing process.[5,6]

Room-temperature irradiations of LiF with energetic ions and high fluences produce not only single defects but also complex defects such as F_n centers (F_2, F_3, and F_4). They absorb in the spectral range between 300 and 600 nm.[2,6] The maxima of the absorption band of the main electron color centers are presented in Table I.

High-fluence irradiations generate defect concentrations well above equilibrium and thus form a supersaturated solid solution.[7–9] During thermal annealing, the supersaturated solid solution decays due to defect diffusion resulting in defect recombination or in the formation of more complex color centers, in particular intrinsic (Li) and impurity (Mg) colloids. The transformation kinetics depends on the initial defect spectrum, the level of supersaturation, as well as the specific diffusion parameters of single defects and thermodynamic properties of defect clusters.

Metallic colloid formation

Metallic colloids in ionic solids including alkali halides were observed in minerals long before the nature of color centers was understood.[10] In the 50s of the last century, the interest in metallic colloids increased due to numerous studies on radiation damage in solids. Metallic colloids and anion clusters (bubbles) were identified and characterized as the final radiolysis products of dielectric materials.[2] Optical properties of colloids in alkali halides were first predicted by Savostianova[11] based on the Mie theory describing the absorption of spherical particles.[12] Experimentally, colloids were evidenced in additive colored crystals produced by doping with excess of metal (see Refs. 13 and 14, and references therein). The absorption maximum of metallic colloid particles depends on their size and compared to bulk material is shifted to shorter wavelengths.[15]

The optical properties of metallic colloids in LiF crystals are less investigated than in other alkali halides[14] because LiF cannot be colored additively.[16] However, they were studied by various other techniques including x-ray diffraction, nuclear and electron-spin resonance (NMR and ESR), and electron microscopy (see Refs. 13 and 14, and references therein). Lambert *et al.*[17] exposed LiF crystals to thermal neutrons and observed Li platelets of atomic thickness instead of spherical colloids. Due to this shape effect, the applicability of the Mie theory for colloids in LiF is therefore limited. The Li platelets embedded in the LiF lattice have fcc structure in contrast to bulk Li of bcc structure (see also Ref.

TABLE I. Absorption maxima of electron color centers produced when irradiating LiF crystals (Ref. 2).

Center	Band maximum (nm)
F	250
F_2	445
F_3	317, 377
F_4	518, 540

TABLE II. Absorption maxima of metallic colloids in LiF crystals irradiated with different beams followed by thermal annealing.

Metal	Absorption maximum (nm)	Irradiation
Li	445	2 MeV Li^+ ions (Ref. 29)
Na	520	0.8 MeV Na^+ ion (Ref. 29)
K	680	0.5 MeV K^+ ion (Ref. 29)
Mg	275–280	(1) 2 MeV electrons (Ref. 15) (2) 100 keV Mg and Ar ion (Refs. 17 and 30) (3) 5 and 10 MeV Au ions (Ref. 31)

18). In LiF irradiated with fast neutrons at nuclear reactors, much larger metallic colloids of several tens of nanometer were observed by means of NMR and ESR.[19–21] Later Beuneu *et al.*[22–24] detected metallic Li colloids in crystals exposed to fast electrons at a dose above 1 GGy. The colloid formation strongly depends on the electron flux. For 2.5×10^{14} electrons cm^{-2} s^{-1} the Li particles have a size above 500 nm.[22] It should be noted, that the same group intensively investigated LiF samples irradiated with 2640 MeV U ions (5×10^{12} cm^{-2}, corresponding to a mean dose of about 85 MGy) but could not observed any ESR signal related to metallic colloids.[25]

The observation of metallic Li colloids was also reported from electron microscopy investigations of LiF irradiated with thermal neutrons.[26–28] Depending on the fluence ($10^{17}-10^{20}$ neutrons/cm^2), the average size of the Li colloids was in the range from several tens up to several hundred of nanometers. For these samples, optical measurements were not possible because the irradiation resulted in strong coloration and thus high optical density. However, the creation of metallic (Li and impurity) colloids was observed after annealing samples irradiated with electrons,[16] low-energy ions,[18,29–31] and megaelectron volt ions (Table II).[32] In all cases, the aggregation process requires temperatures were F centers are mobile ($T>500$ K).

A theory of radiation-induced colloid formation based on F-center cluster nucleation and growth model was developed by Jain and Lidiard[33] and proven in additively colored alkali halides (NaCl, KCl, KBr, KI).[34,35] Additive coloration produces F centers without the complementary hole centers as Schottky anion vacancies. Illumination of additively colored KCl crystals in the F-center absorption band (564 nm) at temperatures 500–770 K creates a new absorption band at 730 nm[35,36] which remains stable after quenching to RT. Subsequent illumination at 730 nm restores the F-center band. Scott *et al.*[37] explained this process by a reversible reaction $F\leftrightarrow nF$, where nF are clusters on n joint F centers with a semimetallic binding between the neighbor Li ions. The number n was assumed to be on the order of 10. Larger nF clusters collapse to metallic colloids.[33] In further investigations, nF clusters were observed in crystals irradiated with x rays or fast electrons.[38] The absorption of these nF clusters is not known because of the inability to perform additive coloration experiments on LiF.[16]

In LiF crystals, intrinsic Li colloids and also the formation of Mg colloids from Mg impurities is known.[13] For annealing temperatures above 700 K, Mg colloids are evidenced by the broad absorption band appearing at 275 nm. Davidson *et al.*[18] supposed a two step process for colloid formation in Mg-doped LiF crystals. In the first step, a Mg^{2+} ion captures electrons from two F centers and converts it into a neutral atom: $Mg^{2+}v_c^- + 2(v_a + e^-) \rightarrow Mg^0 + v_a^+ v_c^-$. In the second step, diffusion of neutral Mg atoms and vacancy pairs $v_a^+ v_c^-$ lead to the formation of the colloid.

This paper concentrates on defects in LiF induced with high-energy heavy ions and processes under thermal annealing. At temperatures below 500 K, the decomposition of V_3 centers leads to the release of free mobile H centers.[6] They can recombine with F and F_n centers ($n=2,3,4$) but they also can form halogen molecules (X_2) and nX_2 clusters. At temperature $T>500$ K, the F centers become mobile. Besides recombination with H centers, F centers can also coagulate. The study demonstrates that the initial irradiation parameters have a strong influence on relaxation kinetics of defects during annealing.

II. Experimental

As samples we used thin platelets of LiF cleaved along one of the (100) planes of a single-crystal block grown from the melt in an inert atmosphere (Korth Kristalle, Germany). According to $K\alpha$ x-ray emission spectra, the crystal contained about 20 ppm ($\sim10^{18}$ cm^{-3}) Mg impurities as well as several ppm Na and Cl. The platelets had a size of 10×10 mm^2 and a thickness between 0.2 and 0.5 mm.

All ion irradiations were performed at the UNILAC linear accelerator of the GSI Helmholtz Center. The energy of the projectiles (^{12}C up to ^{238}U) was between 130 and 2640 MeV. For all ions, the range was smaller than the thickness of the LiF samples. Due to the high energy, the interaction of the ions with the target is dominated by ionization and electronic excitation processes while elastic collisions with target atoms are important only at the end of the ion paths (less than 1 μm) and can be neglected for color center creation.[39,40]

To avoid beam-induced heating of the samples, the flux was limited to less than 10^9 ions cm^{-2} s^{-1} for light ions (C, Cr, and Mo) and to about 2×10^8 cm^{-2} s^{-1} for heavier than Xe. During irradiation, the ion flux was monitored with a secondary electron detector consisting of three 1-μm-thick Al foils placed in front of the sample and calibrated via beam current measurements with a Faraday cup (accuracy $\sim20\%$).[39]

TABLE III. Irradiation parameters and defect data obtained after thermal annealing of irradiated LiF crystals. n_F and $\bar{N}_F$ denote the respective F-center concentration per square centimeter and per cubic centimeter [Eqs. (1) and (4)], ξ is the ratio of the F_2 to F-center concentration, and $T_{1/2}$ describes the temperature at which the initial concentration of the color centers decreases by a factor of 2.

	Ion	Energy E (MeV)	Range R (μm)	E/R (keV/nm)	Fluence Φ (cm^{-2})	n_F (cm^{-2})	$\bar{N}_F$ (cm^{-3})	$\xi=n_{F2}/n_F$	$T_{1/2}$ (F)	$T_{1/2}$ (F_2)	F_n at RT
1	^{12}C	130	236	0.6	10^{11}	7.9×10^{15}	3.3×10^{17}	0.02	510	430	F_2
2	^{12}C	130	236	0.6	10^{12}	3.8×10^{16}	1.6×10^{18}	0.08	530	470	F_2
3	^{52}Cr	577	106	5.5	10^{11}	3.2×10^{17}	3.0×10^{18}	0.13	530	460	F_2
4	^{96}Mo	1066	89	12.6	3×10^{10}	1.8×10^{16}	2.0×10^{18}	0.10	530	460	F_2
5	^{197}Au	709	37	19.2	10^{10}	3.9×10^{15}	1.1×10^{18}	0.10	505	465	F_2, F_3
6	^{197}Au	709	37	19.2	10^{11}	1.6×10^{16}	4.2×10^{18}	0.22	495	505	F_2, F_3, F_4
7	^{197}Au	2187	97	22.5	5×10^{10}	2.8×10^{16}	2.8×10^{18}	0.17	530	500	F_2, F_3, F_4
8	^{197}Au	2187	97	22.5	10^{11}	5.4×10^{16}	5.5×10^{18}	0.20	550	515	F_2, F_3, F_4
9	^{238}U	900	39	23.1	8×10^{10}	7.3×10^{15}	1.9×10^{18}	0.18	505	485	F_2, F_3, F_4
10	^{238}U	2640	94	28.1	8×10^{10}	4.7×10^{16}	5.0×10^{18}	0.28	525	495	F_2, F_3, F_4
11	Electrons	10	5400	0.002	10^{14}		1.8×10^{18}	0.14	595	505	F_2
Enhancement of F_n centers and Li colloid formation											
12	^{136}Xe	800	49	16.4	3×10^{11}	3.9×10^{16}	7.9×10^{18}	0.25	510	585	F_2, F_3, F_4
13	^{208}Pb	2300	97	23.7	5×10^{10}	3.2×10^{16}	3.3×10^{18}	0.13	560	620	F_2, F_3, F_4
14	^{238}U	2640	94	28.1	5×10^{10}	4.0×10^{16}	4.2×10^{18}	0.28	540	605	F_2, F_3, F_4,

All irradiations were performed at RT under normal beam incidence applying fluences (Φ) between 10^{10} and 10^{12} ions/cm^2. For comparison, some crystals were irradiated with 10 MeV electrons at the electron accelerator of the Leibniz Institute of Surface Modification (IOM Leipzig, Germany). The fluence was $\sim10^{14}$ cm^{-2} corresponding to a dose of about 0.5 MGy. The electron range in LiF is approximately 5 cm which is much larger than the sample thickness (0.2 mm). In contrast to the ion irradiation, the dose deposition by electrons is very homogeneous on a microscopic scale. The spatial distribution of the color centers is thus also extremely uniform. The most relevant parameters of all irradiation experiments are summarized in Table III.

For thermal annealing, the irradiated LiF crystals were cut into smaller pieces of size $\sim5\times5$ mm^2. To provide good thermal contact, the crystals were clamped on a gold sample holder and heated in atmosphere to temperatures ranging from 300 to 800 K (stability ±5 K). The heating time was 15 min which was tested to be sufficiently long to establish temperature equilibrium in the samples. Typical annealing experiments consisted of increasing the temperature in steps of ΔT=30–40 K.

The effect of thermal annealing was quantified by recoding absorption spectra of the irradiated samples before and after each annealing step using a double Unicam UV4 spectrometer operating in the spectral range 190–700 nm. Unfortunately, the absorption of V_3 centers could not be investigated because they absorb in the vacuum UV spectral region (maximum at 114 nm),[4,41] which is not accessible with our spectrometer.

F and F_2 centers have their absorption maxima at λ_F =250 nm and λ_{F2}=445 nm, respectively. For low ion fluences, the absorption bands are well separated allowing quantitative analysis. The color center concentration per square centimeter in the irradiated crystals is calculated by using the Smakula-Dexter formula,[39,42]

$$n_F = 9.48 \times 10^{15} \cdot D_F(\mathrm{cm}^{-2}) \quad \text{for F centers}, \qquad (1)$$

$$n_{F2} = 4.42 \times 10^{15} \cdot D_{F2}(\mathrm{cm}^{-2}) \quad \text{for } F_2 \text{ centers}, \qquad (2)$$

where D_F and D_{F2} are the optical densities at the absorption maxima of F and F_2 centers, respectively. To compare the annealing of different samples, we determined the temperature $T_{1/2}$ at which the concentration of the color centers decreased by a factor of 2 (Table III),

$$D(T_{1/2}) = 0.5 \times D(300\ \mathrm{K}). \qquad (3)$$

To determine the average volume defect concentration per cm^{-3}, Eqs. (1) have to be divided by the projected ion range R,

$$\bar{N}_F = n_F/R \quad \text{and} \quad \bar{N}_{F2} = n_{F2}/R. \qquad (4)$$

For most ion-irradiated crystals, the average volume concentration for single F centers before annealing was on the order of few 10^{18} cm^{-3} (Table III). To quantify the relative concentration of F_2 centers and single F centers, we also analyzed the ratio of their concentrations denoted by $\xi=n_{F2}/n_F$ (Table III).

III. RESULTS

The results of the annealing experiments are presented in two groups related to irradiations with (i) light ions (^{12}C, ^{52}Cr, and ^{96}Mo) and 10 MeV electrons and (ii) heavy ions (^{136}Xe, ^{197}Au, ^{208}Pb, and ^{238}U).

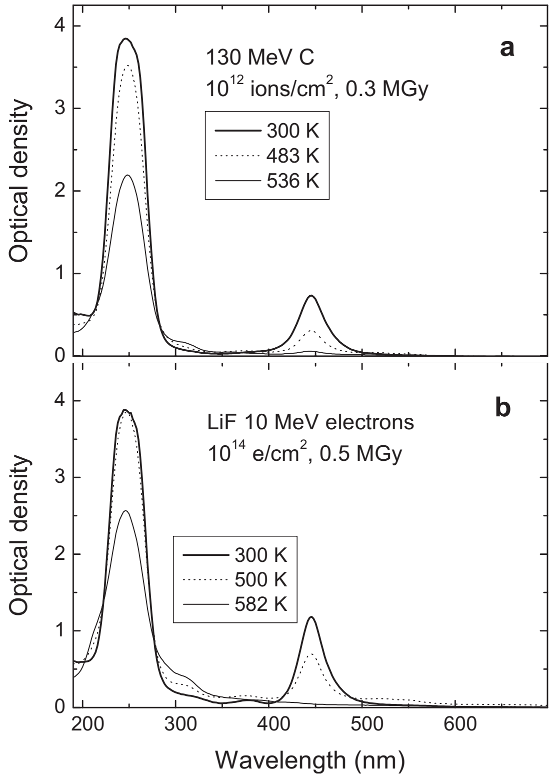

FIG. 1. Absorption spectra of irradiated LiF crystals before (300 K) and after annealing at two different temperatures. The irradiations were performed (a) with 130 MeV C ions (10^{12} cm^{-2}, 0.32 MGy) and (b) 10 MeV electrons (10^{14} cm^{-2}, 0.5 MGy).

A. Light ions and electrons

The initial absorption spectra of crystals irradiated with light ions and electrons are dominated by the F and F_2 absorption bands. During thermal annealing, the intensity of both bands decreases because F centers recombine (annihilate) with mobile H centers produced by the thermal decomposition of V_3 centers. Annealing temperatures above 500 K lead to a slight increase in the absorption at about 310 nm [Fig. 1(a)] indicating the formation of aggregate centers. Above 600 K, an additional absorption band appears at 275 nm, which is assigned to Mg colloids.

The absorption spectra of samples exposed to electrons ($\sim 10^{14}$ cm^{-2}, ~ 0.5 MGy) and C ions (10^{12} cm^{-2}, 0.32 MGy) of comparable dose are both dominated by the absorption bands of the F and F_2 centers with additional weak bands at 317 and 377 nm ascribed to F_3 centers [Fig. 1(b)]. The $T_{1/2}$ values of F and F_2 centers are higher for samples irradiated with electrons than the ones exposed to light ions (Table III). This effect can be explained by the fact that the microscopic dose distribution of the electron irradiation is homogeneous and thus the average distance between V_3 and F centers is larger than in ion tracks.

Comparing the annealing process for irradiations with different light ions, the $T_{1/2}$ values for F centers as well as for F_2 centers agree within 5–10 % accuracy (Table III). For F_2 centers, the $T_{1/2}$ values are in average about 60°–80° lower than those for F centers (Fig. 2). Comparing crystals irradiated with 130 MeV ^{12}C ions of 10^{11} and 10^{12} cm^{-2} shows that the higher fluence shifts $T_{1/2}$ to a slightly higher temperature for F as well as F_2 centers (Fig. 2 and Table III).

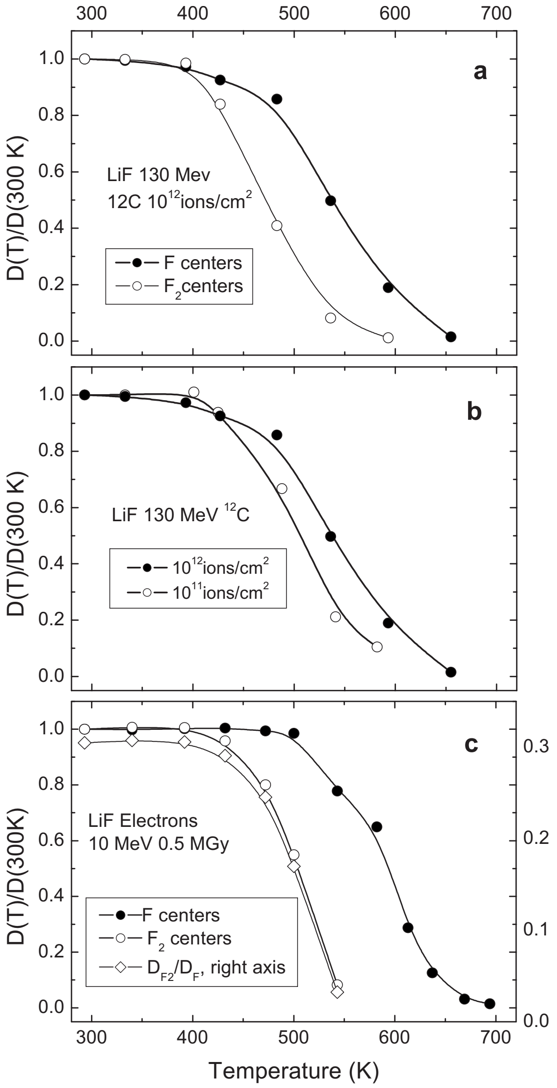

FIG. 2. Thermal annealing of LiF irradiated with 130-MeV ^{12}C ions comparing the band intensity (a) of F and F_2 centers induced at a fixed fluence of 10^{12} ions/cm^2, and (b) of F centers at two different fluences 10^{11} and 10^{12} ions/cm^2, as well as (c) F and F_2 centers (left ordinate) and their ratio (right ordinate) of LiF irradiated with 10 MeV electrons.

B. Heavy ions

Crystals irradiated with heavy ions such as Xe and above exhibit more complicated defect transformation kinetics than those irradiated with light ions. Obviously the energy loss has a significant influence on the defect creation and subsequent transformation. With increasing energy loss, the ratio ξ tends to become larger (Table III). In the following, we separately discuss data from irradiations at low and high ion fluence.

In the single-ion regime ($\Phi < 5 \times 10^{10}$ ions/cm^2), large defect concentrations are produced in the close vicinity of each projectile trajectory where the density of the deposited

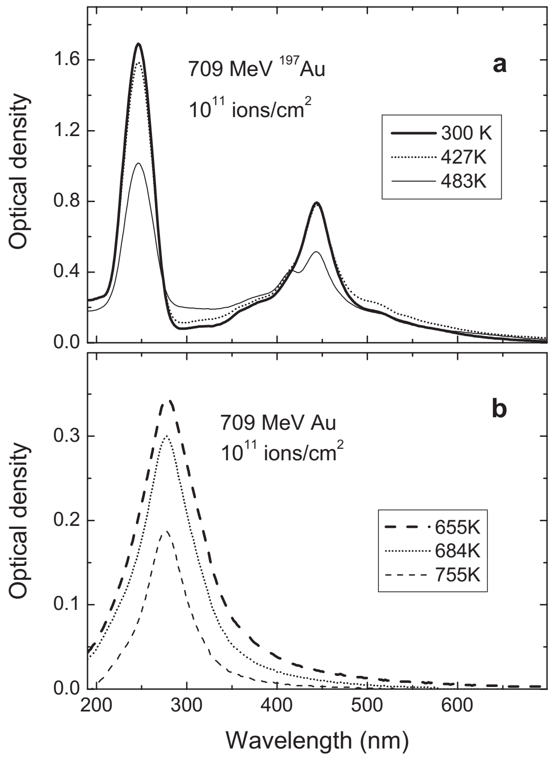

FIG. 3. Absorption spectra of LiF crystals irradiated with 709 MeV Au ions (10^{11} cm^{-2}) before and after annealing at (a) medium and (b) high temperature (note the different scale of the ordinates).

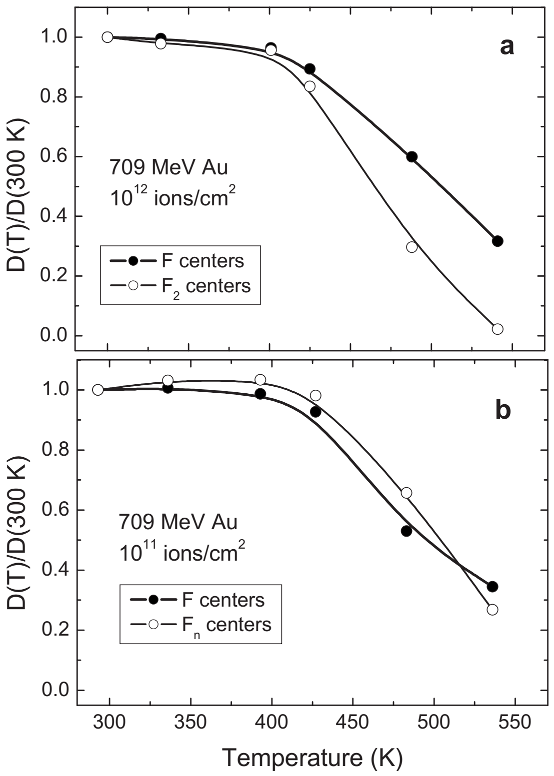

FIG. 4. Thermal annealing of F and F_2 centers in LiF crystals irradiated with 709 MeV Au ions. F- and F_2-center concentration normalized to RT as a function of annealing temperature for samples exposed to low (a) and high ion fluence (b).

energy is high while at high fluences, high dose effects can also result from overlapping tracks.[5,43]

1. Low fluences ($\Phi < 5 \times 10^{10}$ Au ions/cm^2)

At low fluences ξ of the initial absorption spectrum and $T_{1/2}$ are similar to irradiations with light ions (Table III). For annealing temperatures above 600 K, the Mg-colloid absorption band appears at 275 nm, being more pronounced for higher fluences.

2. High fluences ($\Phi \geq 5 \times 10^{10}$ ions/cm, *Xe, Au, Pb, and U ions*)

The absorption spectra of crystals exposed to high fluences show additional bands ascribed to F_3 and F_4 centers [Fig. 3(a), Table I]. At temperatures above 500 K, the thermal evolution of the different color centers leads to increased absorption in the spectral range 290–400 nm [Fig. 3(a)] due to the creation of more complex color centers. They form by diffusion and aggregation of F centers but their microstructure is presently not clear.[39,41] The characteristic temperatures $T_{1/2}$ for F_2 centers are higher than those for light ions or low-fluence irradiations with heavy ions (Table III), probably because of enhanced aggregation of mobile F centers ($F+F \rightarrow F_2$, etc.) at higher temperatures. This process becomes more pronounced at larger fluences (Fig. 4).

3. Thermal annealing and enhancement of F_n *centers*

For crystals irradiated with Xe ions (3×10^{11} cm^{-2}) as well as with Pb and U ions (5×10^{10} cm^{-2}) (Table III, lines 12–14), we found preferential survival of F_n centers (Fig. 5), which is in clear contrast with the observation described earlier for other irradiations. For annealing temperatures below 500 K, the concentrations of F and F_n centers decrease at about the same rate, i.e., the ratio ξ remains approximately constant. Between about 500 and 700 K, ξ increases due to enhanced aggregation of F centers into F_n centers (Fig. 5). During this annealing step, the shape of the absorption band of the F_n centers (300–600 nm) does not change significantly (Fig. 6). At even higher annealing temperatures, the absorption spectrum is dominated by a broad band (half width ~1.3 eV) at ~440 nm (Figs. 7 and 8). According to Refs. 13, 14, and 29, such an absorption band corresponds to Li colloids. The colloid band emerges only in cases where F_n centers ($n > 3$) are formed during annealing, probably because F_n centers act as nuclei for further aggregation.[33] We also noticed that in all those cases where Li colloids are formed, the 275 nm absorption band is much smaller.

When further annealing to 770 K, the shape of the absorption spectrum does not change but the band width slightly decreases and the maximum shifts to a shorter wavelength (Fig. 7). According to the theory of colloid particles,[13,14] such a behavior corresponds to a size decrease in the Li colloids. Finally, at highest temperature around 800 K, the band disappears, i.e., the Li colloids are completely annealed.

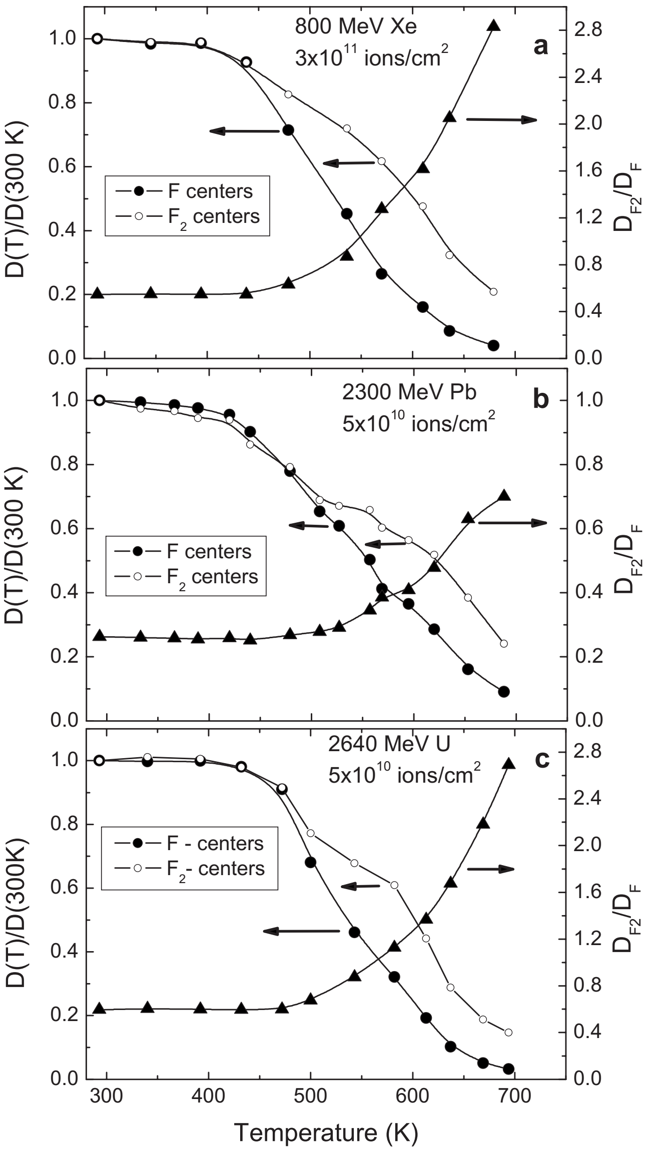

FIG. 5. Normalized concentration of F and F_2-centers after thermal annealing of LiF crystals irradiated with (a) 800 MeV Xe ions, (b) 2300 MeV Pb ions, and (c) 2640 MeV U ions. Triangles represent the ratio D_{F2}/D_F as a function of temperature (right ordinate).

IV. DISCUSSION

A. Thermal annealing processes at various temperatures

The characteristic processes during annealing in different temperatures regimes are summarized in Table IV. At the initial stage of annealing ($T \leq 500$ K), the F centers are not yet mobile and processes related to diffusion of hole centers are dominating. We assume that the migration energy of V_3 centers is higher than their binding energy, thus V_3 centers decompose into H centers.[6] These H centers recombine with F and F_n centers resulting in an intensity decrease in the respective absorption peaks. Also nucleation and growth processes of halogen clusters have to be considered because fluorine-molecule clusters were evidenced by means of NMR in neutron-irradiated LiF crystals.[19,20] The formation of such H-center sinks prevents the complete disappearance of F centers and their complexes.[5,43] The recombination of H centers with electron color centers results in an overall decrease in the F- and F_2-center concentration as well as a drop of the ratio ξ. The lower $T_{1/2}$ value for F_2 than for F centers (Table III) can be explained by a certain bias factor of H centers to complex electron centers. Additional contribution to this effect is provided by the reaction $F_2+H \rightarrow F$. An exemplary case, how irradiation parameters can influence the annealing process is presented in Fig. 4 and Table III (lines 5 and 6) where two LiF crystals were irradiated with the same ions (709 MeV Au) at two different fluences. Under annealing, samples exposed to 10^{10} ions/cm^2 exhibits the typical relation of $T_{1/2}(F) > T_{1/2}(F_2)$ whereas the higher fluence (10^{11} ions/cm^2) produces the opposite effect viz. $T_{1/2}(F) < T_{1/2}(F_2)$. This phenomenon is more pronounced for all crystals with enhanced formation of F_n centers (Fig. 5, Table III, lines 12–14).

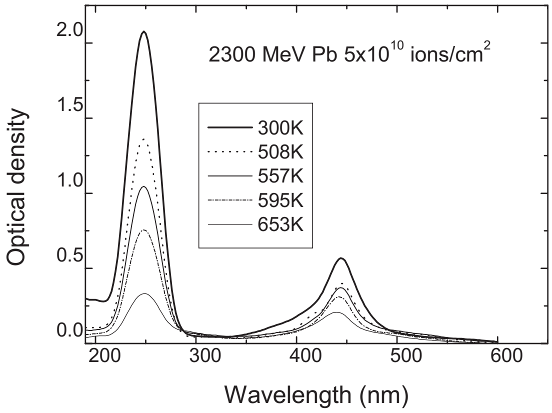

FIG. 6. Absorption spectra of LiF crystals irradiated with 2300 MeV Pb ions at 300 K and after annealing at various temperatures.

When the annealing temperature approaches 500 K, F centers become mobile and the destruction of F_n centers by H centers is partly overcome by F-center aggregation ($F+F \rightarrow F_2$, $F_n+F \rightarrow F_{n+1}$). This aggregation process is responsible for the enhancement of F_n centers, described in Sec. III,

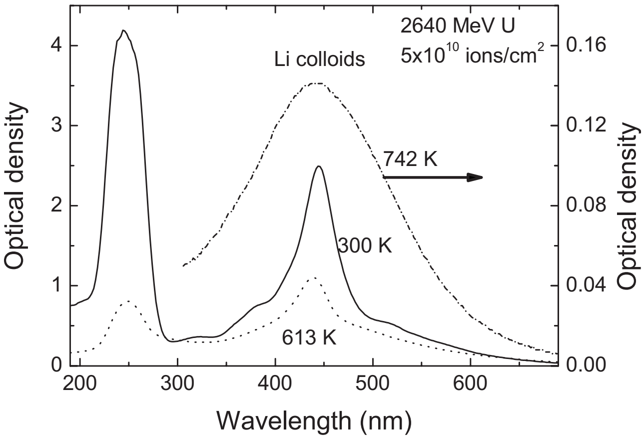

FIG. 7. Absorption spectra of LiF crystals irradiated with 2640 MeV U ions at 300 K and after annealing at various temperatures. The broad absorption band at 440 nm is ascribed to Li colloids (right ordinate).

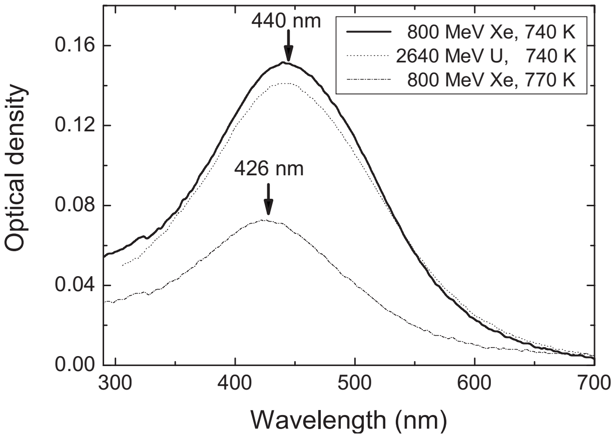

FIG. 8. Absorption spectra of LiF crystals irradiated with 2600 MeV U ions (5×10^{10} cm^2) and 800 MeV Xe ions (3×10^{11} cm^{-2}) annealed at 740 and 770 K. The broad band at 440 nm is assigned to Li colloids. The shift of the absorption maximum to 426 nm at higher temperature occurs probably due to a size decrease in the colloids.

and is only possible if a certain fraction of F centers escapes recombination.

B. Li colloid formation

Formation of metallic colloids in irradiated alkali halides is possible if the volume concentration of F centers is sufficiently high ($10^{18}-10^{19}$ cm^{-3}) and if the temperature provides enough energy for F-center diffusion.[13,14,33] Under such conditions, F centers can aggregate forming *n*F clusters, containing only F centers ($v_a^+e^-$) and lithium ions (Li^+). If such a cluster reaches a critical size, the electrons of the F centers are captured by the Li^+ ions, and the system collapses into a Li colloid.[33] The chance for such a process depends on competitive processes of F-center transformation, in particular recombination with hole centers and their aggregates or impurity cluster formation. High initial supersaturation of defects is thus mandatory but probably not sufficient for intrinsic colloid creation. Suitable nucleation centers can be of great importance.[33,44] According to Ref. 44, F_4 centers play the role of nuclei because the first step of Li-colloid formation requires that larger *n*F cluster are formed.[33,37] Once the F-center cluster has reached a critical size, it collapses into a Li colloid. We assume that such a process takes place in LiF crystals irradiated with a suitable fluence of Xe, Pb, or U ions (Fig. 5, Table III).

Without F_n-center enhancement the number of nuclei created during annealing are not enough and consequently no Li colloids are observed even at higher fluences (Table III, lines 9 and 10). The critical parameter for F_n-center enhancement seems to cover only a small fluence range (Table III). If the fluence is too low, the concentration of F_n centers is not high enough for enhanced aggregation and nucleus creation. On the other hand, at excessively high fluences, the F centers interact with Mg impurities and Mg colloid formation is favored at the expense of the formation of Li colloids. This is supported by the observation that the formation of Li colloids suppressed the formation of Mg colloids.

For all crystals, the Li-colloid absorption band has the same maximum and the same shape (half width) (Fig. 8). Further heating up to 770 K leads to the shift of the band maximum to a shorter wavelength (426 nm) accompanied by a decrease in the half width. At higher temperatures, the area under the absorption band decreases, illustrating a drop of the colloid concentration. This is a typical response of colloid particles during thermal annealing.

For none of the LiF crystals irradiated at RT with various ion species and energies, the appearance of the Li colloid band could be observed without annealing. This is an indication that defect aggregates created in single-ion tracks are not sufficiently large to be transformed into Li colloids. During track formation, the diffusion length of F centers is probably too short to produce large aggregates. The situation is different during thermal annealing in the temperature range 600–700 K, where the diffusion of F centers involves a much larger volume, enhancing aggregation and subsequent sublimation process into metallic Li (see Refs. 13 and 32, and references their in).

C. Mg colloid formation

As illustrated for crystals irradiated with 709 MeV Au ions (10^{11} cm^{-2}), also magnesium colloids can be formed (Fig. 3). The nucleation and growths of metallic Mg colloids is more complex than the formation of Li colloids and require diffusion of three different components, namely, anion vacancies (or F centers), Mg atoms (or ions), and cation vacancies.[2,18] The activation energy for the migration of Mg^{+2} ions is 1.5 eV (Ref. 45) which is too high to allow Mg aggregation during RT irradiation. This is consistent with our observation, that without annealing none of the irradiated crystals exhibited indications for magnesium colloid. In contrast, after annealing at temperatures above 600 K, the Mg colloid band (275 nm) appears in all crystals irradiated either

TABLE IV. Characteristics of thermal annealing process in different temperature regimes.

$300\leq T\leq500$ K	$T\geq500$ K	$T\geq600$ K
(1) Decay of V_3 centers and release of mobile H centers.	(1) Beginning of F-center diffusion.	(1) Diffusion of F centers to larger distances.
(2) Diffusion of H centers, recombination with F centers, and reactions $F_n+H\rightarrow F_{n-1}$.	(2) Recombination of mobile F centers with hole centers.	(2) F-center aggregation and Li-colloid formation.
(3) Aggregation of H centers, formation of fluorine molecules and their clusters.	(3) Aggregation of F centers $F_n+F\rightarrow F_{n+1}$, formation of F_n centers and *n*F aggregates.	(3) Mg-colloid formation by F-center and Mg diffusion and interaction.

with ions or 10 MeV electrons. The Mg colloids are completely annealed at temperature above 850 K.

The observation suggests that Mg coagulation is energetically favored compared to the formation of intrinsic Li colloids. The activation energy for diffusion of Mg is higher than that of F centers (1 eV).[14,45] For Mg-colloid formation it is thus important that the concentration of F centers remains high enough up to temperatures where the Mg impurities become mobile. On the other hand, the formation of Li colloids leads to a depletion of F-centers which suppresses the formation of Mg colloids. The low concentration of F centers plays also a decisive role in the case of irradiation with light ions or with heavy ions at lower fluences, where the 275 nm absorption band is consistently weak and overlaps with the 250 nm absorption band of the F-centers.

V. CONCLUSIONS

The annihilation and transformation of color centers during thermal annealing of LiF crystals irradiated with high-energy ion projectiles are complex processes depending on the initial defect spectrum and on the annealing temperature. Below 500 K, the recombination of electron color centers with hole centers takes place without the formation of new electron centers. At temperatures between 500 and 600 K, F centers become mobile and aggregation of single F centers to complex F_n centers occurs. At temperatures above 600 K, larger aggregates are created including metallic colloids. For crystals irradiated with heavy ions within a medium fluence window, annealing between 500 and 700 K leads to the enhanced creation of F_n centers They are probably essential as nuclei for, the formation of Li colloids occurring above 700 K.

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