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Color centers aggregation kinetics in lithium fluoride after gamma irradiation

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ABSTRACT

Lithium fluoride crystals are irradiated at various doses by gamma rays at 77 K. The time evolution of photoluminescence signals from aggregated F_2^+ , F_2 , F_3^+ and F_3 color centers, and of the absorption intensity of primary F centers are measured at various annealing temperatures. The lifetimes of anionic vacancies v_a and F_2^+ centers, the characteristic times of concentration growth of F_2 , F_3^+ and F_3 centers, and also the activation energies of diffusion of vacancies and F_2^+ centers together with various processes of aggregation are determined. It is found that lifetime decreases for vacancies while increases for F_2^+ centers by increasing the irradiation dose. It is also shown that, after irradiation during annealing, vacancies are formed as a result of the reaction $F_2^+ + H \rightarrow v_a + \text{Fl}^-$, where Fl^- is a fluorine ion in a lattice site and H is a fluorine interstitial atom. Then these vacancies participate in color centers aggregation kinetics. The presence of F^- centers in the irradiated crystal is established, and the processes which lead to the formation of F_2 , F_3^+ and F_3 centers after irradiation, are unveiled.

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1. Introduction

Lithium fluoride (LiF) containing color centers (CCs) is widely used as an active medium in tunable solid-state lasers operating at room temperature (RT) in the visible and near infrared spectral range [1]. Pure [2] and doped [3] LiF crystals are well-known dosimeter materials. Recently, new radiation detectors based on microcrystalline LiF in polymer matrix have been proposed for gamma and electrons high-dose dosimetry [4], as well as polycrystalline LiF films for nuclear sensors of neutrons [5]. Applications of LiF with CCs for the fabrication of light-emitting micro-structures with high spatial resolution are studied [6–9]. Also the properties of polycrystalline LiF (ceramics) are investigated [10]. So, in order to optimize the characteristics of LiF for laser technologies and dosimeter applications, a more detailed knowledge of the formation processes of radiation-induced CCs is necessary.

Processes of CCs formation in LiF have been analyzed since long times [11–14]. It has been found that the kinetic of coloration is

complex and strongly dependent on a large number of variables, i.e. type of ionizing radiation and its characteristics, conditions of irradiation like radiation intensity (dose-rate), as well as chemical purity and mechanical and thermal history of the crystal, irradiation temperature, etc. However, still now some processes of CCs aggregation and disaggregation remain essentially unknown experimentally. For example, not all possible processes in which F_2^+ centers participate were analyzed as far as their role in the formation of aggregated CCs is concerned. It is not known whether anionic vacancies are produced in a crystal well after irradiation, or whether F^- centers after gamma irradiation are present, and the dependence of F_2^+ centers lifetime upon dose of irradiation. We also noted that a previous study of F_2 centers generated after irradiation with electron beams is misleading [14]. Indeed, the change of the M absorption band (with a maximum at 446 nm), which is formed by the superposition of F_3^+ and F_2 centers, was measured. Extraction of F_2 centers absorption band from the M-band was carried out by assuming the presence of two close F_3^+ centers absorption bands with maxima at 420 and 460 nm. However, this assumption is not supported by well assessed literature [12,15,16,17], which attributes to F_3^+ centers only one fundamental absorption band with a maximum at 448 nm in the M spectral range. Then numerical estimates and conclusions about the kinetics of F_2 centers concentrations should be reconsidered.

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In order to provide further insights on the formation rates of various types of aggregated CCs after irradiation, which are of practical and basic interest, in this paper the CCs aggregation kinetics are measured after low-temperature irradiation of LiF crystals by gamma rays at various doses. On the basis of several experiments, reactions providing formation of F_2 , F_3 and F_3^+ centers in LiF crystals during annealing after gamma irradiation at liquid nitrogen temperature (LNT) are determined. The experimental investigation after irradiation has been chosen because of a smaller number of processes occurring than during the irradiation, and these processes are more easily defined. However, the obtained data can also be used to go back to the aggregation during the irradiation. In particular, the nature of electronic defects participating in the aggregation processes after irradiation is specified, and the influence of the irradiation dose on the lifetime of F_2^+ centers is established. Moreover, the relationship between rates of F_2 , F_3 and F_3^+ centers formation, and increase and decrease of F_2^+ centers are unveiled. Finally, a critical comparison of the activation energies estimated for the various processes is utilized as a survey procedure.

2. Experimental Procedures

From a nominally pure single crystal of lithium fluoride, containing oxygen impurities of the order $(2-5)10^{16} \text{ cm}^{-3}$, plates with side dimensions between 5 and 10 mm and of thickness in the range (0.7–1.1) mm were cleaved along a {100} plane. These samples were irradiated in identical experimental conditions by gamma rays from a ^{60}Co source at $T_{\text{irrad}}=77 \text{ K}$. For each batch of plates the irradiation times, and then the irradiation doses, were varied. The samples were placed in a metal cryostat filled with liquid nitrogen, a non-standard condition for irradiations.

After irradiation, the samples from the same batch were taken each one at the time out of liquid nitrogen, and mounted in a holder device providing a definite stabilized temperature T at which optical measurements were carried out. The time required for moving the samples from T_{irrad} to T was 1–1.5 min, and this measurement (annealing) temperature varied in the range 283–313 K (10–40 °C). For each temperature, the photoluminescence (PL) intensities of F_2^+ , F_2 , F_3 (R_2) and F_3^+ centers at the recording wavelength λ_{rec} , equal to 890, 680, 480 and 530 nm, respectively, were measured with a spectrofluorimeter SFL-1211A (SOLAR, Belarus). For these light-emitting electronic defects, the PL excitations were carried out at $\lambda_{\text{exc}}=630, 446, 380$ and 420 nm , respectively. In order to maximize the CCs PL signal, the recording wavelengths were close to the peaks of their broad emission bands [6,11]. The excitation wavelengths were selected close to their optical absorption maximum for F_2^+ and F_3 . As optical absorption bands of F_2 and F_3^+ centers strongly overlap, the values of λ_{exc} for these defects have been chosen by taking into account their specific spectral features [15] in order to maximize the selectivity of excitation. Data about PL spectra of F_3 (R_2) centers and the other CCs have been taken by the known literature [18,6]. The chosen wavelengths of PL excitation and registration and also relative positions of these wavelengths and with respect to the absorption and luminescence bands of the CCs in LiF, provided possibility of selective investigation of each type of the defects.

The optical densities values of the absorption spectra for the investigated samples are considerably less than unity in the visible spectral range; then the emission re-absorption is absent, or negligible, and the PL intensity is proportional to the CCs concentration. Emission intensities were measured by averaging the signal every 2 s. For F_2 and F_3^+ centers, PL was registered as it follows. At the beginning, the PL signal of one type of center was measured and then after two seconds the other type of center was

measured, and then again the first one and so on. Thus, after several hours the PL time evolutions of the two CCs from the same sample were measured at the same temperature, allowing us to compare PL intensities of both CCs at the same time after the initial annealing. PL spectra of F_2^+ and F_3 centers were measured by using other samples from the same batch.

Time dependence of the optical density D_1 at $\lambda_{\text{abs}}=248 \text{ nm}$, the maximum of F -center absorption [6,19], (or at another wavelength within this band for large values of D_1) was measured at various temperatures T with a spectrophotometer Cary-500 Scan (Varian, USA). The signal was averaged every 1 s. The measured optical densities are proportional to the F -center concentrations, according with the Smakula formula [19], and give an estimate about the irradiation dose of the various batches [20]. The typical F -center concentrations under used irradiation doses were in the range of 10^{18} cm^{-3} , much more than oxygen content in the crystals.

The measured time dependences of PL intensities and optical density values are directly proportional to the concentration kinetics of F_2^+ , F_2 , F_3 , F_3^+ and F centers, and they provided the experimental basis in the analysis of CCs aggregation processes soon after irradiation. The obtained results characterize the processes among the bulk defects inside the crystal volume.

3. Color centers aggregation processes

The irradiation temperature ($T_{\text{irrad}}=77 \text{ K}$) is well below the mobility temperatures of V_k hole centers ($T_v \approx 140 \text{ K}$) and anionic vacancies ($T_v \approx 250 \text{ K}$) [21]. Therefore during irradiation both V_k hole centers and anionic vacancies (vacancies from now on) are localized. Under these specific conditions, after the irradiation there are the following point defects in the crystals: probably electrons in traps (e), vacancies (v_a), V_k centers, F and probably F^- centers, as well as interstitial fluorine ions (I) and interstitial fluorine atoms (H). It is further supposed that the irradiation doses are low enough that the probability of CCs aggregation during irradiation, as a result of binary and higher order processes, is negligible.

During the sample heating from T_{irrad} to T , electrons from shallow traps and V_k centers disappear. Processes of CCs formation at the beginning of annealing are defined by vacancies, electrons in deep traps (probably), F and, eventually, F^- centers, interstitial fluorine ions and interstitial fluorine atoms. Concentrations of these defects at the beginning are limited by the requirement of electrical neutrality of the sample and balance of interstitial and vacancy defects:

$$n_v = n'_1 + n_I + n_e, \quad (1)$$

$$n_H + n_I = n_1 + n'_1 + n_v, \quad (2)$$

where n_v , n_e , n_1 , n'_1 , n_I , and n_H are the concentrations of vacancies, electrons, F and F^- centers, interstitial fluorine ions and interstitial fluorine atoms, respectively. In Eq. (1) the cationic component is not taken into account, and will not be considered further in the present work.

After their formation, complex CCs also participate in subsequent processes of transformation, and we assume that only vacancies and F_2^+ centers migrate over the crystal. As a matter of fact, the observed long-term stability of concentrations of F , F_2 , F_3^+ , F_3 centers, measured during more than a year after the end of all transformation reactions, allows us to conclude that it is possible to neglect diffusion and destruction of these primary and aggregated centers, and also the diffusion of interstitial fluorine ions and atoms at the temperatures used in the present experiments. So, CCs aggregation and transformation after

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