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Effect of electron beam irradiation dose on luminescence and optical absorption of LiF crystals

Elena A. Ilina [a], Alexander I. Sidorov [a,*], Uliana V. Yurina [b], Oleg A. Podsvirov [b]

[a] ITMO University, Birzhevaya line, 4, 199034 St. Petersburg, Russian Federation
[b] Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya str., 29, 195251 St. Petersburg, Russian Federation

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ABSTRACT

It is shown experimentally that local electron irradiation of LiF crystals by focused electron beam with relatively low electrons energy (E = 50 keV) and doses of Q = 10–100 mC/cm^2 results in the formation of Li nanoparticles and luminescent centers in near-surface layer less than 30 μm thick. The formation of spherical Li nanoparticles is confirmed by computer simulation in dipole quasistatic approximation. When electron irradiation dose increases from 10 mC/cm^2 up to 35 mC/cm^2 the amplitude of plasmon absorption band of Li nanoparticles increases by 6 times and luminescence intensity increases by 30–40 times. Local Li nanoparticles and luminescent centers formation in LiF crystals by focused electron beam may be promising in integrated optics for fabrication of non-linear optical elements, elements with metamaterial properties, submicrometer two-color light sources and for multilevel optical information recording.

1. Introduction

Electron beam is the powerful instrument for modification of optical materials properties and for the creation of novel functional materials with specified characteristics. The advantage of electron beam technology is that using focused electron beam and scanning technique the modification can be obtained locally, even in nanometer scale. Metal-containing glasses and crystals are widely used in optics and photonics. Processing of these materials by electron beam with relatively low electron energies makes possible to create metal nanoparticles (NPs) and to change refractive index in the near-surface layers [1–5].

It was shown in Refs. [1,2] that the irradiation by electrons with energies E = 5–50 keV of Ag- or Na-containing silicate glasses and the subsequent thermal treatment above the glass transition temperature results in the formation of Ag or Na NPs in the near-surface layers of glasses. The local action of electrons with E = 50 keV on MgF_2, CaF_2 and BaF_2 crystals produces in them Mg, Ca and Ba nanoparticles even at room temperature [3]. The main mechanisms of these effects are as follows [1–5]: (i) the accumulation during electron irradiation of thermalized electrons and the resultant formation of negatively charged region under the glass (or crystal) surface; (ii) the field migration of mobile positive metal ions into this negatively charged region. This is the main peculiarity of low energy electron irradiation – in contradiction to γ- or X-ray, high energy electron and UV laser irradiation. The appearance of local charged region and field migration of metal ions result in their spatial redistribution in crystal – the concentration of metal ions in the irradiated zone increases, and in the surrounding areas decreases; (iii) the reduction of metal ions to neutral state; and (iv) the growth of metal nanoparticles during the subsequent thermal treatment in the case of glass. It must be mentioned that low-energy electron beam can be focused into a spot less than 10 nm in diameter. The main advantage of this method is the possibility of nanoparticles formation locally, in the region with the required shape and located at the required depth.

It was shown in Refs. [6–15] that irradiation of LiF, NaF, NaCl and CaF_2 crystals by γ- or X-ray radiation, by electrons with energies of 1–200 MeV, or by UV laser intense radiation results in metal NPs formation in crystal bulk. As metal NPs possess plasmon resonances [16,17] the coloration of irradiated area appears. In CaF_2 crystals colloids of Ca NPs can be formed by additive coloring – i.e. by thermal treatment in Ca vapor [18]. X-ray irradiation of LiF and MgF_2 crystals also produces in them luminescent centers, such as F_2 and F_3^+ defects [7,10].

The formation of colored and luminescent centers in the mentioned crystals by irradiation makes it possible to use them in integrated optics, nanoplasmonic devices and for optical information recording. Metal NPs formation in crystals can be

* Corresponding author..
E-mail address: sidorov@oi.ifmo.ru (A.I. Sidorov).

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applied in creation of non-linear optical materials and metamaterials. But in an integrated optical and nanoplasmonic devices and in optical information recording it is important to form NPs locally in nanoscale region and near the substrate surface. The use of electrons with high energy, or ionization radiations, which penetrate through the crystal bulk, makes that impossible. That's why for the mentioned applications scanning electron microscope with relatively low electron energies is mostly preferred.

For most practical applications of materials with color and luminescent centers it is important to control the intensity of coloration or luminescence. An example of such applications is multilevel optical information recording in high-order codes [19]. So, the aim of the present work is the study of the influence of electron irradiation dose on the formation of color and luminescent centers in LiF crystals and investigation of the processes, which take place in LiF crystals under the local electron irradiation with relatively low electron energies.

2. Materials and methods

LiF crystals are widely used for optical elements fabrication. They are durable, transparent in a wide spectral range – from UV to middle IR, and do not change their properties under the action of atmosphere. In our experiments we used polished plates of LiF single crystal 2 mm thick. The electron irradiation was carried out in JEBD-2 scanning electron microscope, the electron energy E was 50 keV, the irradiation doses Q were 10–100 mC/cm^2 for the electron current density of 50 μA/cm^2. The electron irradiation was carried out at a room temperature. The calculation has shown that the temperature of near-surface crystal layers during the electron irradiation for E = 50 keV and Q = 50 mC/cm^2 does not exceed 150–200 °C. The electron beam diameter on the glass surface was 1.5–2 mm. Electron beam diameter was chosen for the convenience of the subsequent optical measurements. In some experiments we formed the irradiated zone in a shape of a line by electron beam scanning. Al films of 80 nm thick were deposited on the samples surfaces for removing the surface charge, which appear on a crystal surface during electron irradiation. After irradiation, these films were removed by etching in an aqueous solution of KOH. The optical density spectra of samples under study were recorded within the 200–700 nm spectral region using Lambda 650 (Perkin–Elmer) spectrophotometer at room temperature. For luminescence measurements EPP2000-UVN-SR (StellarNet) fiber spectrometer was used, the luminescence being excited by a semiconductor lasers with λ = 405 and 450 nm.

3. Experimental results and discussion

LiF crystals before electron irradiation were transparent and colorless. Electron irradiation of LiF crystals with E = 50 keV results in the appearance of pronounced absorption band on optical density spectra at λ = 445 nm (Fig. 1). For Q = 15–35 mC/cm^2 the increase of irradiation dose led to the increase of optical density by 2.1 times (Fig. 1a). Irradiated zones in this case change the color from light-yellow to yellow (inset in Fig. 1a). For Q > 50 mC/cm^2 the absorption significantly increases in the whole spectral range of measurements with maximum in 400–470 nm spectral range. The spectral position of absorption band maximum does not change with the increase of irradiation dose. At λ = 400–470 nm for Q = 100 mC/cm^2 the value of optical density exceeds 4 (Fig. 1b). For electron energy of 50 keV all processes during irradiation take place in the near-surface layer approximately of 15–30 μm thick (see below). It means that the absorption coefficient in this case exceeds 5000 cm^{-1}. Arise of absorption bands led to the coloration of crystals from yellow for Q < 50 mC/cm^2 to

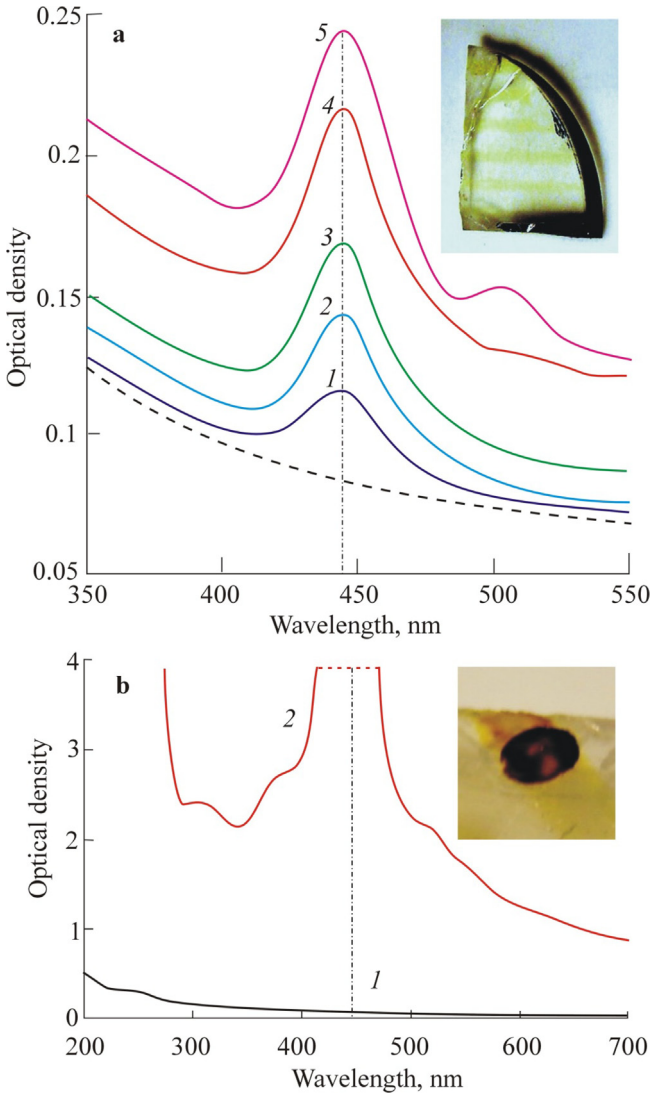

Fig. 1. Optical density spectra of irradiated LiF crystals. a: 1 – Q = 15 mC/cm^2, 2 – 20, 3 – 25, 4 – 30, 5 – 35, dashed line – before irradiation. b: 1 – before irradiation, 2 – Q = 100 mC/cm^2. Insets: photos of irradiated zones.

brown-black for Q = 100 mC/cm^2 (see inset in Fig. 1b). The absorption bands at λ = 300–350 nm (Fig. 1b) can be attributed to irradiation-induced crystal defects, such as R_1, F- and F_3 – centers, absorption bands at 500–520 nm (Fig. 1a, b) – to N-centers [6,11,20,21]. It is also known [6] that the agglomeration of F-centers (cation vacancy) gives rise to formation of metallic colloidal NPs.

For the definition of the thickness of layer, in which the processes take place, we used by Monte-Carlo method. Simulation was performed for 10^4 electrons using Mott's expression for scattering cross-section. For the calculation of ionization cross-section we used the empirical method, described in Ref. [22]. In the simulation we have taken into account electron energy losses in Al film on LiF crystal. The calculation have shown that the maximum of electron energy losses in LiF crystal for E = 50 keV is at 15–20 μm depth (Fig. 2) and maximum electrons penetration depth is approximately 30 μm. These define the location of negatively charged region formed by thermalized electrons and the thickness of near surface layer where the main processes take place. It must be mentioned that for relatively low electron energies the charged region does not have homogenous spatial