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Near-surface layer radiation color centers in lithium fluoride nanocrystals: Luminescence and composition

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ABSTRACT

Lithium fluoride nanocrystals are irradiated by gamma quanta at 77 K. The radiation color centers formed in a near-surface layer of nanocrystals are studied. Absorption, luminescence and luminescence excitation spectra of the surface defects have been measured. It has been found that the luminescence excitation spectra for aggregated surface centers consist of two or three bands with not very much different intensities. Reactions of the surface centers separately with electrons and with anion vacancies have been investigated. Numbers of anion vacancies and electrons entering into the centers composition have been established and it has been found that F_{S1}, F_{S1}^-, F_{S2}, F_{S2}^-, F_{S3}^+ and F_{S3} types of the surface centers are formed. The degree of luminescence polarization has been defined and it has been determined that the polarization degree for F_{S2}^+ centers changes sign under transition from one excitation band to another. It has been shown that during irradiation at 77 K radiation-induced defects are formed more efficiently on the surface than in the bulk.

1. Introduction

Radiation modified crystals are widely used in Prod. Type: FTPelectronics, dosimetry and laser technology [1–3]. Therefore, radiation-induced defects in them have been intensively investigated. The defects formed in the bulk of crystals are predominantly applied and studied. Lithium fluoride (LiF), due to its physical and optical properties, is one of the often-used crystals with radiation defects (color centers (CCs)). CCs formation processes in the LiF bulk have been investigated for many years and are well studied [4–7]. For such applications as waveguides and structures with high spatial resolution [8] LiF crystals with CCs in near-surface and surface layers are used. The defects in surface layers can also influence catalytic properties of the surface, serve as nucleation centers and favor the nanostructures creation [9,10].

In the majority of alkali halide crystals, with the exception of lithium and sodium fluorides, radiation CCs in surface and near-surface layers have been found relatively long ago [10,11]. Hereinafter we will designate them as surface color centers (SCCs) or surface defects (SDs). Their optical characteristics differ from the characteristics of defects in the bulk. Recently one of the SDs types in the near-surface layer and in nanocrystals (NCs) of LiF has been detected and its photoluminescence (PL) and photoluminescence excitation (PLE) spectra have been measured [12,13]. The basic measurements have been carried out with NCs that increase the ratio of surface area to volume as well as SDs concentration.

Many questions about the SCCs in LiF remains unclear: i) the presence of other types of SDs, their composition and characteristics; ii) peculiar properties and efficiency of SDs formation when crystals are exposed to ionizing radiation; iii) the possibilities to use LiF crystals based on the availability of SDs, etc. The results of the first stage of listed problems research are presented in this article. The formation of other types of radiation SCCs in LiF in addition to the type described in [12] is discovered. The absorption, PL and PLE spectra for irradiated NCs are presented. These characteristics are inherent in SDs and were not observed previously in irradiated LiF bulks. Transformations of such defects as a result of their reactions separately with electrons and with vacancies are determined. Conclusions about the processes of SCCs formation are being drawn. Their PL polarization is being measured. The findings are used to establish the number of anion vacancies (hereinafter referred to as vacancies) and electrons entering into the composition of the detected SCCs.

2. Samples and study technique

As follows from the data of [9], nanocrystals exposed to ionizing radiation at temperatures T_{irrad}, which are lower than temperature T_v of the vacancies mobility, are the convenient objects for observation and investigation of SCCs in LiF. NCs have

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been produced by mechanical fragmentation of a nominally pure LiF monocrystal. For experimental convenience they have been pressed into pellets. CCs have been also investigated in crystal plates cut out from the same LiF monocrystal. Radiation defects in samples were created by gamma rays from a ^{60}Co source. The irradiation was carried out at liquid nitrogen temperature (LNT), i.e. provided $T_{irrad}=77\ \mathrm{K}<T_v$. It was impossible to determine irradiation dose since samples were placed in front of a ^{60}Co source in a metal container filled with liquid nitrogen.

The majority of manufactured pellets were opaque. This circumstance did not allow to measure defects absorption spectra and limited information acquisition about them. To remove this restriction, some pellets of NCs have been pressed at high pressure ($\sim 3.7\times 10^9$ Pa) which ensured their transparency in the spectral region where the defects absorption is being observed. Also, absorption spectra have been registered for NCs, placed in an immersion liquid consisting of a mixture of ethanol and glycerin. The ratio of mixture components was chosen in such a way as to minimize scattering of light by NCs. In both types of measurements at room temperature (RT) the corresponding unirradiated sample (a transparent pellet or a cuvette with NCs in an immersion liquid) has been installed in the spectrophotometer reference channel. Absorption spectra registration at LNT was carried out without the unirradiated sample in the reference channel because of impossibility to install two cryostats in spectrophotometer cuvette compartment. Therefore, the spectra have been recorded on a background of radiation attenuation in the cryostat. To account for this attenuation, absorption of unirradiated transparent pellet has been subtracted from absorption of the same irradiated pellet while in both measurement procedures the samples were placed in a cryostat with liquid nitrogen.

PL measurements were carried out using two types of spectrofluorimeters which operated in the visible and near infrared spectral regions. The PL and PLE spectra were registered. Particular attention was given to the choice of wavelengths of PL registration and excitation in order to minimize the impact of different CCs spectra overlapping on measurements results. The PL polarization degree $P=(I_{||}-I_{\perp})/(I_{||}+I_{\perp})$ was defined, where $I_{||}$ и $I_{\perp}$ are PL intensities with polarizations respectively parallel and perpendicular to the polarization of the exciting radiation. When determining the value of P, Glan prisms were used as polarizers and nanocrystals have been placed in an immersion liquid between two quartz plates. For technical reasons the PL polarization could only be measured at RT. There were also technical restrictions on the range of wavelengths in which polarization has been determined.

The characteristics of unannealed samples with the defects formed by the end of irradiation at LNT have been measured. Influence of ultraviolet (UV) radiation on unannealed pellets characteristics at LNT has been studied. It will be shown in the next section that free electrons are generated as a result of samples exposure to UV radiation. These electrons diffuse in the NCs and enter into the reactions with the defects formed during γ-irradiation at LNT. The samples extracted from a vessel with liquid nitrogen were annealed at temperatures $T_{ann}>T_v$ ($T_{ann}\approx$ RT). At these temperatures vacancies diffuse in the NCs and, as a result, defects aggregation takes place during annealing in the post-radiation period. Reactions of defects with electrons and vacancies have been investigated.

3. Results and discussion

3.1. CCs formation during irradiation at LNT

Absorption, PL and PLE spectra of unannealed crystalline plates and pellets of NCs irradiated at LNT have been measured. The received absorption spectra are presented in Fig. 1. Spectral bands with maxima at 245 (F-band) and 345–350 nm belonging to centers F_1 and V_k, respectively, [14] have been detected both in a crystalline plate and in a pellet (Fig. 1, spectra 1 and 2). No other bands have been registered in the absorption spectrum of the plate. In the spectra 1 and 4 in Fig. 1 band with a maximum at 245 nm was cut off at about 0.5 so that it does not interfere with a clear view of difference in the same band in the spectra of 2 and 3, Fig. 1. For the unannealed plate the PL intensity at various excitation wavelengths is very weak and obvious emission bands are absent. It is known that bulk LiF crystals F_1 centers do not luminesce and aggregated CCs possess the characteristic PL spectra [4,5]. Thus, aggregated CCs have not been formed in the bulk during irradiation at LNT. The received results testify that probability of formation of two vacancies in the adjacent lattice sites is rather small in the bulk, irradiated at LNT with used doses of gamma rays. This conclusion confirms the correctness of the assumption made in a paper [7] and used in the studies of CCs aggregation in the post-radiation period.

Spectral bands with maxima approximately at 510, 600, 900 nm and particularities at 425, 540 and 800 nm, which indicate presence of three more bands, are observed in absorption of NCs unlike the crystal plate (Fig. 1, spectra 2 and 1). The PL and PLE spectra measured at LNT are shown in Fig. 2 for NCs irradiated at LNT and unannealed. Three PL bands with maxima at wavelengths $\lambda_{0,lum}=617$, 770 and 1100 nm have been registered. Luminescence has been measured at excitation wavelengths $\lambda_{exc}=425$ or 540 (Fig. 2a), 540 (Fig. 2b) and 600 or 900 nm (Fig. 2c). In the PLE spectra the following bands have been observed: the bands with maxima at 425 and 540 nm at registration wavelength $\lambda_{reg}=617$ nm (Fig. 2a), two bands with maxima at 560 and 635 nm at $\lambda_{reg}=770$ nm (Fig. 2b), the bands with maxima at 500, 600 and 910 nm at $\lambda_{reg}=1100$ nm (Fig. 2c). From the data presented in Fig. 1 (curve 2) and in Fig. 2 we can conclude that absorption spectra of NCs are in accordance with their PLE spectra. The CCs types with luminescent characteristics shown in Fig. 2a–c will be called types I, II, III, respectively, for convenience before the defects composition determination.

The findings indicate that during irradiation at LNT color centers are formed in NCs with the characteristics which are not

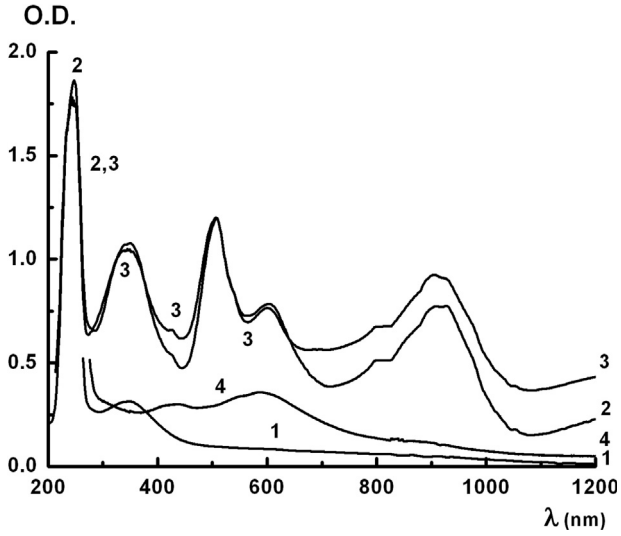

Fig. 1. Measured at LNT absorption spectra of samples irradiated at the same temperature and unannealed: a crystal plate (1), a pellet of NCs before (2) and after (3) exposure to ultraviolet radiation. The measured at RT absorption spectrum after annealing and termination of the CCs transformation processes in a pellet, not subjected to ultraviolet irradiation (4).