

Photoluminescence behavior of surface radiation induced color centers in lithium fluoride and influence of nanosized clusters

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ABSTRACT

Influence of pre-irradiation annealing temperature on the efficiency of the subsurface color center formation in lithium fluoride nanocrystals at their γ -irradiation has been studied. Increase of the annealing temperature reduces the efficiency of formation of these centers. Nanocrystals lose their ability to form subsurface color centers after pre-irradiation annealing at the temperatures above 623 K. The formed subsurface color centers are partially transformed into the usual centers of the same composition during the post-radiation annealing at certain temperatures. The mechanical fragmentation of lithium fluoride crystals leads to the formation of nanosized clusters in their subsurface layers. Subsurface radiation color centers which are located near the clusters are subjected to the modified crystal field. This circumstance causes strong differences between the luminescent characteristics of subsurface color centers and usual centers of the same composition in the crystal bulk, where there are no clusters. The clusters are completely destroyed after annealing the samples at the temperatures above 623 K. The obtained results indicate that the presence of nanoclusters is a prerequisite for the formation of subsurface radiation color centers with specific fluorescent properties. The thickness of the subsurface layer, where subsurface color centers can be formed, has been estimated.

Keywords: subsurface color center; nanosized cluster; photoluminescence; annealing; lithium fluoride nanocrystals

1. Introduction

An introduction of extrinsic or intrinsic point defects into solid-state matrices promotes a broad variety of novel properties of these materials and opens new possibilities for their applications [1]. Materials with such defects are used as gain media in solid-state lasers [2,3], for ionizing radiation dosimetry [4] etc. Lithium fluoride (LiF) with radiation point defects – color centers (CCs) – serves as an active medium in tunable solid-state lasers emitting in the visible and near infrared spectral ranges [3]. Pure and doped LiF crystals are the well-known dosimeter materials [5]. Radiation-induced CCs formation processes in LiF crystal bulk have been investigated for many years and they are well studied [6–8].

Recently the radiation CCs in near-surface layers of the crystal plates and in the nanocrystals (NCs) of LiF have been observed [9,10]. We will denote them as subsurface color centers (SCCs) or subsurface defects (SDs). The presence of the following types of SDs has been defined to date: F_{S1} , F_{S1}^- , F_{S2}^+ , F_{S2} , F_{S2}^- , F_{S3}^+ and F_{S3} [10] (here we exploit the commonly-used notations for CCs [6–8] and the subscript “S” is added for the SCCs). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of aggregate SCCs are substantially different from ones determined for CCs with the same composition but formed in the crystal bulk [10].

To date, the reasons of SCCs generation and features in their absorption and PL characteristics are still unclear. The aim of the present work is the investigation of these reasons. We have studied the effect of pre-irradiation annealing of mechanically fragmented LiF samples on the efficiency of SCCs formation, as well as the decomposition and transformation of SCCs and CCs due to the annealing of already irradiated samples. The structure of NCs is investigated with and without the thermal treatment. The correlation between the structure of NCs and the efficiency of SCCs formation in them is analyzed. Estimations of the subsurface layer thickness where radiation SCCs are formed are carried out.

2. Samples and study technique

As it was shown in [9,10], very suitable materials for the observation and study of SCCs in LiF are NCs, exposed to ionizing radiation at the temperature $T_{irr} < T_v$, where T_v is the temperature of the anion vacancies mobility. In this work we used NCs, manufactured by mechanical fragmentation of plates from a nominally pure non-irradiated LiF single crystal.

NCs dimensions were not more than a micrometer. In some cases for the convenience the nanocrystalline powder was pressed to pellets; most of them were opaque. During the preparation of some of the pellets, an increased pressure was applied ($\sim 3.7 \times 10^9$ Pa) resulting in the pellet transparency. The properties of irradiated plate cut from the LiF single crystal along the $\{100\}$ plane were studied as well for the sake of comparison. The radiation defects in samples were formed by gamma rays from a ^{60}Co source. The irradiation was carried out at the liquid nitrogen temperature, thus providing the condition $T_{irr} < T_v$. It was impossible to determine the irradiation dose accurately as the samples were placed in a dewar filled with a liquid nitrogen. An estimation of the irradiation dose gave a value of about $5 \cdot 10^4$ Gy. After the irradiation, all samples were kept at room temperature, which is higher than the temperature T_v , until the finalization of the post-radiation aggregation processes of CCs and SCCs.

Some of samples were annealed before or after the γ -irradiation. The annealing temperature, T_{ann} , is the constant temperature at which the samples are kept in the furnace for a fixed time.

The PL and PLE spectra were measured with a spectrofluorimeter SM-2203 (SOLAR, Belarus). Previously it was shown that the PL intensity for the samples similar to those used in the present work is proportional to the concentration of emission centers [11]. Using a laser scanning confocal microscope LSM 510 NLO (Zeiss, Germany), we inspected the depth distribution of SCCs in the transparent pellet and in the crystalline plate.

The structural characteristics of LiF nanocrystals were studied with X-ray diffraction (XRD) analysis. For this, we used a diffractometer DRON-3M (Russia) with X-ray wavelength 0.15405 nm (Cu K_α line). The measurements were performed in Bragg-Brentano configuration. The structure of samples was also studied by the Transmission Electron Microscopy (TEM). A microscope JEOL TEM-1011 with an acceleration voltage up to 200 kV and a point resolution up to 0.5 nm was used. The nanocrystalline powder fabricated with the mechanical grinding was poured in ethanol and this mixture was put into ultrasonic disperser. After extra grinding of nanocrystals within the disperser, a small part of the mixture was dropped onto a metal grid. Then it was dried in air at room temperature and has been used to produce images. Samples of nanocrystals without and with the preliminary γ -irradiation were studied. After receiving images, some samples were additionally annealed at 623 K for 1 h and the TEM studies were repeated.

All measurements were performed at room temperature.

3. Results and discussion

3.1. Effect of pre-irradiation annealing on SCCs formation

PLE spectra of NCs, γ -irradiated with the same dose, were measured for the registration wavelengths $\lambda_{reg} = 670, 535$ and 850 nm. All used NCs were fabricated in the same manner from LiF single crystal and then pressed to opaque pellets. Before the irradiation, each pellet was annealed at the given temperature for one hour. For the first sample, the annealing temperature was 323 K. For each subsequent sample it was increased at 50 K, up to 623 K. One of samples was annealed at $T_{ann} = 623$ K, ground again and then pressed to an opaque pellet. The data obtained are presented in Fig. 1. The spectra shown in Fig. 1 by solid lines are normalized to their maximum values. This is done to facilitate their comparison and highlight their similarities and distinctions. The remaining spectra shown by dashed lines are given in the same relative units to show the difference of their intensities.

In Fig. 1a, we show some of the PLE spectra corresponding to $\lambda_{reg} = 670$ nm. For the sample annealed at 323 K (spectra 1, 1'), the excitation bands of the subsurface F_{S3}^+ centers are observed (the bands with the maxima at $\lambda_m = 393, 493$ and 564 nm) [10]. For the same sample, the band ascribed to the F_2 defects in the crystal bulk is also recorded (the band peaking at $\lambda_m = 444$ nm) [6]. Our measurements indicated that annealing at the temperatures of $T_{ann} \leq 423$ K does not affect significantly the PL intensity (and, hence, the concentration) of F_{S3}^+ SCCs. Further rise of the annealing temperature results in the decrease of the concentration of these centers and in the increase of the concentration of F_2 CCs (see spectrum 2'). In the sample annealed at $T_{ann} = 623$ K, F_{S3}^+ centers are not formed under the γ -irradiation (spectrum 3'). The PLE spectrum of NCs, annealed at $T_{ann} = 623$ K and subsequently grinded, is very similar to the spectra of the samples annealed at $T_{ann} \leq 423$ K or unannealed (compare the spectra 4 and 1 in Fig. 1a).

When the temperature of the preliminary annealing is increased, a behavior similar to the one described above is observed for the F_{S3} SDs as well. In Fig. 1b, the PLE spectra measured for $\lambda_{reg} = 535$ nm are presented. For this λ_{reg} and for the sample annealed at $T_{ann} = 323$ K (spectrum 1), we detected the luminescence of F_3 (R_2) and F_3^+ CCs (the bands with the maxima at $\lambda_m = 380$ and 448 nm, respectively) [6], and the luminescence of F_{S3} SCCs (bands with the maxima at $\lambda_m = 463, 400$ and 355 nm) [10]. By comparing the spectra 1 and 3, we conclude that after the preliminary annealing of the samples at $T_{ann} = 623$ K, the subsequent γ -irradiation does not lead to the formation of the F_{S3} centers. However, secondary grinding of the sample

annealed at this temperature recovers the ability of γ -rays to form the F_{S3} SDs in the NCs (see Fig 1b, spectrum 4).

PLE spectra measured for $\lambda_{reg} = 850$ nm are shown in Fig. 1c. In these spectra, the bands with the maxima at $\lambda_m = 420$ and 570 nm (spectra 1, 1' and 4) are ascribed to the F_{S2}^+ SCCs [10] and the band peaking at $\lambda_m = 444$ nm (spectrum 3') is due to the F_2 CCs [6]. The small intensity of the latter band is due to very weak PL of the F_2 CCs at $\lambda_{reg} = 850$ nm. The dependence of the concentration of the F_{S2}^+ SCCs formed under the γ -irradiation upon the temperature of the preliminary annealing of NCs is similar to the corresponding dependences for the F_{S3}^+ and F_{S3} centers. In the NCs annealed at $T_{ann} = 623$ K, the F_{S2}^+ SCCs cannot be formed by the subsequent γ -irradiation (spectrum 3'). Again, the secondary grinding of these NCs recovers this ability of γ -rays (Fig. 1c, spectrum 4).

Let us note that the F_{S2} SCCs concentration changes with increasing pre-irradiation annealing temperature in the same manner as the concentrations of F_{S2}^+ , F_{S3}^+ and F_{S3} centers.

Summarizing the results of the pre-irradiation annealing on the efficiency of SDs formation, we can make the following conclusions. The increase of the annealing temperature reduces the efficiency of SCC formation. After the annealing at $T_{ann} \geq 623$ K, nanocrystals lose their ability to form SCCs while the secondary mechanical grinding recovers this ability. The experiments performed on LiF crystal plates have also demonstrated that the heat-treatment at $T_{ann} \geq 623$ K makes it impossible to form SCCs in the subsurface layers as a result of the γ -irradiation.

One of the possible reasons for the formation of radiation defects in LiF nanocrystals with new PL characteristics can be the development of aggregates in the subsurface layer with atmosphere components. Indeed, it is known that the water vapors transform the surface radiation centers in NaCl [12]. The presence of carbon and oxygen was detected on the air cleaved surface of LiF [13]. To clarify the possible effect of atmosphere on the formation of radiation-induced SDs the following experiment has been carried out. Half of the LiF single crystal was irradiated by a focused laser beam. For this, we used a Q-switched Nd:YAG laser with the following parameters: laser wavelength $\lambda = 1.064$ μm , pulse duration $\tau = 8$ ns, pulse energy $E = 16$ mJ. Each laser pulse structurally destroyed the crystal in the area of the focal spot. We have controlled that the defects formed by the laser pulses were located in the crystal volume and did not propagate to the surface. Two identical LiF single crystals were prepared in this way. Each crystal was half-damaged (a part of the crystal contained caverns and non-point defects and the remaining part was not damaged). One of these crystals was then annealed at $T_{ann} = 623$ K. Then both samples (annealed and unannealed) were irradiated by γ -rays. The PLE

spectra of these samples were studied for $\lambda_{\text{reg}} = 670$ nm. The F_{S3}^+ SCCs exist only in the part of non-annealed crystal which was damaged by the laser radiation. In the annealed crystal, SDs are not found after the γ -irradiation. Thus, the contact of the crystal surface with the atmosphere is not the prerequisite for the formation of radiation-induced SCCs with the characteristic PL properties.

3.2. Effect of post-radiation annealing on SCCs and CCs

The changes in the concentrations of the F_{S2}^+ , F_{S3}^+ , F_2 and F_3^+ centers were studied in opaque pellets of NCs annealed at different temperatures T_{ann} after the γ -irradiation. Three series of measurements corresponding to different annealing duration τ_{ann} have been performed. The durations τ_{ann} we selected to be 1 h, 10 min and 1 min. The annealing temperature was sequentially increased. After each annealing, the sample was cooled to room temperature and the PL intensity was measured. Two pellets were used in each of measurements series. One of them was not annealed before the γ -irradiation. The second pellet was annealed at $T_{\text{ann}} = 623$ K for 1 h and consequently there were no SCCs in this pellet after the γ -irradiation. The results on variation of the PL intensity due to the post-radiation annealing are shown in Fig. 2. They were obtained as following: (i) for the F_{S3}^+ and F_2 centers – from the PLE spectra measured for $\lambda_{\text{reg}} = 670$ nm, (ii) for the F_{S2}^+ centers – from the PLE spectra measured for $\lambda_{\text{reg}} = 850$ nm, (iii) for the F_3^+ centers – from both the PL spectra and PLE ones recorded under $\lambda_{\text{exc}} = 445$ nm and $\lambda_{\text{reg}} = 535$ nm, respectively. If necessary, the measured spectra were decomposed into components.

In pellets which were not annealed before the γ -irradiation, an increase in the temperature of the post-radiation annealing leads to a rapid drop in concentrations of the F_{S2}^+ and F_{S3}^+ SCCs (Fig. 2a,b, spectra 1 and 2). By comparing the spectra 1, 2 and 3, 4 in Fig. 2a,b, one can see that a decrease in the SCCs concentration is always accompanied by an increase in the F_2 and F_3^+ CCs concentration. After the destruction of F_{S2}^+ and F_{S3}^+ SCCs, the increase of the F_3^+ CCs concentration stops, while it is still ongoing for the concentration of the F_2 CCs.

For the samples pre-annealed at 623 K for one hour before the γ -irradiation, the increase of the temperature of the post-radiation annealing T_{ann} reduces the F_3^+ CCs concentration up to their complete disappearance (Fig. 2c). With the increase of T_{ann} , the F_2 CCs concentration first does not change, then increases, and finally drops to zero. The increase of the F_2 CCs concentration starts at the higher temperatures than in the case of the unannealed pellets, compare spectra 3 in Fig. 2c and in Fig. 2a. The results similar to those shown in Fig. 2c were also obtained for $\tau_{\text{ann}} = 1$ h and 1 min. Let us emphasize that in the NCs without SCCs, no

growth of the F_3^+ CCs concentration is observed for any temperature range and for all used durations of the post-radiation annealing.

From the presented results we can conclude that the post-radiation annealing of the pellets which were not subjected to a heat-treatment before the γ -irradiation results in a transformation of some of the F_{S3}^+ SCCs into the F_3^+ CCs. This fact may indicate that the heat-treatment destroys some aggregates which are formed in the NCs as a result of the cleaving (or grinding) of the crystal and opens possibilities for the formation and stabilization of SCCs. This assumption does not disagree to the data of Section 3.1 and the previous results of Ref. [10]. To validate this assumption, one needs to study the NCs structure.

3.3. Structure features of NCs

The XRD patterns were measured for the following LiF powder samples: (i) unannealed and annealed at $T_{ann} = 623$ K for 1 h, both fabricated by the mechanical grinding, and (ii) two samples fabricated by a chemical method. The diffraction lines with indices h, k, l of (111), (200), (220), (311) and (222) have been observed for all of the samples. Here, the indices h, k, l characterize crystallographic planes of the X-rays reflections. They are in accordance with the standard data for LiF powders (JCPDS card No. 4-857). We measured the widths for the diffraction lines of (111) and (200) at 38.74° and 45.04° , respectively. The widths for the annealed samples ($\sim 0.22^\circ$) are slightly less than ones for the unannealed samples ($\sim 0.25^\circ$). We refer this difference to the relaxation of small stresses during annealing.

TEM studies have shown that the NCs produced by the mechanical grinding have mean size ranging from few hundreds of nm up to ~ 1 μm and different shape. They also proved the existence of small irregularities (clusters or aggregates) within the NCs which are presented in TEM image as dark spots in large-area samples, Fig. 3. Let us note that large dark areas in the TEM image presented in Fig. 3 is due to the large thickness of the individual sample that makes it almost non-transparent for TEM. The developed clusters are uniformly distributed in the sample volume and they are randomly oriented. Their shape is irregular. The typical size distribution for clusters was obtained using the ImageJ software by analyzing clearly resolved clusters from several TEM images (total number of clusters analyzed, ~ 200), the mean cluster dimension was considered, see Fig. 4. Their mean sizes are in the range 5–17 nm.

After the mechanical grinding in an ultrasonic disperser, some of the samples studied with TEM were subjected to a heat-treatment at 623 K for 1 h. These samples were then again studied with TEM. The image of one of them is shown in Fig. 5. The nanosized clusters can be

hardly found in the TEM image of the annealed NCs. The destruction of clusters during the annealing may eliminate small stresses in the NCs as it was discussed above based on the XRD studies.

Thus, radiation-induced SCCs are observed in the samples with the nanosized clusters. The destruction of these clusters leads to the impossibility of such centers formation. This correlation allows us to conclude that the presence of nanosized clusters is a prerequisite for the formation and stabilization of radiation-induced SCCs in LiF nanocrystals and in the subsurface layers of LiF crystals. The distortion of the crystal field near these clusters determines the specificity of the PL characteristics of SCCs observed before in Ref. [10].

TEM image in Fig. 3 does not give an indication of the subsurface layer depth where the nanosized clusters are developed and, consequently, the SCCs are formed. In order to evaluate this depth, the PL related to the F_{S3}^+ SCCs was measured using a transparent pellet of the LiF nanocrystals and a single-crystal LiF plate. This PL is located in the red spectral region, and it is excited by green radiation [11]. In our experiments, we used two sources for the excitation of such PL: (i) a He-Ne laser with a wavelength of 543 nm and with a power of 1 mW and (ii) a mercury lamp emitting a line with a wavelength of 546 nm. Radiation with such wavelengths is not absorbed by the F_2 defects in the crystal bulk (see Fig. 1(a) and the related explanations in the text) and therefore does not excite PL of these defects.

A scanning confocal microscope was used in the first part of experiments to determine the depth where the SCCs are formed. In these studies, PL of the F_{S3}^+ centers was excited by the He-Ne laser emitting at 543 nm. Some of the obtained data are shown in Fig. 6 where the surface of studied samples is located at the beginning of the emission region. The color lines are from the coordinate frame of the camera. As is seen in Fig. 6(a), PL is observed throughout the whole pellet thickness. The emission from the single-crystal plate is detected from a narrow subsurface layer only, Fig. 6b. Evaluation of the depth of this layer leads to the value of $h \sim 9$ μm . The same value of h is obtained from the measurements of the excitation light reflected from the plate surface, Fig. 6c. This value can be thus referred to the instrumental function of the microscope, so the real depth of the luminescent layer in the plate satisfies the relation $h < 9$ μm . Here in conclusion, we note another two things. First, there is no PL of the F_{S3}^+ SCCs in the single-crystal plate which is annealed at $T_{ann} = 623$ K for 1 h and γ -irradiated after that. Second, the picture of green light reflection from the transparent pellet is similar to that shown in Fig. 6(c).

In the second part of experiments, the value of h was estimated from the ratio of PL intensities associated with the F_{S3}^+ SCCs for a transparent pellet of NCs (thickness of 350 μm)

and a single-crystal plate. Both samples were exposed to the same radiation dose and studied under identical conditions of PL excitation ($\lambda_{exc} = 546$ nm) and registration. The reduced density of the pellet (2.32 g/cm^3) with respect to the single-crystal (2.60 g/cm^3) was also taken into account. In this way, the depth of the subsurface layer where the SCCs are formed is estimated as $h \approx 2.5 \text{ }\mu\text{m}$.

It is known [13] that during the cleavage of the LiF crystals, partial dissociation of the LiF molecules and desorption of atoms from the surface can occur. During this process, the halogen and metal atoms are lost not in the stoichiometric relation. The cleavage of crystal is also accompanied by the emission of electrons [14]. This process participates in the variation of the near-surface properties of the crystal too.

Irradiation of LiF crystals with all types of ionizing radiation (ions, neutrons, electrons, γ -rays) leads to the formation of lithium colloids [15-19]. These colloids are characterized with the optical absorption band with the maximum at 450–430 nm depending on their size [16,17,19,20]. In the absorption spectrum of the transparent LiF nanocrystalline pellet, we have observed a band peaking at 433 nm, see spectrum 4 in Fig. 1 of Ref. [10]. The width of this band did not change with the cooling of the sample from room temperature down to the liquid nitrogen temperature. This indicates that this band is not related to the color centers. One may ascribe this band to the colloids of lithium created in the NCs during or (and) soon after the crystal cleavage.

In Ref. [15] it was shown that the concentration of lithium colloids decreases significantly with the sample heating to the temperatures exceeding 423 K and these colloids completely disappear at 623–723 K. In Refs. [16,18,19], the temperatures corresponding to the decomposition of these colloids are estimated as 630–730 K. Our data on the temperature corresponding to the decomposition of non-uniformities appeared in the prepared NCs (Section 3.3) and on the effect of the heat-treatment on the efficiency of formation of SCCs (Section 3.1), are in agreement with the previously reported results [15,16,18,19] concerning decomposition of lithium colloids. Thus, we expect the existence of such colloids in the studied samples.

The presence of metal colloids is a clear indication of the separation of halogen and metal atoms in the crystal. In Ref. [21], it was demonstrated that the irradiation of CaF_2 crystals with the low-energy electrons leads to the crystal decomposition, as well as formation of calcium colloids on the crystal surface and in the near-surface layer and subsurface fluorine gas bubbles. Similar situation may be observed in our samples. Further experiments and complementary

techniques are necessary for the clarification of the composition and structure of the nanosized clusters observed in the TEM image (Fig. 3).

4. Conclusions

Cleavage of the LiF crystals leads to the formation of nanosized clusters in their subsurface layer. According to the TEM studies of the LiF nanocrystals obtained with the mechanical grinding, the mean size of these clusters is in the range 5–17 nm. Estimates of the subsurface layer depth, in which nanosized clusters are formed, give a value of several microns. This value needs to be further clarified.

The preliminary annealing of LiF crystals and NCs at $T_{ann} \geq 423$ K leads to the drop of the efficiency of SCCs formation under γ -irradiation. The ability to form SCCs is lost after the pre-annealing at $T_{ann} \geq 623$ K due to the decomposition of nanosized clusters. Thus, the presence of these clusters is the prerequisite for the formation of radiation-induced SCCs in the LiF nanocrystals and subsurface layers of LiF single-crystals.

The existence of nanosized clusters implies the variation of the crystal field. XRD studies indicate the effect of these clusters on the crystal field. Consequently, absorption and emission characteristics of SCCs adjacent to clusters are changed compared to the characteristics of CCs with the same composition, as it was observed previously [9–11].

The results on annealing of the samples after the complete post-radiative aggregation of SCCs and CCs indicate that during the annealing, SCCs are transformed into CCs of the same composition. This process is associated to the decomposition or size reduction of major part of the nanosized clusters. In the parts of the crystal with the decomposed clusters, the parameters of non-distorted crystal field are recovered and, consequently, the parameters of radiation-induced defects specific for the crystal bulk are observed.

The temperatures corresponding to the cluster decomposition are in agreement with the temperatures reported in the previous studies [15,16,18,19] for the decomposition of lithium colloids.

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Figure captions

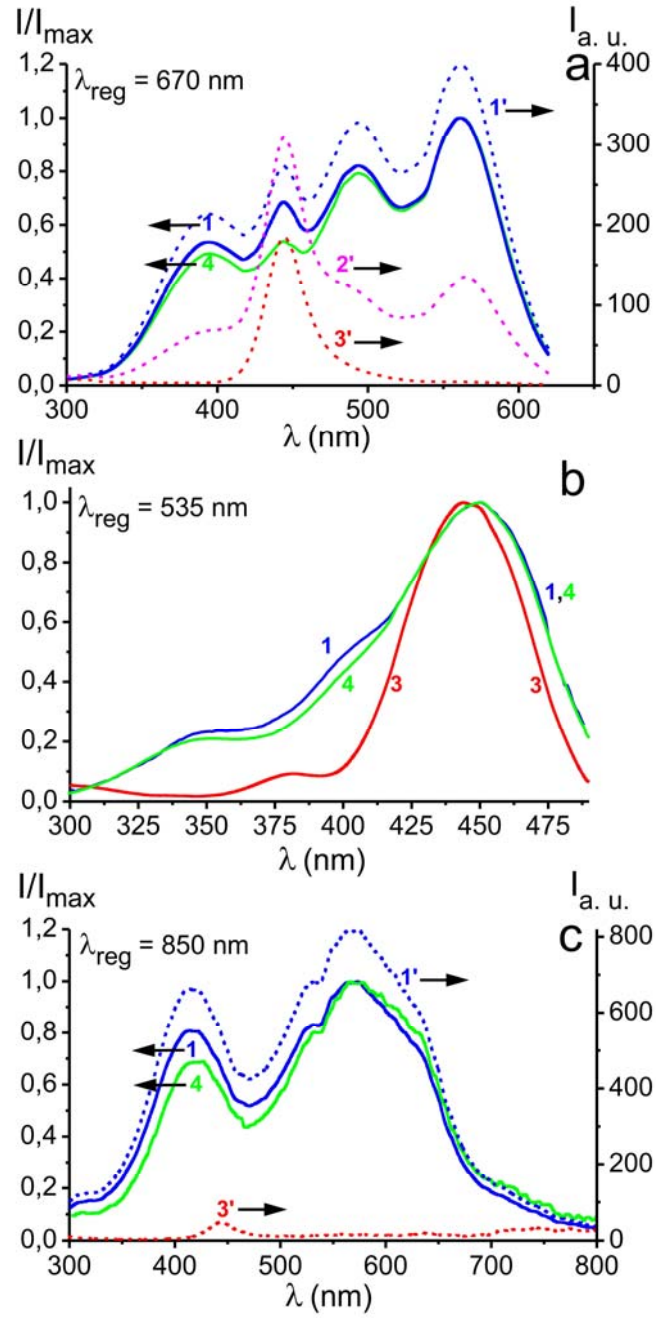


Figure 1. PLE spectra measured for $\lambda_{\text{reg}} = 670 \text{ nm}$ (a), 535 nm (b) and 850 nm (c) for the following nanocrystalline LiF samples: pre-annealed before the γ -irradiation for 1 h at $T_{\text{ann}} = 323$ (1, 1'), 473 (2') and 623 K (3, 3'); pre-annealed before the γ -irradiation for 1 h at $T_{\text{ann}} = 623 \text{ K}$ and then again mechanically grinded (4).

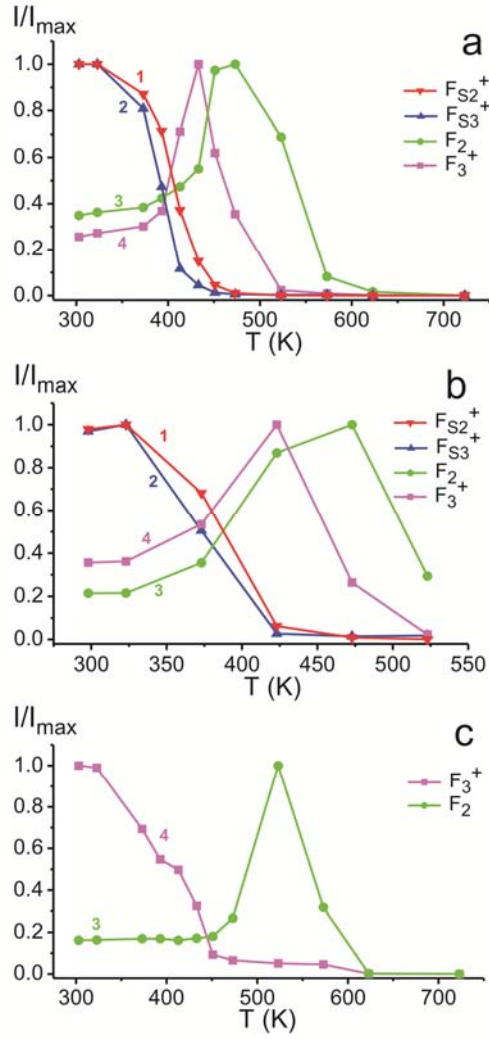


Figure 2. PL intensity changes for the F_{S2}^+ (1), F_{S3}^+ (2), F_2 (3) and F_3^+ (4) centers within opaque nanocrystalline LiF pellets non-annealed (a, b) and pre-annealed at $T_{\text{ann}} = 623$ K for 1 h before the γ -irradiation (c) as a result of the post-radiation heat-treatment for 10 min (a, c) or 1 h (b) at each temperature. Lines are drawn for the convenience of interpretation.

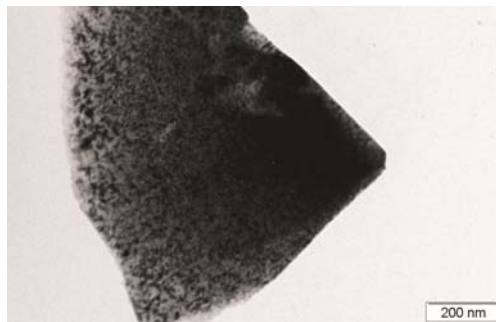


Figure 3. TEM image of a single LiF nanocrystal (unannealed, after the fabrication by mechanical grinding).

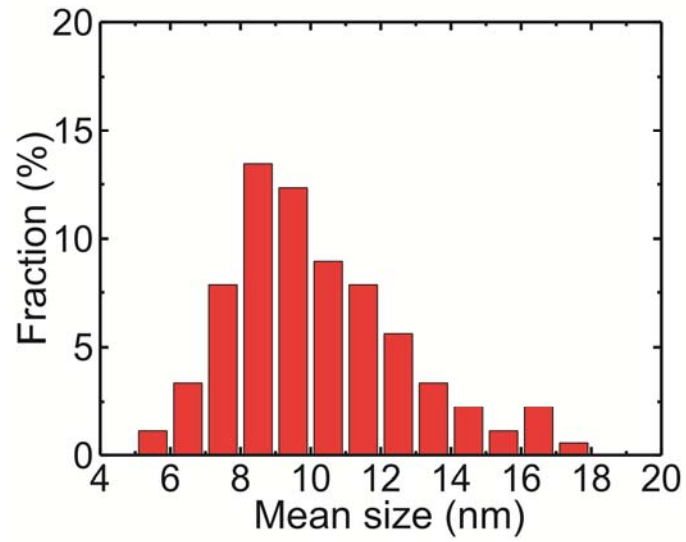


Figure 4. Size distribution of the nanosized clusters in LiF nanocrystals.

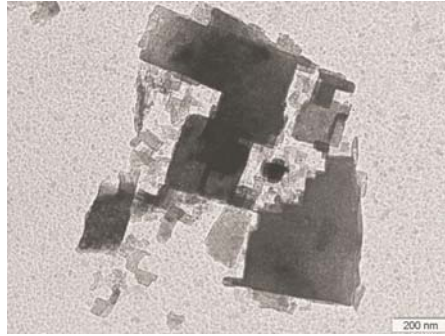


Figure 5. TEM image of LiF nanocrystals annealed at 623 K for 1 h.

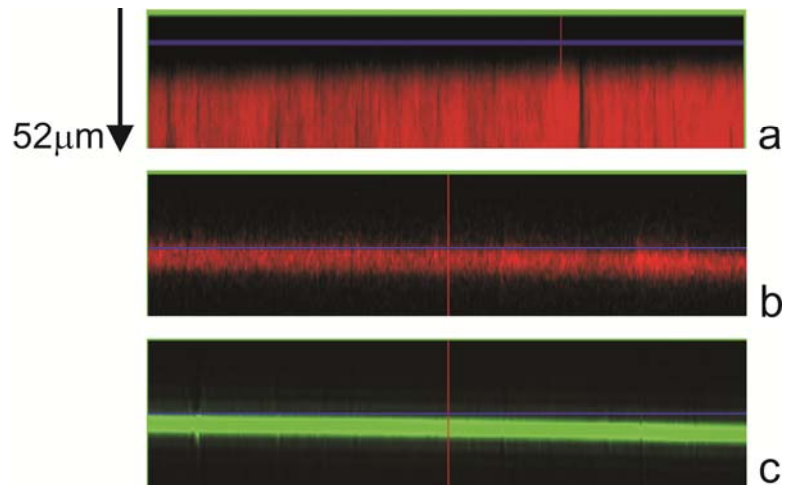


Figure 6. PL related to the F_{S3}^+ SCCs from a transparent pellet of LiF nanocrystals (a) and from a LiF single-crystal plate (b); radiation at $\lambda = 543$ nm reflected from the surface of the crystal plate (c).