Formation and transformation of the radiation-induced near-surface color centers in sodium and lithium fluorides nanocrystals

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Abstract. Near-surface color centers in sodium fluoride nanocrystals have been formed. At pre-irradiation annealing of sodium and lithium fluorides samples at temperatures of 623 K and above, the near-surface color centers in them have not been found after γ-irradiation. Annealing lithium fluoride nanocrystals with the near-surface defects leads to their transformation into bulk ones of the same composition.

1. Introduction
Lithium fluoride (LiF) due to its physical and optical properties is one of the often used crystals in dosimetry of ionizing radiation. Processes of radiation-induced color centers (CCs) formation in the LiF bulk have been investigated for many years and are well studied [1–4]. Recently new radiation CCs in near-surface layers of crystalline plates and in nanocrystals (NCs) of LiF have been found [5, 6]. Their absorption and luminescence characteristics are significantly different from similar characteristics of CCs of the same composition formed in the LiF bulk. Hereinafter we will designate them as near-surface color centers (SCCs). It is shown [7] that presence of nanoscale clusters in the samples is a necessary condition for the formation of SCCs.

The possibility of creating radiation SCCs in other crystals is shown in this work. Sodium fluoride (NaF) crystal was chosen for experiments. It has a cubic lattice, as well as LiF crystal. The influence of pre-irradiation annealing on radiation defects formation in LiF is presented. The effect of after-irradiation annealing on radiation defects transformation in LiF is also investigated.

2. Samples and methods
The experiments were carried out with samples consisting of NCs with dimensions less than 1 μm (at least in one dimension). NCs were prepared by mechanical grinding of nominally pure NaF or LiF crystals. For convenience NCs were pressed into tablets. Radiation defects in tablets were created by γ-rays from a 60Co source. Samples were irradiated at liquid nitrogen temperature T irr = 77 K < Tυ, where Tυ is the temperature of anion vacancies mobility. Estimated radiation dose was about 5·10⁴ Gy. All samples were kept at room temperature after irradiation until the aggregation processes of created defects was completed.
Tablets were annealed at different temperatures before irradiation. Annealing temperature $T_{\text{ann}}$ is a constant temperature at which the sample is held in an oven for 1 hour. Unannealed tablets were also investigated.

Two tablets of LiF were used for other experiment. One was annealed before the $\gamma$-irradiation at $T_{\text{ann}} = 623$ K for 1 h, the other was not annealed. These samples were annealed at different temperatures after irradiation and aggregation of bulk CCs and SCCs. Annealing was carried out as follows. Sample was annealed 1 minute at a constant temperature. Then the sample was quickly cooled to room temperature and the photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured. After that the sample was annealed, but at a different, higher temperature. The photoluminescence measurements were repeated. This measurement procedure was repeated several times until it has reached the annealing temperature 553 K.

PL and PLE spectra were recorded by SM-2203 spectrophotometer (SOLAR, Belarus). In all cases, the PL intensities were proportional to the concentrations of the corresponding color centers. All spectral measurements were performed at room temperature.

3. Results and discussion

3.1. Effect of pre-irradiation annealing on SCCs formation in LiF nanocrystals

The PLE spectra were detected at registration wavelengths $\lambda_{\text{reg}} = 540$ and 670 nm for the $\gamma$-irradiated LiF tablets and for a crystal. Before the irradiation one tablet was annealed at temperature 623 K for one hour. The spectra obtained at $\lambda_{\text{reg}} = 670$ nm are presented in figure 1, a. The spectrum 1 in figure 1, a demonstrates intense bands belonging to bulk $F_2$ (the band with the maximum at $\lambda_m = 444$ nm) and near-surface $F_{S3}^+$ (the bands with the maxima at $\lambda_m = 393, 493$ and 564 nm) centers [1, 2, 4, 6]. This means that both surface and bulk CCs appear in this tablet after irradiation. SCCs are not formed in a tablet pre-annealed at temperature 623 K and then $\gamma$-irradiated (figure 1, a, spectrum 2). Furthermore, the PLE spectrum of this sample (figure 1, a, spectrum 2) is very similar to the spectrum of a LiF crystalline plate (figure 1, a, spectrum 3) which was not subjected to a preliminary heat treatment. There is only one band belonging to $F_2$ centers in spectra 2 and 3.

![Figure 1](image_url). Normalized to their maximum values PLE spectra measured at $\lambda_{\text{reg}} = 670$ (a) and 540 nm (b) for the following $\gamma$-irradiated LiF samples: unannealed (1) and annealed before the $\gamma$-irradiation for 1 h at $T_{\text{ann}} = 623$ K (2) tablets, unannealed crystalline plate (3); all spectra were registered after the termination of post-radiation CCs aggregation processes. Explanations are given in text.

The PLE spectra measured at $\lambda_{\text{reg}} = 540$ nm are presented in figure 1, b. Spectrum 1 belongs to a tablet which was unannealed before $\gamma$-irradiation. This complex spectrum was decomposed into separate components, which are represented by dashed lines in the figure 1, b. The PLE bands with the maxima at $\lambda_m = 355, 400$ and 463 nm (spectrum 5) belong to $F_{S3}^+$ SCCs [6], the band with the maximum at $\lambda_m = 448$ nm (spectrum 4) belong to $F_{3}^+$ CCs [1, 4]. Therefore, both surface and bulk...
defects observed in this sample. PLE spectrum of crystalline plate (spectrum 3 in figure 1, b) was also decomposed into individual components, which are represented by dashed lines. It contains spectral bands with the maxima at $\lambda_m = 380$ and 448 nm, which belong to $F_3$ (R2) and $F_3^+$ CCs, respectively [1,4]. The first band practically coincides with the measured spectrum in the range 400-490 nm. PLE spectrum of a tablet (spectrum 2 in figure 1, b) which is pre-annealed at temperature $T_{\text{ann}} = 623$ K before $\gamma$-irradiation, is similar to the spectrum of a crystalline plate. Therefore, after the pre-annealing of the samples at $T_{\text{ann}} = 623$ K, the subsequent $\gamma$-irradiation does not lead to the formation of the $F_{33}$ centers. The other measurements show that $F_{32}$ and $F_{32}^+$ SCCs are also not formed in a tablet pre-annealed at temperature 623 K for 1 hour and then $\gamma$-irradiated [8].

A similar method was used to detect SCCs in $\gamma$-irradiated NaF samples.

3.2. Observation of SCCs in NaF nanocrystals
The PLE spectra were measured at $\lambda_{\text{reg}} = 590$ nm for the NaF crystalline plate and NCs irradiated at $T_{\text{irr}} = 77$ K (figure 2, a). Before the irradiation, one pellet was annealed at temperature 623 K for one hour. Another pellet was not annealed. The wavelength $\lambda_{\text{reg}}$ of the PL detection was chosen because it is located in the luminescence bands of the $F_2$ and $F_3^+$ CCs [9,10].

Figure 2. Normalized to their maximum values PLE spectra measured for $\lambda_{\text{reg}} = 590$ nm (a) and PL spectra at $\lambda_{\text{exc}} = 310$ nm (b) for the following $\gamma$-irradiated NaF samples: unannealed (1) and annealed before the $\gamma$-irradiation for 1 h at $T_{\text{ann}} = 623$ K (2) pellets, unannealed crystalline plate (3); all spectra were registered after the termination of post-radiation CCs aggregation processes.

In the PLE spectrum of crystalline plate (figure 2, a, spectrum 3), we observe only spectral bands belonging to bulk $F_2$, $F_3^+$ CCs. The most intensive bands are located in the region of 500–520 nm [10]. Also, there are the less intense second absorption bands of $F_2$ and $F_3^+$ CCs with maxima at 344 and 310 nm, respectively [10]. The spectrum of the pellet (spectrum 1 in figure 2, a) differs from the spectrum of the crystalline plate. Decomposition of this spectrum into components (not presented here) shows that except the above-mentioned bands, it contains other spectral bands. We consider that these spectral bands belong to near-surface CCs in NaF. The PLE spectrum of pre-annealed before irradiation pellet (spectrum 2 in figure 2, a) contains the same bands as the spectrum of the crystal. The distinction between the intensities of the bands in spectra 2 and 3 can be explained by distortions due to the difference of the scattering in different spectral ranges. We have a strongly scattering sample of nanocrystals (2) and practically no scattering crystalline plate (3).

The PL spectra were measured at $\lambda_{\text{exc}} = 310$ nm for $\gamma$-irradiated at $T_{\text{irr}} = 77$ K NaF crystal and NCs pellets (figure 2, b). We can see that PL spectrum of the annealed before the $\gamma$-irradiation pellet differs from that has not been annealed. There is one band with a maximum 590 nm in the PL spectrum of the unannealed pellet (spectrum 1 in figure 2, b). On the other hand PL spectrum of annealed pellet contains two overlapping bands (spectrum 2 in figure 2, b). The decomposition of this spectrum into components indicates the presence of two bands with maxima at 590 and 650 nm, which are PL bands.
of bulk F$_2$ and F$_3^+$ CCs, respectively [10]. Spectrum of the crystalline plate (spectrum 3 in figure 2, b) is similar to the one of the annealed pellet.

Thus, SCCs are present in the NaF pellet. Additional studies are required to establish the composition of these SCCs.

3.3. Effect of after-irradiation annealing on SCCs transformation in LiF nanocrystals

The changes in the concentrations of the F$_{33}^+$, F$_2$ and F$_3^+$ centers were studied in pellets of LiF NCs annealed at different temperatures $T_{\text{ann}}$ after the $\gamma$-irradiation. Two pellets were used in each of measurements series. One of them was not annealed before the $\gamma$-irradiation. The second pellet was annealed at $T_{\text{ann}} = 623$ K for 1 h and there were no SCCs in this pellet after the $\gamma$-irradiation. The results of the PL intensity changes due to the post-radiation annealing are shown in figure 3. They were obtained from the PLE spectra measured for $\lambda_{\text{reg}} = 670$ nm for the F$_{33}^+$ and F$_2$ centers and from both PL spectra at $\lambda_{\text{exc}} = 445$ nm and PLE at $\lambda_{\text{reg}} = 535$ nm for the F$_3^+$ centers. If necessary, the measured spectra were decomposed into components.

In the pellet which was not annealed before the $\gamma$-irradiation an increase in the temperature of the post-radiation annealing above 393 K leads to a rapid drop in concentrations of the F$_{33}^+$ SCCs (figure 3 a, data 3). By comparing the data 1, 2 and 3 in figure 3, a, we can see the following: a decrease in the F$_{33}^+$ SCCs concentration is accompanied by an increase in the F$_2$ and F$_3^+$ CCs concentrations. After the destruction of F$_{33}^+$ SCCs, the increase of the F$_3^+$ CCs concentration stops, while it is still ongoing for the concentration of the F$_2$ CCs. A similar situation is observed for other samples subjected to the longer duration of the post-radiation annealing [7].

![Figure 3](image)

**Figure 3.** PL intensity changes for the F$_2$ (1), F$_3^+$ (2), F$_{33}^+$ (3) centers in $\gamma$-irradiated non-annealed (a) and annealed at $T_{\text{ann}} = 623$ K for 1 h before the irradiation (b) LiF pellets as a result of the post-radiation heat-treatment for 1 min at each temperature. Points are experimental results. Lines are drawn for the convenience of interpretation.

In the pellet which was annealed before the $\gamma$-irradiation, there is a completely different situation. We observe only a monotonic decrease in the concentration of F$_3^+$ centers with temperature growth (data 2 in figure 3, b). The growth stage of these centers is not observed in contrast to the previous case. An increase in the concentration of F$_2$ centers is fixed in the temperature range from 493 to 553 K (data 1 in figure 3, b).

Based on these results, we can conclude that post-radiation annealing of the pellets which were not exposed to pre-radiation annealing leads to a transformation of some of the F$_{33}^+$ SCCs into the F$_3^+$ CCs.
4. Conclusion

New spectral bands in PLE spectra of NaF nanocrystals, not subjected to pre-radiation annealing, were found. These bands belong to near-surface color centers in NaF. Near-surface color centers in NaF and LiF nanocrystals not annealed before irradiation are formed as a result of γ-irradiation. For NaF as well as for LiF, pre-annealing at temperatures 623 K and more makes it impossible to create the SCCs as a result of γ-rays exposure.

It was shown [7] that an unannealed pellet of NCs contains clusters with size ranged from 5 to 17 nm. The similar clusters are absent in annealed samples. Mechanical fragmentation of the crystal leads to the creation of clusters. The formation of surface color centers is impossible without these clusters. Pre-irradiation annealing leads to the destruction of clusters and eliminate the conditions necessary for the formation of the surface centers.

Post-radiation annealing of the pellets which were not exposed to pre-radiation annealing leads to a transformation of some of the F$_{33}^+$ SCCs into the F$_3^+$ CCs. It means that SCCs are transformed into CCs of the same composition.

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