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Spectral properties of radiation-induced near-cluster color centers in LiF, NaF and MgF_2 nanocrystals

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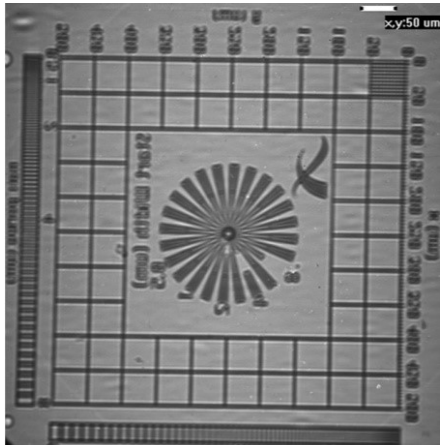
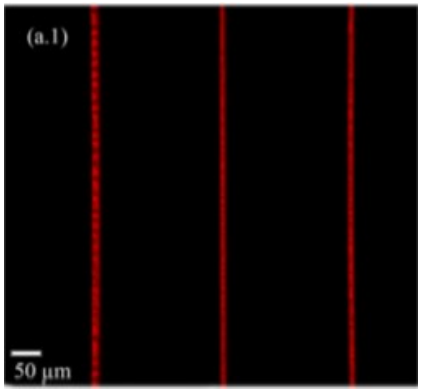
Institute of Physics NAS Belarus

Conference on Physics of Defects in Solids: Quantum Mechanics Meets Topology
9–13.7.2018 ICTP, Trieste, Italy

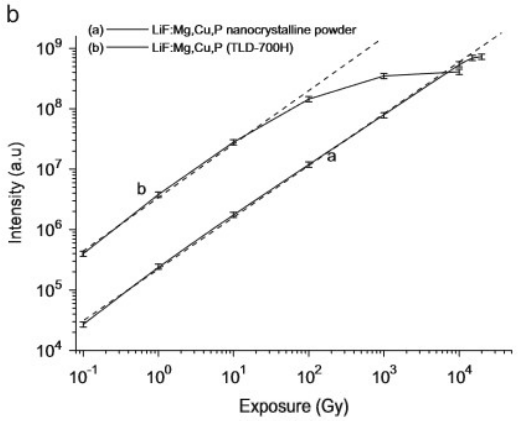
Application

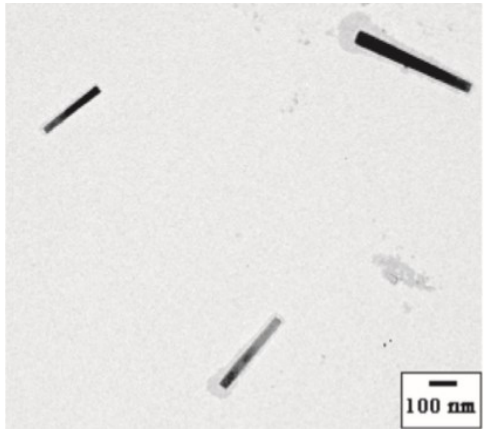


Rad. Meas. 56 (2013) 277-280



J. Appl Phys. 115, 023108 (2014)

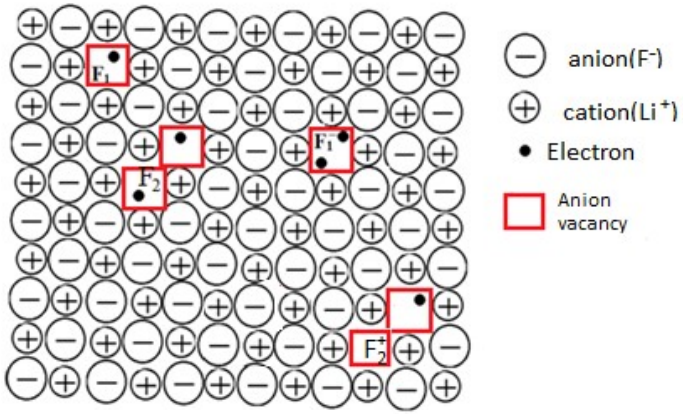




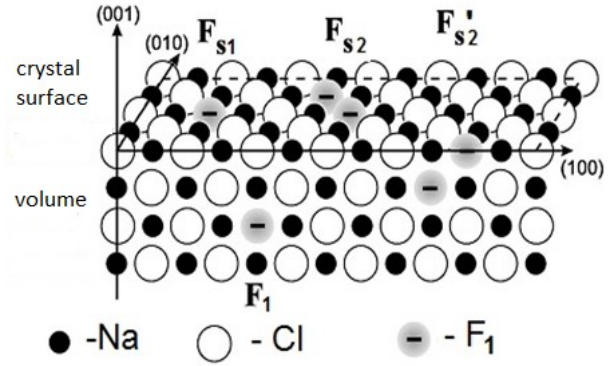
Rad. Phys. Chem. 80 (2011) 1–10

- detection and dosimetry of ionizing radiation.
- electronics and laser technologies.
- detectors of images for X-ray, electron, ion and neutron radiography and microscopy.

Radiation defects in bulk and near-cluster layer



Variations of color centers in alkali halide crystals are formed under the influence of ionizing radiation



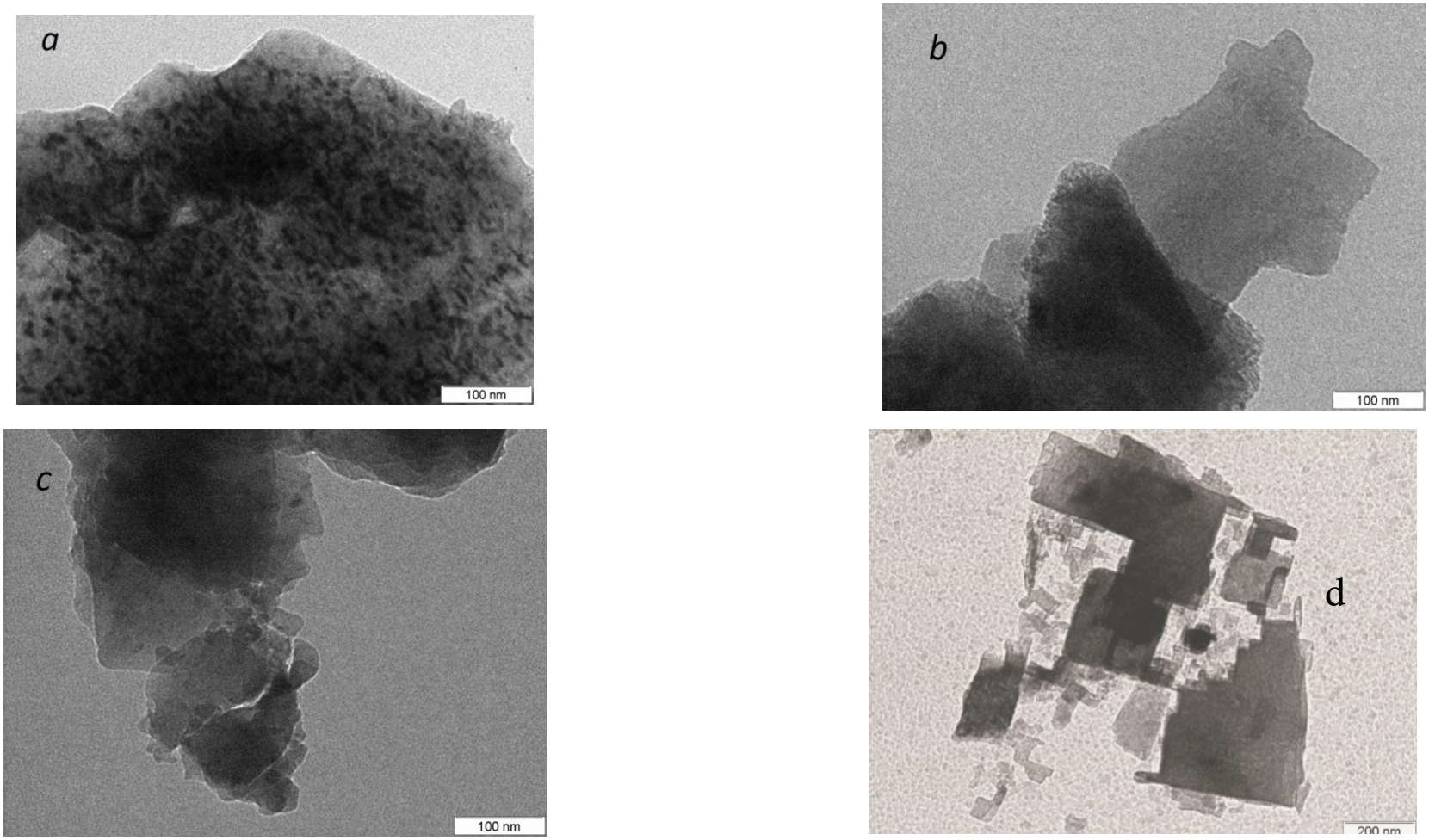
Model of surface color centers (*)

Phys. Rev. B. Vol. 62, № 4. (2000). P. 2912–2919.

The Goals of this work

- To investigate radiation near-cluster centers in LiF, NaF and MgF_2
- To determine types and compositions of near-clusters color centers and their spectral properties in LiF and NaF nanocrystals
- To compare the characteristics of the color centers of the same composition located in the bulk and in the near-cluster layers of LiF and NaF

TEM images



TEM images of LiF (a), NaF (b) and MgF_2 (c) nanocrystals which were not annealed before study; TEM image of LiF nanocrystal (d) annealed before study

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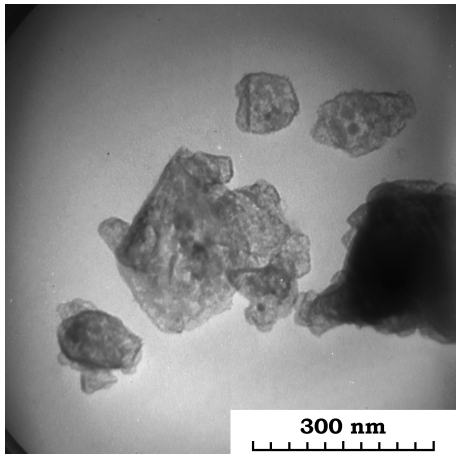
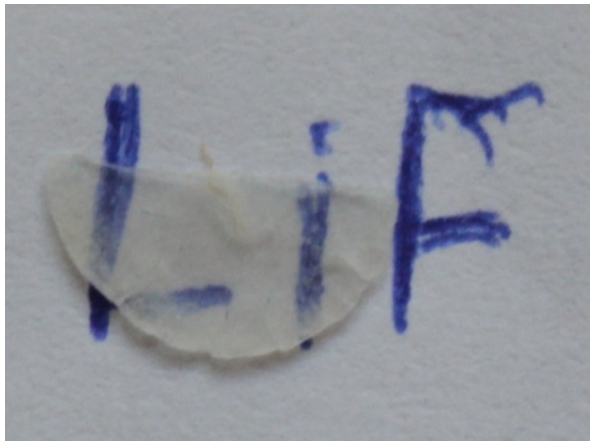
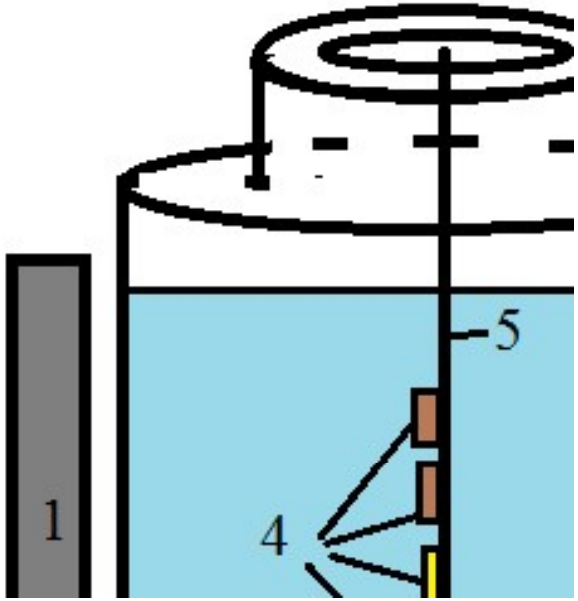
The samples and methods



nanocrystals



pellet



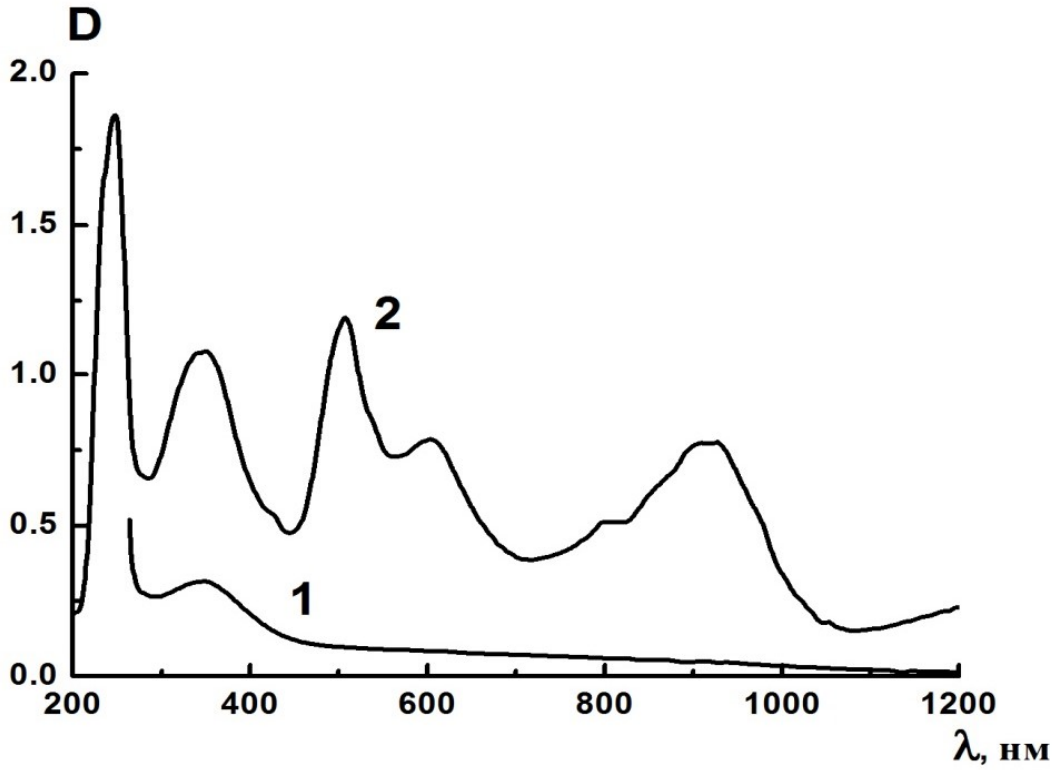
Irradiation technique

Measurements:
Absorption Cary 500 Scan (Varian, USA).
Luminescence SM-2203 (SOLAR, Belarus)
TEM measurements
Luminescence life-time measurements

1- plate with ^{60}Co cassettes
2 - dewar filled with liquid nitrogen
3 - liquid nitrogen
4 – samples
5 – sample holder

LiF

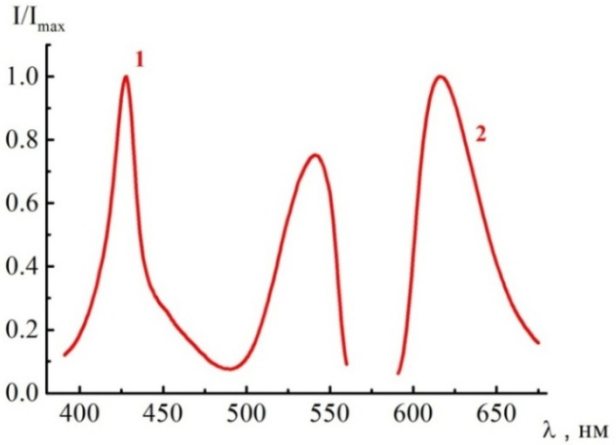
Absorption spectra of LiF bulk crystal (1) and pellet (2)

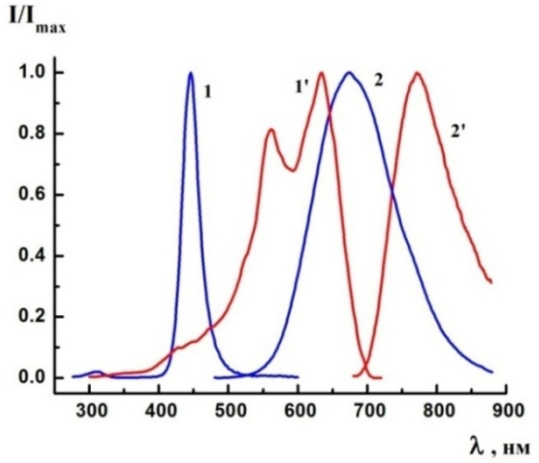


Measured at LNT absorption spectra of samples irradiated at the same temperature and unannealed: a crystal plate (1), a pellet of NCs (2).

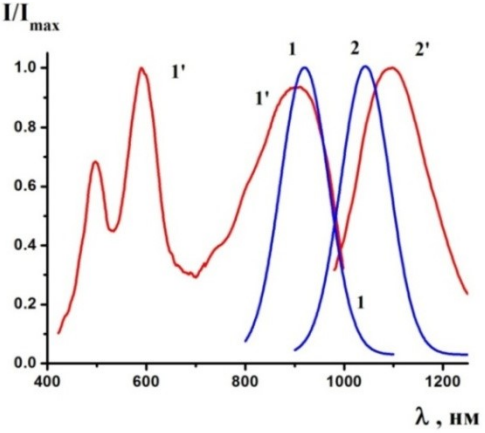
Color centers in LiF (1)

a





b



c

F_2 and F_{C2}

τ (F_2) = 16.2 ns

c

F_2^- and F_{C2}^-

Measured at LNT and normalized to their maximum values PLE (1') and PL (2') spectra of CCs type 1 (a), F_{C2} (b), F_{C2}^- (c) in LiF in a pellet irradiated at LNT and unannealed (red); for comparison, spectra of defects of the same composition in the bulk crystal are shown on the same spectrum (blue)

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Color centers in LiF (2)

aggregation processes

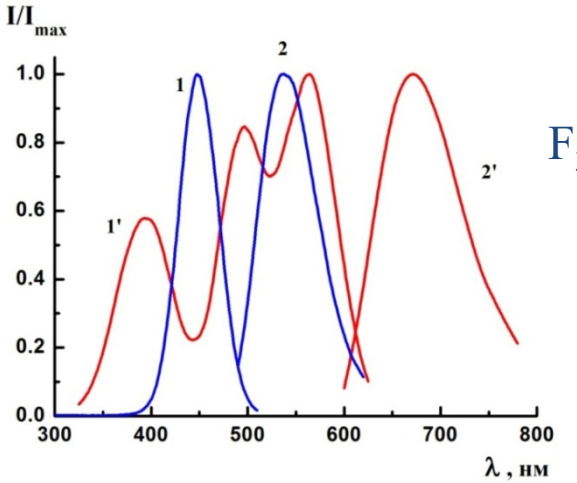
$$\upsilon_a + F_{C1} \rightarrow F_{C2}^{+}, \quad (1)$$

$$\upsilon_a + F_{C1}^{-} \rightarrow F_{C2}, \quad (2)$$

$$\upsilon_a + F_{C2} \rightarrow F_{C3}^{+}, \quad (3)$$

$$\upsilon_a + F_{C2}^{-} \rightarrow F_{C3}. \quad (4)$$

a



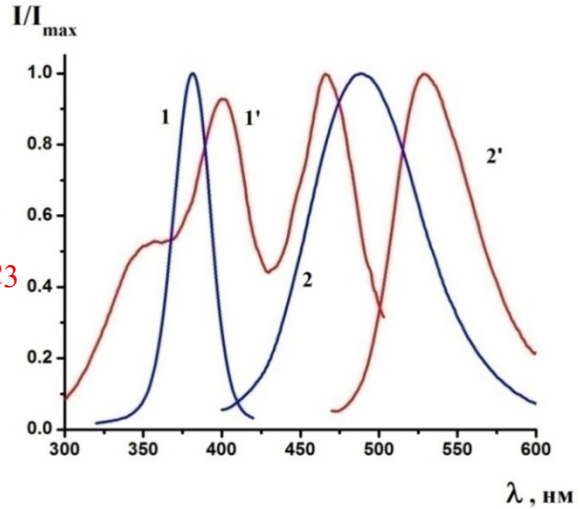
F_3^+ and F_{C3}^+

$\tau\ (F_3^+) = 8.5$ ns

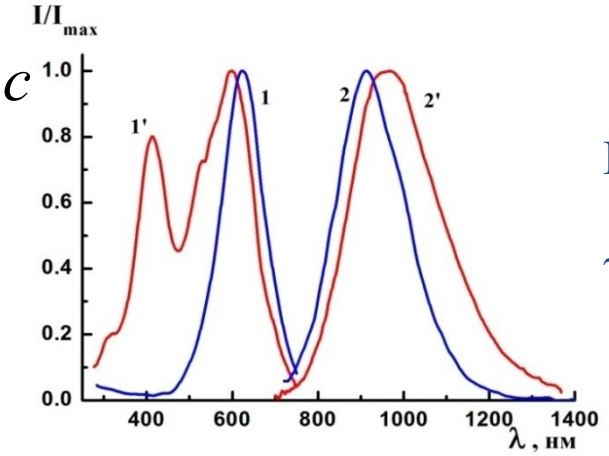
$\tau\ (F_{C3}^+) = 13.5$ ns

b

F_3 and F_{C3}



c



F_2^+ and F_{C2}^+

$\tau\ (F_2^+) = 21.9$ ns

Measured at RT and normalized to the maximum values PLE (1, 1′) and PL (2, 2′) spectra of near-clusters (′) and bulk color centers with same composition in LiF. All the spectra were measured at RT after termination of aggregation processes in them.

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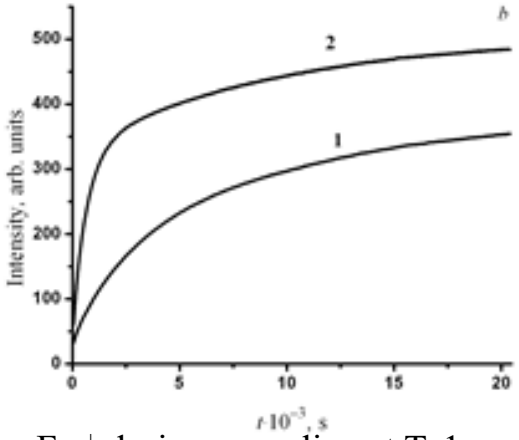
Diffusion of near-cluster and bulk defects

$$L^2 = 6Dt, \qquad (1)$$

$$D = D_0 \exp\left(-\frac{E_a}{kT}\right) \qquad (2)$$

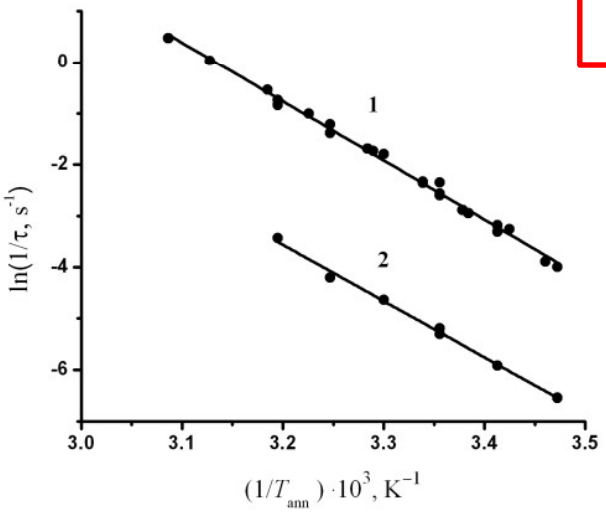
$$\ln(1/\tau) = \ln(6D_0/L^2) - (E_a/k)(1/T) \qquad (3)$$



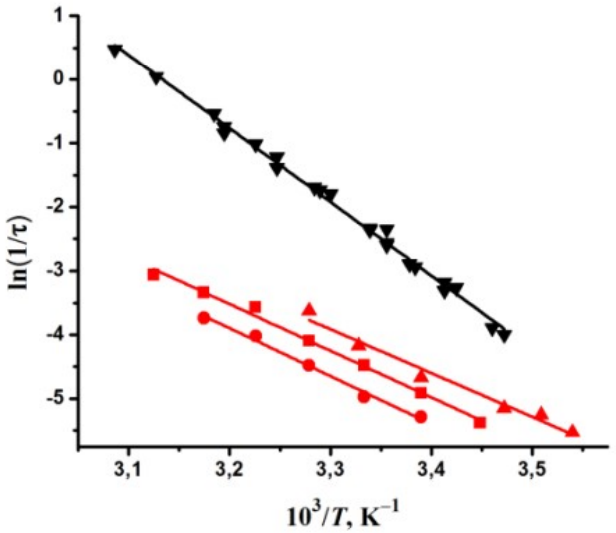
PL I (t) for the F_{S3}^+ during annealing at T. 1 — 288, 2 — 298 K;

E_{sav} = 1.00eV

E_{av} = 0.60eV



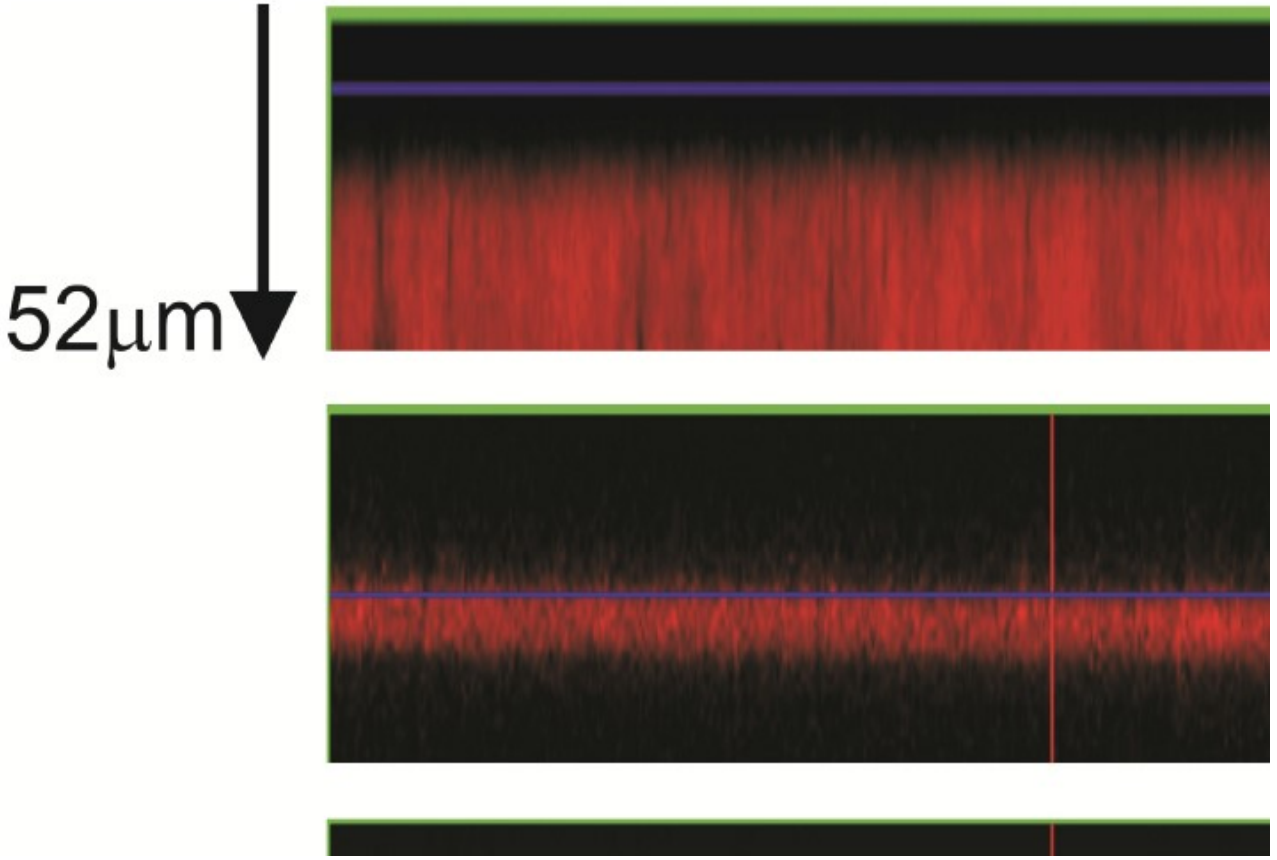
The dependences ln (1/τ) = f (1/T_{ann}) for the first stage of the concentration changes of the centers F_{C2} and F_{C3}^+ (1) and for the second stage of growth of the concentration of the F_{C3}^+



The dependences ln (1/τ) = f (1/T_{ann}) for the first stage of the concentration changes of the centers F_{C2} and F_{C3}^+ (black), for the initial stage of F_2^+ centers formation at different irradiation doses (red)

Phys. Solid State 57, 9 (2015) 1752–1758

Scanning confocal microscope measurements in LiF



Photoluminescence related to the F_{c3}^{+} CCCs from a transparent pellet of LiF nanocrystals (a) and from a LiF single-crystal plate (b); radiation at λ = 543 nm reflected from the surface of the crystal plate (c).

Evaluation of subsurface layer's depth result to the value of h ~ 9 μm.

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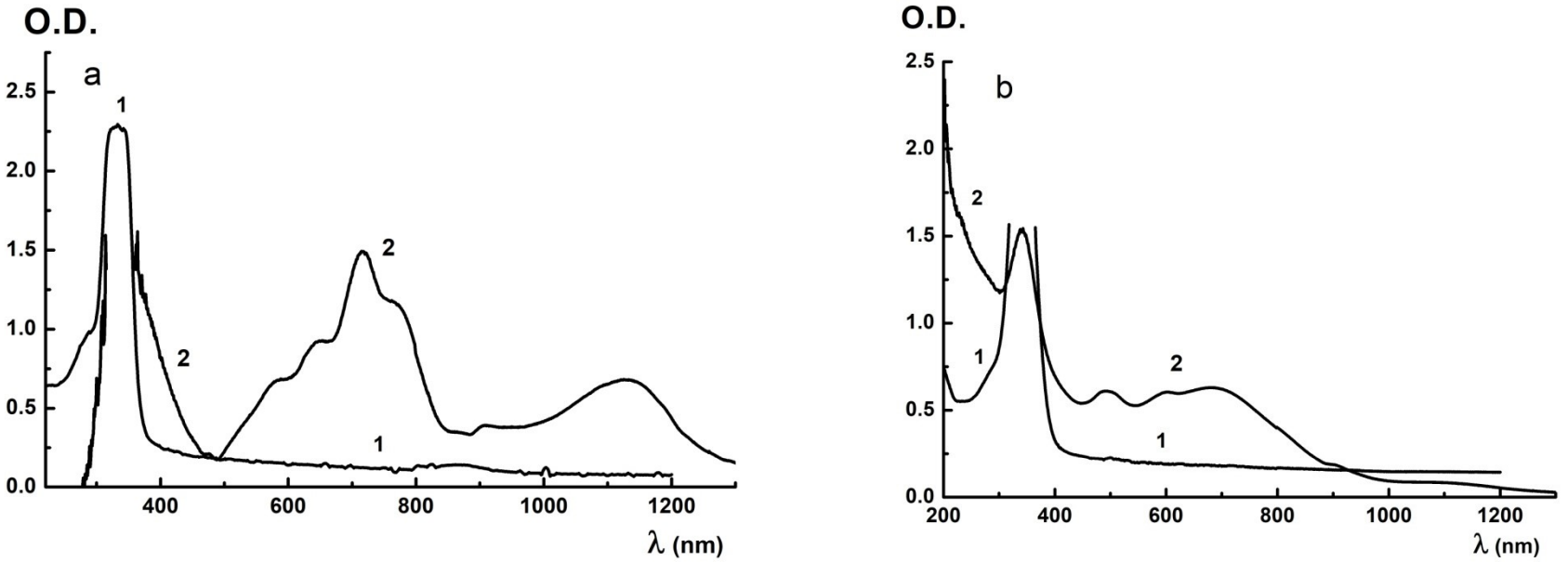
NaF



Absorption spectra for NaF crystalline plate (1) and non-annealed transparent pellet of NCs (2) irradiated at LNT and measured without defrosting (a) and after termination of the defects aggregation processes at RT (b).

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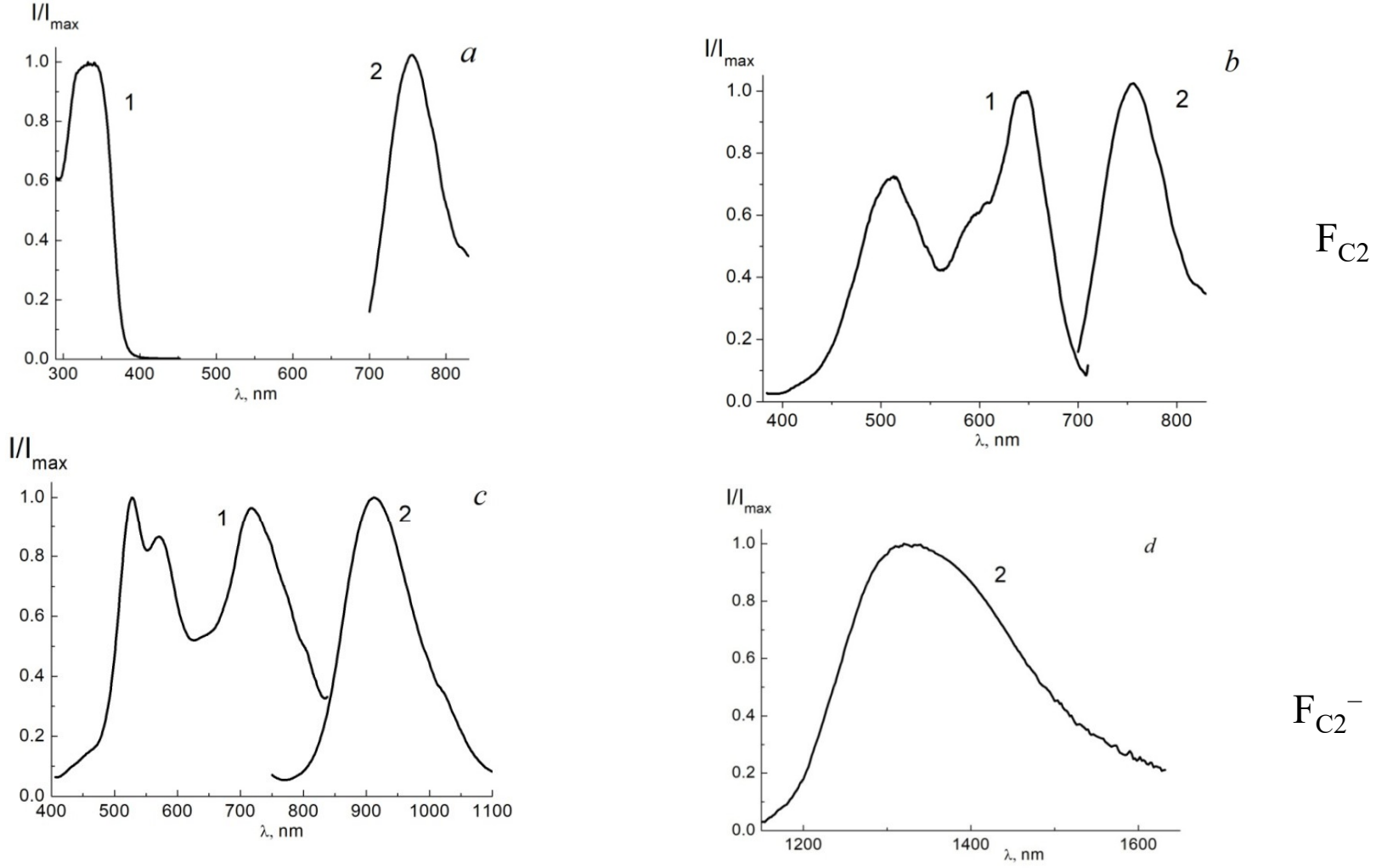
Color centers in NaF (1)



F_{C2}

F_{C2}^{+}

F_{C2}^{-}

PLE (1) and PL (2) spectra for NaF crystalline plate (a) and non-annealed pellet (b – d) irradiated at LNT and non-defrosted before measurements at the following wavelengths λ_{reg} and λ_{exc} respectively: 765 and 340 (a), 750 and 645 (b), 930 and 710 (c), 1064 nm (d).

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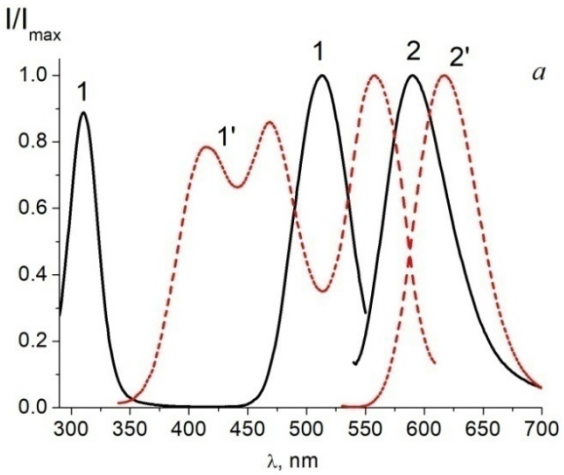
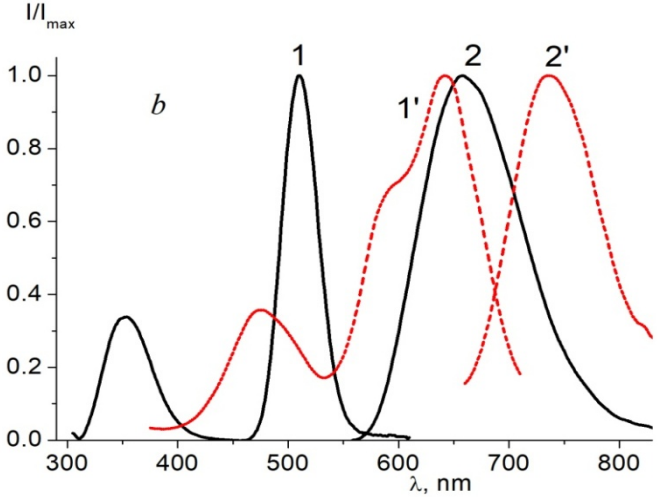
Luminescent properties of bulk and near-clusters color centers in NaF

б

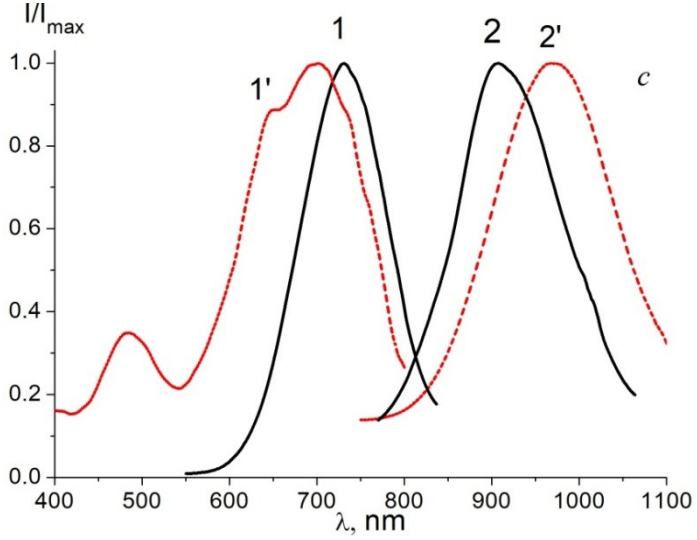




F_3^+ and F_{C3}^+

τ (F_3^+) = 8.0 ns

τ (F_{C3}^+) = 10.8 ns



F_2 and F_{C2}

τ (F_2) = 9.8 ns

τ (F_{C2}) = 14.3 ns

F_2^+ and F_{C2}^+

Normalized to their maximum values PLE (1, 1') and PL (2, 2') spectra in NaF for CCs (1, 2) and CCCs (1',2') of the following types: F_3^+ and F_{C3}^+ (a), F_2 and F_{C2} (b), F_2^+ and F_{C2}^+ (c).

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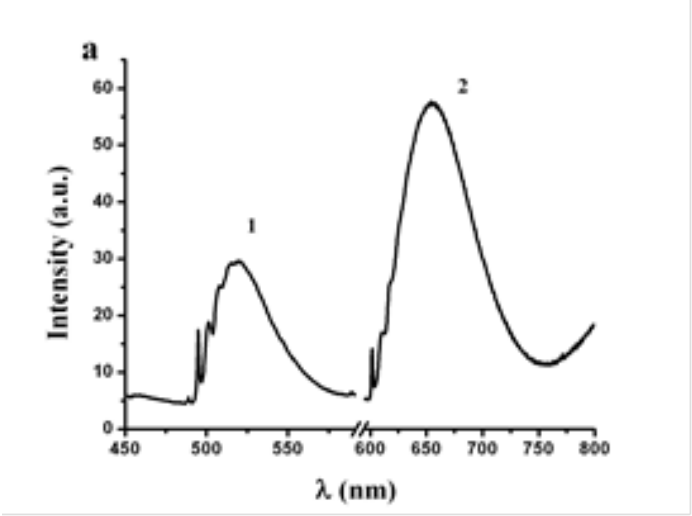
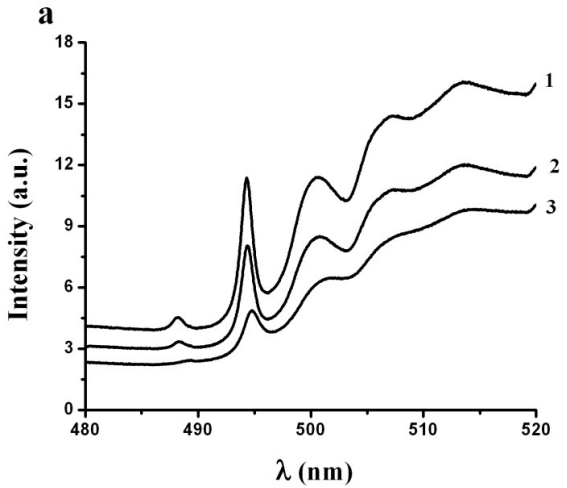
Zero-phonon lines and electron-phonon interaction characteristics of CCCs in LiF and NaF



Pellets PL spectra: F_{S3} (1) and F_{S3}^{+}(2) SCCs, λ_{exc}=405 (1) and 532 nm (2), T=20 K (a)



Pellets PL spectra for centers F_{S3} (a) at T=10 (1), 50 (2) and 90 K (3) and λ_{ex}=405

$$\Delta E = E_{abs} - E_{lum} = 2Sh\nu_{ph},$$

The ratios of the Huang-Rhys parameters for transitions in CCs and CCCs of the same composition in LiF and NaF

	$S(F_2^+)/S(F_{C2}^+)$	$S(F_2)/S(F_{C2})$	$S(F_3^+)/S(F_{C3}^+)$
NaF	0.70	2.28	1.48
LiF	0.78	2.63	1.42

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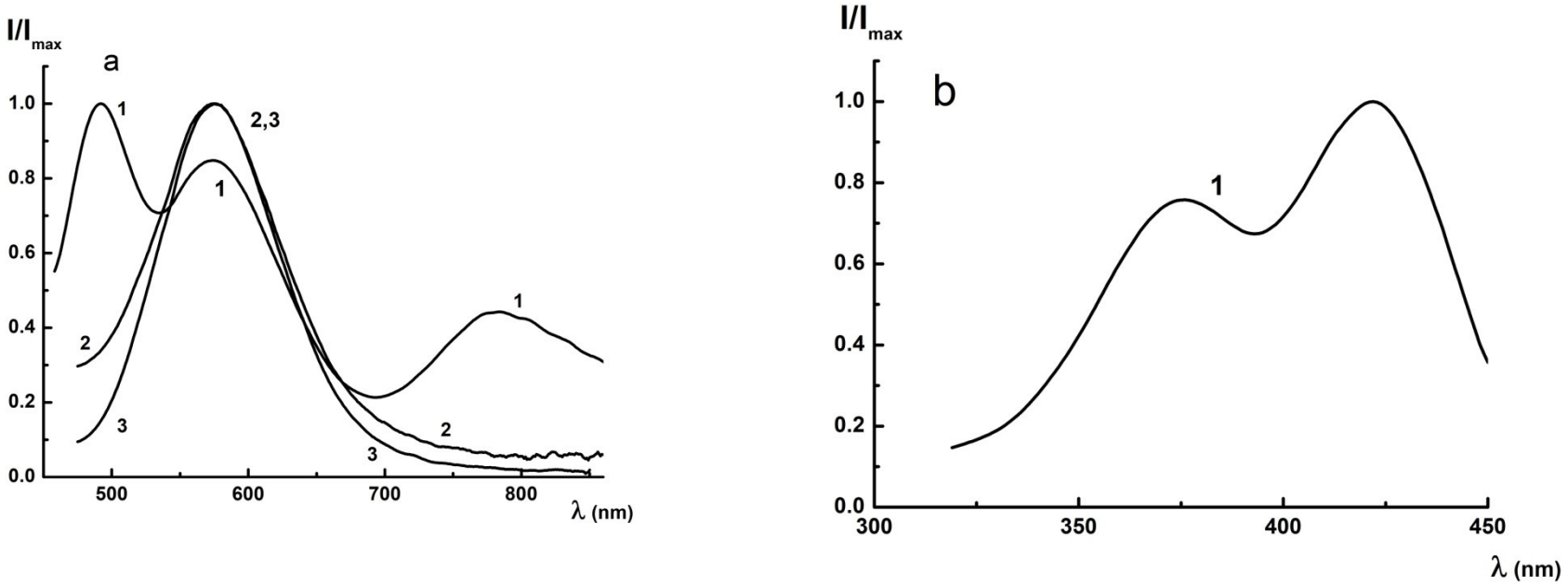
MgF_2



Normalized to their maximum values PL (a) and PLE (b) spectra for the following MgF_2 samples: non-annealed NCs (1), pre-annealed NCs (2) and polycrystalline plate (3). Excitation and registration wavelengths are 403 (a) and 500 (b) nm, respectively.

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Results

- The presence of the following types of the near-clusters color centers has been defined in LiF: F_{C1}, F_{C1}^{-}, F_{C2}^{+}, F_{C2}, F_{C2}^{-}, F_{C3}^{+} and F_{C3}.
- The same types of near-clusters color centers (except F_{C3}) were found in NaF nanocrystals.
- The photoluminescence and photoluminescence excitation spectra for near-clusters color centers which contain more than one anion vacancy differ from the corresponding spectra for the centers in the bulk (valid both for LiF and for NaF).
- In nanocrystals of MgF_2 the center has been found with optical characteristics that are absent in single crystals.

Thank you for attention!