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Effect of doping with Ce^{3+} ions on color centers in KY_3F_{10} crystal induced by x-ray radiation

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The results of investigations into the optical properties of color centers formed under X-ray irradiation in nominally pure KY_3F_{10} crystals and those doped with Ce^{3+} ions are presented. The types of color centers and their characteristic evolution time constants have been studied. The influence of Ce^{3+} ion doping on the evolution of color centers has been examined. A comparison of the parameters of color centers in the doped and nominally pure crystals is provided. X-ray induced color centers in the nominally pure crystal have been identified as F- and F_2-type centers, whereas in the doped crystal, — F-, F_2-, and F_A-type centers are observed. In KY_3F_{10} crystals doped with Ce^{3+} ions, the recombination times of free charge carriers associated with F-type color centers differ significantly from the recombination times of charges associated with these types of color centers in the nominally pure crystal. In the doped crystal (in comparison to the nominally pure one), the maxima of the absorption bands of the color centers are shifted towards the shorter wavelength region.

Keywords: KY_3F_{10}, Ce, color centers, types of color centers, optical transmission spectra, energy state diagram.

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Introduction

Currently, fluoride crystals, as materials for scintillators, play one of the primary roles due to their wide band gap extending into the short-wavelength region with a cutoff up to 100 nm. These crystals, doped with trivalent cerium ions, possess high light output owing to the allowed $5d \leftrightarrow 4f$-transitions of this dopant, as well as short (no more than tens of nanoseconds) luminescence. They are characterized by the typical localization of interconfigurational $4f \leftrightarrow 5d$-transitions of Ce^{3+} ions predominantly in the UV spectral region [1]. For this reason, these crystals have long been used as scintillators converting hard radiation into optical range radiation [2–4]. Moreover, recently, fluoride crystals doped with Ce^{3+} ions have been employed in lasers as UV active media [5].

Scintillator crystals are susceptible to coloration under the influence of hard radiation. This phenomenon has a dual significance: on one hand, the formation of color centers (CCs) in crystals degrades their light output in the UV spectral region the main one for scintillators; on the other hand, precisely due to the formation and accumulation of CCs, these crystals find applications in dosimetry, determined by the density of crystal coloration and/or thermoluminescence [6]. It should be noted that, in some cases, the CCs themselves in crystals are used as active media for IR lasers [7].

For all these reasons, knowledge of the mechanisms of formation and destruction of CCs in doped and nominally pure fluoride crystals under X-ray irradiation, as well as studying their optical properties, is highly relevant for their use as scintillators, dosimeters, or active media for UV and VUV lasers.

The choice of the KY_3F_{10} crystal with a simple cubic structure as the research object, to exclude problems related to spectrum property dependencies on light polarization in anisotropic crystals, allows simplifying the study of properties and analysis of CC behavior in nominally pure and doped crystals formed under X-ray irradiation.

Samples

The KYF crystal has a wide band gap (~ 10 eV [8]), its structure is cubic, space group $Fm\overline{3}m$ (O_h^5). When activated by rare earth ions, they predominantly occupy the yttrium site [9]. The KYF:Ce^{3+} crystal samples were grown by the vertical directed crystallization method in graphite crucibles under an overpressure of fluorinated argon atmosphere. All

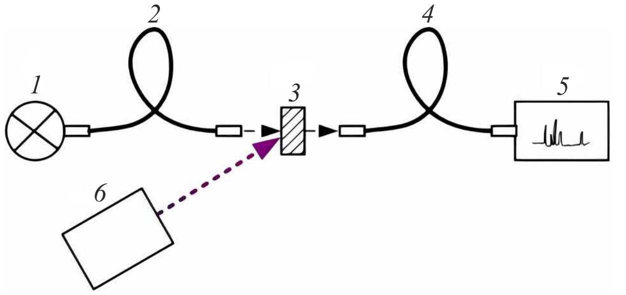

Figure 1. Experimental setup scheme: *1* — lamp, *2*, *4* — light guides, *3* — sample, *5* —spectrometer, *6* — X-ray source.

initial batch components had a purity of about 99.99 %. For doped crystal samples, CeF_3 compound was introduced into the batch at 1 at.%.

Disks 6 mm in diameter and 2 mm thick with polished flat-parallel surfaces were fabricated from the grown boules for optical research.

Experimental setup

The setup for studying CC relaxation in crystals at room temperature, induced by X-ray irradiation, was based on a StellarNet spectrometer capable of recording spectra in the 190–1100 nm range with 0.5 nm resolution. This was fully sufficient for recording absorption and luminescence spectra of CCs that have broad spectral bands. Additionally, this spectrometer could automatically register series of spectra at set time intervals. Exposure time per spectrum registration was 3 s. A schematic of the experimental setup is shown in Fig. 1.

In all experiments, an X-ray tube with a tungsten cathode ($I = 16$ mA, $U = 55$ kV) was used as the source of X-ray radiation.

X-ray Induced Color Centers and Their Evolution in the Nominally Pure KYF Crystal Sample

To induce CCs and subsequently study their evolution in KYF crystals, KYF crystal samples were exposed to continuous X-ray radiation from the tungsten cathode tube for 10 min, after which the irradiated area of the sample acquired a yellow color.

The sample was placed in the measuring system with minimal delay and measurement was started. The transmission spectrum registration process lasted 6 h. Spectra were automatically recorded by spectrometer *5* (Fig. 1) at set time intervals. The first spectrum in this series corresponded to a few seconds after exposure ended, and the last — several days after stopping irradiation of the samples.

Fig. 2 shows the result of recording a series of transmission spectra of the nominally pure KYF crystal sample (NPS) during the first 45 min after X-ray irradiation. The shape of the obtained spectra, their maximum positions by wavelength, and widths are characteristic of CCs in crystals. The fading yellow color of the irradiated sample area over time also supports this.

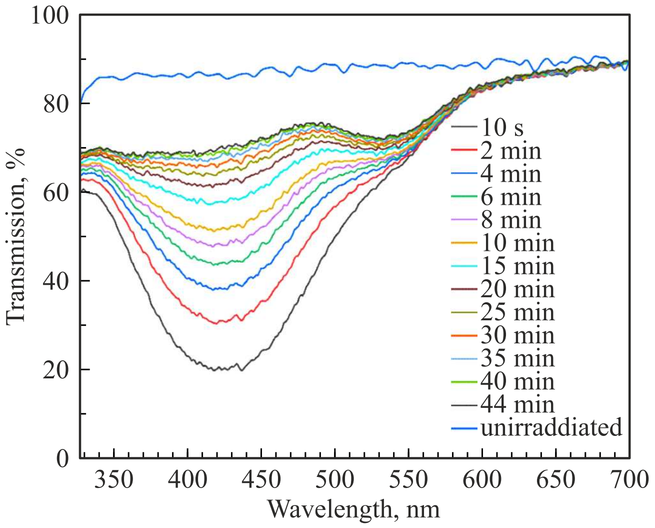

Figure 2. Series of transmission spectra of undoped KYF crystal recorded at different times after X-ray irradiation.

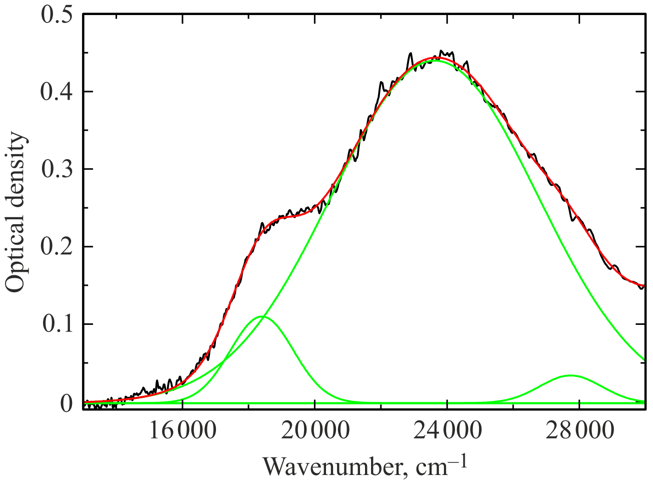

Figure 3. Result of decomposing the optical density spectrum of the NPS KYF crystal into three Gaussian contours.

From Fig. 2 it can be seen that transmission spectra of the NPS KYF crystal after X-ray irradiation consist of several overlapping spectral bands. The transmission spectra were converted into optical density spectra, and the wavelengths were converted into wavenumbers. Using a spectrum processing and analysis program, these spectra were mathematically decomposed into Gaussian contours. Fig. 3 presents the result of this mathematical decomposition corresponding to the transmission spectrum recorded 15 min after the X-ray exposure ended. The figure shows that the spectrum is well described by three

Table 1. Parameters of Gaussian contours

№	Area	Center, cm^{-1}	Width, cm^{-1}	Height, rel. units
1	268	18400	1914.3	0.11
2	3448	23620	6230.4	0.44
3	84	27740	1870.4	0.04

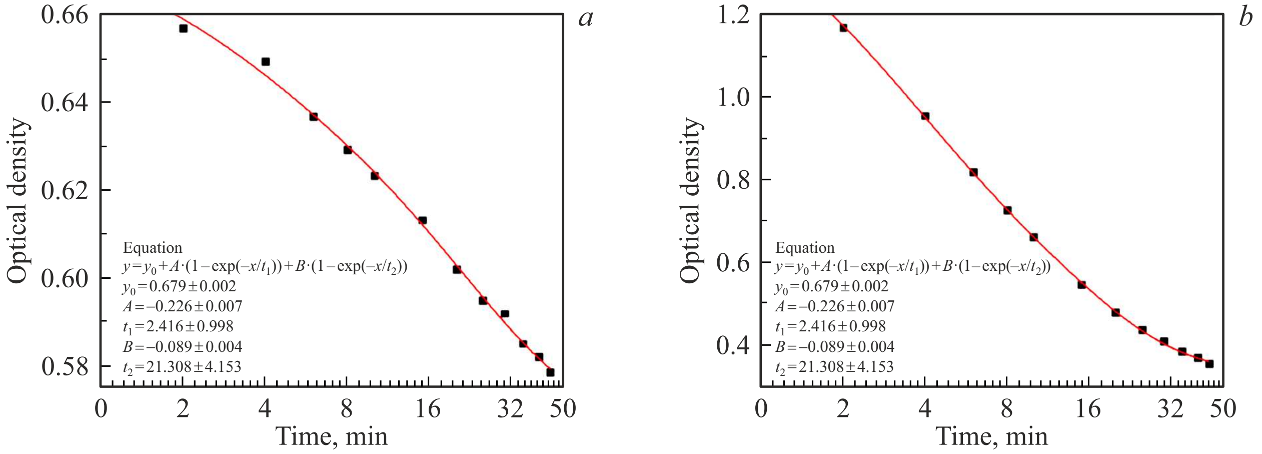

Figure 4. Dependences of optical density of the NPS KYF sample on time after X-ray irradiation (*a*) at the spectral band with the wavenumber 27740 cm^{-1}, (*b*) at the spectral band with the wavenumber 23620 cm^{-1}.

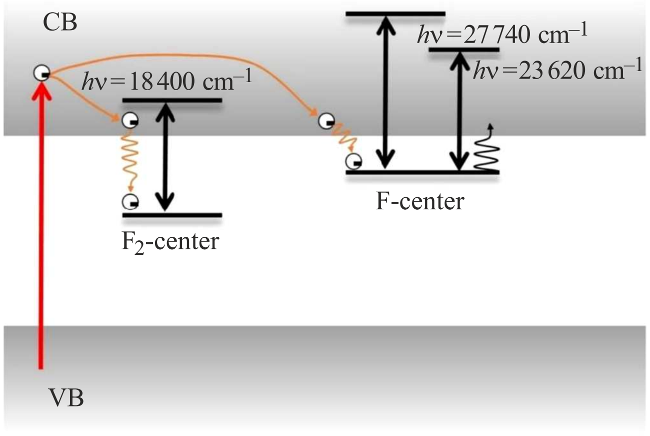

Figure 5. Energy state diagram of color centers in the undoped KYF crystal sample relative to fundamental bands (VB and CB), and transitions between them after X-ray irradiation.

Gaussian components with maxima at 18400, 23620, and 27740 cm^{-1} the parameters of which are listed in Table 1.

A close examination of the series of irradiated KYF crystal spectra shown in Fig. 2 reveals that the intensity of the spectral band with a maximum at 18400 cm^{-1} practically does not change over time and is present in all spectra, while the intensities of the bands with maxima at 23620 and 27740 cm^{-1} decrease over time.

For these bands, dependencies of optical densities at frequencies 23620 and 27740 cm^{-1}corresponding to the maxima, on time after irradiation were constructed, shown in Fig. 4. These dependencies were approximated by biexponential curves with characteristic times21 ± 4 and 2 ± 1 min for the band with the maximum at 27740 cm^{-1} and 13 ± 2 and 2.0 ± 0.5 min for the band with the maximum at 23620 cm^{-1}.

In Fig. 4, *a* the contribution from the exponent with the longer time (21 min) is several times greater than that from the exponent with the shorter time (2 min), while for the dependence in Fig. 4, *b* the contributions from the two exponents to the overall dependence also differ significantly: 13 and 2 min.

The appearance of additional bands in the absorption spectrum of the sample after X-ray irradiation is due to the formation of CCs in the crystal. Thus, based on the obtained results, one can conclude that several types of CCs are presumably formed in the NPS KYF crystal during its X-ray irradiation. The most intense band in the optical density spectrum with a maximum at 27740 cm^{-1} s due to the presence of the simplest electronic type of color centers the F-center. The spectrum of this center consists of a single broad bell-shaped band characteristic of F-type centers, and the maximum of this band closely coincides with the maxima of F-center bands in other crystals with similar structures [10]. The short-wavelength band with a maximum at 23620 cm^{-1} is interpreted as the K-band of a higher-lying excited state of F-centers, arising as a result of its excitation. The band that does not change over time, with a maximum at 18400 cm^{-1} most likely belongs to a more complex F_2-type electronic color center, which represents two closely located F-centers.

Based on the analysis of experimental data, a diagram in the form of a model of an open quantum system with ongoing processes in the nominally pure KYF crystal after X-ray irradiation was constructed, as shown in Fig. 5. The occurring processes can be explained as follows. As a result of the crystal sample absorbing X-ray quanta, an interband transition occurs: the valence band → conduction band (CB). The electron state in the CB is nonequilibrium. Due to electron movement (diffusion) in the CB, electrons can be captured by localized defect states of the crystal forming color centers of two types F-centers with absorption bands at 23620 and 27740 cm^{-1} and F_2-centers with an absorption band at 18400 cm^{-1}. Depending on the position of the ground state relative to the crystal bands, these color centers can be stable or unstable at room temperature. Since the absorption band with a maximum at 18400 cm^{-1} interpreted as the absorption band of F_2-centers, does not change intensity over time, while the F-center bands with maxima at 23620 and 27740 cm^{-1} have limited lifetimes, it can be concluded that the ground state of the F_2-centers lies deeper in the band gap than the ground state of the F-centers.

Thus, as a result of X-ray irradiation, two types of color centers are formed in the nominally pure KYF crystal presumably F- and F_2-centers. Moreover, judging by the longer lifetime of the F_2-centers at room temperature compared to the F-centers, it can be concluded that their ground state lies deeper within the band gap than that of the F-centers.

Formation of Color Centers under X-ray Irradiation in KYF Crystal Doped with Ce^{3+} Ions and their Evolution

Similar procedures applied to the nominally pure sample were performed with the KYF crystal doped with Ce^{3+} ions. A series of transmission spectra of the KYF:Ce^{3+} crystal after X-ray irradiation was obtained and recorded at specific time intervals after irradiation. These spectra are shown in Fig. 6.

Fig. 6 shows that the transmission of the KYF:Ce crystal sample after X-ray irradiation consists of several overlapping bands. It is also evident that the intensities of some of these bands decrease over time. The transmission spectra were converted to optical density spectra as a function of wavenumber and then mathematically decomposed into Gaussian contours. Fig. 7 shows an example of this decomposition. The spectra are well described by four Gaussian contours with maxima at wavenumbers 17600, 18400, 23580 and 27300 cm^{-1}. The parameters of these contours are given in Table 2.

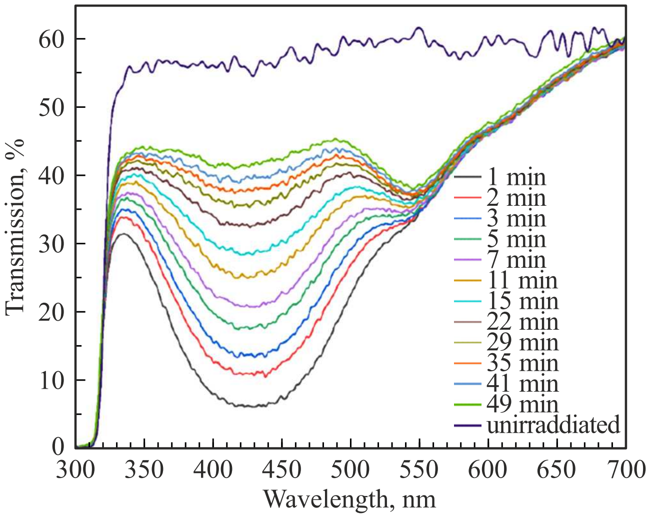

Figure 6. Transmission spectra of the KYF:Ce^{3+} crystal recorded at different times after X-ray irradiation.

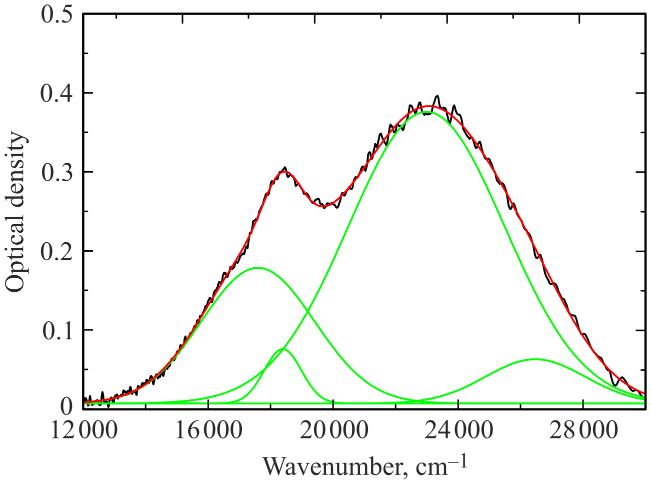

Figure 7. Result of decomposition of the optical density spectrum of the KYF:Ce^{3+} crystal sample into four Gaussian components.

From Fig. 7 it can be seen that the bands with maxima at 17600 and 18400 cm^{-1} practically do not change intensity over time, while the intensities of bands with maxima at 23580 and 27300 cm^{-1} decrease. For these decaying bands, dependencies of optical densities at wavenumbers 23580 and 27300 cm^{-1} on time after irradiation were constructed (Fig. 8). Each of these dependencies was approximated by biexponential curves with characteristic times 14 ± 2, 1.5 ± 0.5 min for the band with maximum at 23580 cm^{-1} and 15 ± 2, 1.5 ± 0.5 min for the band with maximum at 27300 cm^{-1}.

The bands with maxima at 18400, 23580, and 27300 cm^{-1} in the KYF:Ce^{3+} crystal coincide with bands observed after X-ray irradiation in the nominally pure crystal. This means that the same color centers form in

Table 2. Parameters of Gaussian contours of the color center spectrum in the KYF:Ce^{3+} crystal sample after X-ray irradiation

№	Area	Center, cm^{-1}	Width, cm^{-1}	Height, rel. units
1	778	17600	3618.1	0.17
2	103	18400	1194.4	0.07
3	2316	23580	5006.9	0.37
4	224	27300	3185.2	0.06

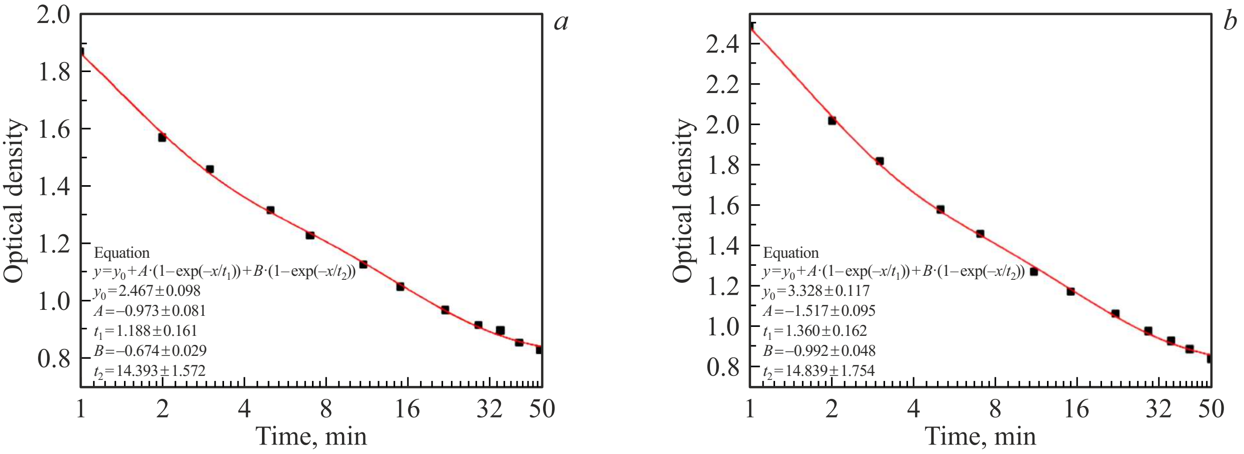

Figure 8. Dependencies of optical density of the KYF:Ce^{3+} crystal on time after X-ray irradiation: (*a*) at the spectral band with wavenumber 27300 cm^{-1}, (*b*) at the spectral band with wavenumber 23580 cm^{-1}.

the KYF crystal doped with Ce^{3+} ions as in the pure KYF. However, the spectrum of the Ce^{3+} ion doped crystal contains a band absent in the pure crystal spectrum. The maximum of this band is at frequency 17600 cm^{-1} (Fig. 7). This band is presumably attributed to impurity-related electronic color centers localized in the crystal lattice near the dopant Ce^{3+} ion. Supporting evidence is that this color center appears only upon doping. The lifetimes of the F-centers were shorter than in the nominally pure KYF crystal, suggesting that the Ce^{3+} impurity ions accelerate the recombination process of free charge carriers.

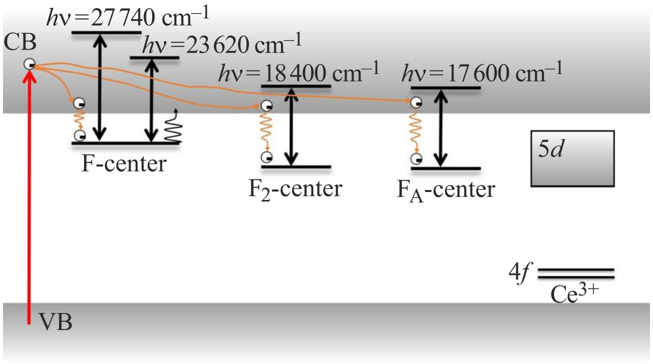

Figure 9. Energy state diagram of color centers in the KYF:Ce^{3+} crystal sample relative to fundamental bands and transitions between them formed after X-ray irradiation.

Based on the analysis of experimental data, a diagram was created presenting a model of the processes occurring in the doped KYF:Ce^{3+} crystal after X-ray irradiation, shown in Fig. 9. Upon absorption of X-ray quanta, an interband transition takes place inside the KYF:Ce^{3+} crystal, causing electrons to move from the valence band to the conduction band of the crystal. From the conduction band, electrons can be captured by local defects in the KYF:Ce^{3+} crystal lattice, forming three types of color centers: F-centers with absorption bands at 23620 and 27740 cm^{-1}, F_2-centers with an absorption band at 18400 cm^{-1} and F_A-centers with an absorption band at 17600 cm^{-1}. The absorption band with a maximum at 17600 cm^{-1} interpreted as the absorption band of F_A-centers, does not change intensity over time, whereas the F-center bands with maxima at 23580 and 27300 cm^{-1} have limited lifetimes. From this, it can be concluded that the ground state of F_A-centers in the KYF:Ce^{3+} crystal lies deeper within the band gap than the ground state of the F-centers.

Thus, under X-ray irradiation, three types of color centers are formed in the crystal: F-, F_2- and F_A-centers. In the case of UV irradiation of the KYF:Ce^{3+} crystal [11] the same types of centers are formed.

Conclusion

This work identified the types and parameters of color center evolution in nominally pure KYF crystal and in the KYF crystal sample doped with Ce^{3+} ions.

Thus, upon X-ray irradiation, nominally pure KYF crystal forms two types of color centers — presumably F- and F_2-centers. The most intense absorption band is observed at the maximum with wavenumber 23620 cm^{-1}. The absorption bands with maxima at wavenumbers 23620 and 27740 cm^{-1} are assigned to F-type color centers. The absorption band with a maximum at 18400 cm^{-1} is assigned to F_2 type color centers.

Upon X-ray irradiation of the doped KYF:Ce^{3+} crystal sample, three types of color centers are formed: along with F-centers (23580 and 27300 cm^{-1}) and F_2-centers (18400 cm^{-1}), which were found in the nominally pure crystal, impurity centers — presumably — F_A-type with a maximum near 17600 cm^{-1} — also appear in the doped crystal. There is consistency in the types of color centers in the studied sample with those in other fluoride crystals of similar crystal structure [12,13]. It is demonstrated that under UV irradiation of the KYF:Ce^{3+} crystal [11], the same types of centers form as under X-ray irradiation, i.e., these color centers have the same nature. The Ce^{3+} ions act as „triggers" for the formation of color centers in the crystal via a two-step excitation mechanism.

The research results revealed that F_2- and F_A-centers are more stable at room temperature, from which it is concluded that their ground states lie deeper within the forbidden band than the ground state of the F-centers.

Finally, in the KYF crystal, doping with Ce^{3+} ions facilitates the acceleration of the recombination process of free charge carriers of the F-type color centers corresponding to the band at 23580–23620 cm^{-1}, which manifests as a reduction in lifetime from 21 to 14 minutes. In the case of the shorter-wavelength K-band, a slight increase from 13 to 15 minutes is observed, which may indicate charge transfer. Doping also affects the shift of the maxima of these bands toward the shorter wavelength region.

Moreover, alongside the formation of F-type centers in the crystal doped with Ce^{3+}, ions, stable color centers — impurity F_A-type centers associated with the presence of the dopant — are formed.

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Conflict of interest

The authors declare that they have no conflict of interest.

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