Radiation Defects in CaF$_2$–CaO Crystals

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The spectral and kinetic parameters of electron-pulse-initiated transient absorption of oxygen-doped CaF$_2$ crystals were studied using pulsed spectrometry with a nanosecond time resolution. It is shown that the formation of a M$_A^+$ color centers in CaF$_2$–0.01 M%CaO crystals occurs by thermally activated diffusion of the vacancies. Activation energy of M$_A^+$ color centers formation process of 0.4 eV is established.

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1. Introduction

The study of radiation stimulated processes of defects formation and accumulation in doped CaF$_2$ crystals is of high urgency due to their prospective application as active media for optical quantum generators, materials for optical memory, thermo-luminescence dosimetry and solid-state electric batteries. Nominally pure CaF$_2$ crystals have a high transparency in a wide spectral range and are prospective as constructional optical material for transfer of high power UV and VUV-radiation fluxes (beams) from sources of coherent and incoherent type [1].

The presence of “biographic” [2] impurity of oxygen in fluorite crystals shifts the transparency cutoff into the long-wave region of a spectrum and leads to occurrence of selective absorption bands at 150 nm and 180–200 nm in vacuum ultraviolet region of the spectrum. Presence of oxygen impurity causes well investigated absorption bands of the F$_A$ color centers in visible region of the spectrum in case of low-temperature irradiation (below 80 K). At subsequent heating of the crystals up to room temperature, the F$_A$ centers participate in formation of complex electronic centers such as M$_A^+$ by reaction:

$$F_A + V_A^+ \rightarrow M_A^+$$  \hspace{1cm} (1)

M$_A^+$ center represents a complex bivalent impurity anion–two anion vacancies where an electron is located. However, the mechanism of anion vacancy ($V_A^+$) formation has been investigated insufficiently. Clarification of this question is the subject of the present paper.

The purpose of the work is a study of spectral and kinetic characteristics of optical absorption induced by an accelerated electrons pulse in oxygen-doped CaF$_2$ crystals by a method of pulse spectroscopy with nanosecond resolution. The objects of study are crystals grown by the Stockbarger method. The pulsed measurement method is similar to that in Ref. [3]. However, in present experiments a more advanced accelerator design was used, which incorporated strict requirements on stabilization of the parameters of the supply circuit and control of the capacitor bank (a thermally stabilized comparator).

An electron accelerator used as a source ionizing irradiation has the following parameters: maximal energy of electrons is 0.28 MeV, time resolution is 7 ns, pulse width at half-height is 12 ns, and density of energy in the pulse is 0.1 J cm$^{-2}$. Measurements are carried out in temperature range of 80–500 K. The extrapolated electron range in the CaF$_2$ is 0.26 mm. Dosimetry was carried out using a calorimetric method. To measure a full absorption spectrum in photoelectric registration mode, the re-iterative irradiation of the sample is necessary. To eliminate the influence of dose loading on the shape of the spectrum of the transient absorption of boiling of liquid nitrogen the sample was bleached by unfiltered light from a mercury high-pressure lamp.

When measuring the spectra at room temperature the samples were annealed at a fixed temperature with adjustable heating and cooling rates. Small values of optical density (below 0.1) were measured by directing the probe light at an angle of 7° to the irradiated surface of the crystal. Control was provided by measurements on parallel cleaves of fresh samples. The samples were thermostatically controlled during irradiation.

2. Low-temperature irradiation

Figure 1 shows the optical absorption spectra of CaF$_2$–0.01 M%CaO crystal, measured at 80 K in 10 ns and 1 ms after the end of an accelerated electron pulse. Centers responsible for induced absorption have different thermal stability. Relaxation of unstable absorption in the dominant bands at $\approx 2.76$ and 4.1 eV is well described by exponential dependence with a time constant of 40 $\mu$s

$$D(t) = D_0 \exp(-t/\tau).$$  \hspace{1cm} (2)

The spectral and kinetic characteristics of unstable absorption (the characteristic lifetime of defects at fixed
temperature, the spectral positions of maxima in the dominant absorption) are close to the well-known parameters of self-trapped excitons (STE) [4], which usually comprise pairs of closely spaced F and H centers.

The electronic excitations effectively interact with defects of the lattice caused by the introduction of an oxygen impurity in CaF$_2$ crystals. Presence of the additional channel of relaxation for electronic excitations results in a reduction of STE creation efficiency in doped crystals in comparison with pure CaF$_2$. Quantitative estimates are made from the amplitude values of optical density measured at the moment of the pulse end at the maximum (2.76 eV) of electronic component of STE absorption [4]. The stable absorption was not taken into account.

With increase of the time after the end of irradiation there is a change of the induced absorption spectrum structure (Fig. 1, curve 2). As follows from the results given, for time 1 ms after the end of irradiation pulse one can define bands at 2.64 eV and 3.87 eV in the spectrum due to creation of the F centers perturbed by oxygen impurity (F$_2$). Spectral position and the half-width (0.94 eV) of absorption band at 3.9 eV (Fig. 1, curve 2) is close to known characteristics of V$_k$ color centers (optical σ-transition $^{2}\Sigma_g^{+}\rightarrow^{2}\Sigma_i^{+}$) in CaF$_2$ crystals [5].

F$_A$ and V$_k$ color centers formation occurs noninertially after electrons ($e^-$) localization at $(O^{2-}-V_a^+$) dipoles and holes ($p^+$) self-trapping in anion sublattice, respectively:

$$e^- + (O^{2-}-V_a^+) \rightarrow F_A \quad p^+ \rightarrow V_k.$$  

(3)

The centers at 80 K are thermally stable, but they can be efficiently destroyed under the action of unfiltered light of a mercury lamp. The nature of the centers responsible for absorption band with the maximum at 4.6 eV (Fig. 1, curve 2) is unknown. However, absorption in the given spectral region is observed at irradiation of pure CaF$_2$ crystals as in spectra of stable absorption at the low-temperature coloration (4 K) [5], as in short-lived absorption spectra at the high-temperature (500 K) irradiation [6]. It is possible to conclude that the defects responsible for absorption at 4.6 eV are formed in the lattice undisturbed by an impurity. We assume that in CaF$_2$–0.01 M%CaO crystals absorption in higher energy range than absorption of V$_k$ and H color centers (3.87 eV and 4.03 eV, respectively [5]) is caused by formation of hole defects with a complex structure (such as X$_3$ or di–H centers).

3. High-temperature irradiation

The spectra of optical absorption of CaF$_2$–0.01 M%CaO crystal, measured at room temperature with various delays after the end of irradiation pulse are presented in Fig. 2. A relaxation of unstable absorption is well fitted by exponential dependence with a time constant of 1 µs. The lifetime of STE at room temperature is about 1 µs [6]. Comparison of the data presented in Fig. 1 (curve 2) and in Fig. 2 (curve 2) shows that the spectra of optical absorption induced by an electron pulse at various (80 K and 295 K, respectively) temperatures of irradiation are qualitatively similar. The obtained experimental data allow to make a conclusion that for time 4 µs after the electron pulse end at room temperature (Fig. 2, curve 2) absorption of the V$_k$ and F$_A$ color centers dominates.

Figure 2 presents the absorption spectrum (curve 4) obtained by subtraction of the curve 3 from the curve 2. As follows from the data shown in Fig. 2, in the time interval (4 µs–1 s) there is a destruction of the V$_k$ centers and centers giving rise to band with maximum at 3.1 eV. The nature of the centers responsible for absorption band with the maximum at 3.1 eV (Fig. 3, curve 4) is unknown. Since in the given interval of times only destruction of V$_k$ centers and centers absorbing at 3.1 eV takes place, it is possible to draw a conclusion that the type and concentration of F$_A$ centers in this interval of times remain constant. According to the literature [7], absorption band at 3.1 eV is caused by F centers perturbed by some defect, namely V$_k$ center, i.e., F and V$_k$ centers are formed at
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a neighbourhood. Recombination of an electron from F center with a trapped hole is accompanied by excitation of STE or oxygen ions emission and formation of free anion vacancies.

![Image](https://example.com/image1.png)

Fig. 3. Optical absorption spectra for the CaF$_2$–0.01 M%CaO crystal, measured 1 s (1) and 6 s (2) after the end of electrons pulse, at 295 K.

![Image](https://example.com/image2.png)

Fig. 4. The kinetic curve of increase of M$^+_A$ in CaF$_2$–0.01 M%CaO crystal. Measurements are performed at a fixed wavelength of 520 nm at 352 K. The lines represent a best fit of exponentials.

Appearance of free anion vacancies in CaF$_2$–0.01 M%CaO crystal is a consequence of non-local compensation of an excess charge of oxygen impurity. The spectra of optical absorption of CaF$_2$–0.01 M%CaO crystal, measured at room temperature in the second range are presented in Fig. 3. With increase of time up to 6 s the originally induced spectrum of optical absorption (Fig. 3, curve 1) is transformed in so-called “spectrum Mollvo” (curve 2) which is caused by created M$^+_A$ color centers. It has been established, that kinetic curves of increase of M$^+_A$ optical absorption are well described by the first order reaction (Fig. 4):

$$D(t) = D_0 + D_\infty [1 - \exp(-t/\tau)],$$  \hspace{1cm} (4)

where $D_0$ — optical density caused by capture of electrons on dipoles ($O^2-\rightarrow V^+_A$), $\tau$ — lifetime of anion vacancies in relation to thermally activated recombination with the F$A$ centers.

Measurements are performed at a fixed wavelength of 520 nm. The temperature dependence of characteristic times of M$^+_A$ formation in CaF$_2$–0.01 M%CaO crystal is presented in Fig. 5. In the Arrhenius coordinates this dependence looks like a straight line with the activation energy of the process $E_a = 0.4$ eV which coincides with activation energy for an anion vacancy migration [8]. The obtained experimental data allow to make a conclusion that the accumulation of M$^+_A$ in CaF$_2$–0.01 M%CaO crystal occurs at the thermally activated diffusion of anion vacancies. On the basis of the experimental data submitted above it is possible to draw the following conclusions.

![Image](https://example.com/image3.png)

Fig. 5. Temperature dependence of the characteristic times of the formation of the M$^+_A$ color centers in CaF$_2$–0.01 M%CaO crystal.

In CaF$_2$–0.01 M%CaO crystal under pulsed electron irradiation STE and color centers such as F$A$ and V$_k$ are formed noninertially. It is assumed that formation of free vacancies is a result of interactions of mobile V$_k$ centers with the F-like centers. Activation energy of inertial process of M$^+_A$ centers accumulation (0.4 eV) is close to activation energy of anion vacancies migration.

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References


