

Mechanisms of nonlinear absorption of UV laser radiation in CaF₂

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Abstract. A numerical model is proposed for the interaction of ionising and UV laser radiation with CaF₂ crystals. It is shown that the appearance of short-lived electronic excitations in the crystal has a strong effect on the nonlinear absorption of laser radiation for pulse durations exceeding 30 ps. The consequences of this absorption for the crystal structure are analysed.

Keywords: fluorite, UV laser radiation, nonlinear absorption, colour centres.

1. Introduction

An analysis of the behaviour of alkaline-earth fluoride crystals (MgF₂, CaF₂, BaF₂) irradiated by UV and VUV lasers is very important for understanding the prospects of developing excimer lasers. The windows of these lasers, especially with an electron-beam excitation, as well as other optical elements in the path of the beam, lose their transparency and suffer optical degradation when exposed to ionising and laser radiation. One of the main reasons behind this is the production of colour centres in the crystals. These centres are formed during the relaxation of electronic excitations produced by ionising radiation or due to nonlinear absorption of laser radiation [1–5]. The two-photon absorption thresholds in MgF₂, CaF₂, BaF₂ are 5.5, 5.0 and 4.5 eV respectively. However, the absence of other suitable materials necessitates the use of these crystals for preparing transmission optical elements both for UV and VUV ranges, especially for lithographic systems based on a 157-nm F₂ laser [6–9]. Thus, it is very important to study the problem of the efficiency of these wide-band optical materials exposed to laser radiation at wavelengths shorter than 250 nm.

The diversity of experimental results on this subject requires a theoretical generalisation. One of the approaches in this direction is the development of numerical models for describing the kinetics of interaction of laser radiation with crystals, which is important for revealing the most general regularities in the behaviour of the crystal–radiation open system.

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Systems of kinetic equations describing the interaction of UV laser radiation with alkaline-earth fluorides were proposed in Refs [10, 11], in which the model of interaction of KrF-laser radiation with defects of the MgF₂ structure was considered in greater detail. This paper aims at demonstrating the potentialities of the approach being developed by considering the behaviour of CaF₂ crystals irradiated by ionising and 248-nm UV laser pulses of duration $\sim 10 - 100$ ns. The results presented here reveal, in particular, the mechanisms of nonlinear absorption of radiation in fluorite and indicate the consequences of this absorption for the crystal itself.

2. Model of defect-formation kinetics in fluorite

The exposure of the electronic subsystem of fluorite crystals to radiation leads to the perturbation of their anion sublattice. The relaxation of free electrons and holes produced under the action of ionising radiation results in the appearance of autolocalised excitons, which decay by producing two pairs of Frenkel anion defects. These processes are reflected in the ionisation-induced absorption spectra [12–15]. Fig. 1 shows such a spectrum taken from Ref. [15]. This spectrum has a complex structure due to the superposition of absorptions from all the electronic states of the crystal over which recombination takes place.

If the crystal is simultaneously exposed to laser radiation along with the ionising radiation, the recombination processes will be modified. The case when laser radiation falls into the absorption band of F centres is studied in detail in Ref. [11]. In CaF₂, this band lies at 450 nm (2.75 eV, see Fig. 1). This band is a result of superposition of the

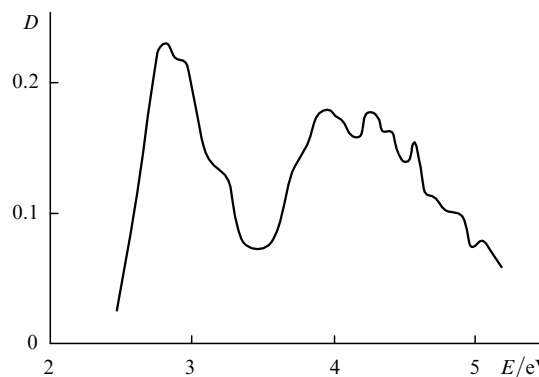


Figure 1. Optical density of CaF₂ ($T = 295$ K) 10 ns after irradiation by a 0.28-MeV pulsed electron beam of duration 12 ns [15].

absorption by F centres and the electron component of the absorption of self-trapped excitons in the S₁ singlet or S₃ triplet state [11]. The absorption of a photon with energy 5 eV by these quasiparticles leads to their ionisation. The absorption cross sections at 248 nm are almost identical and rather small for these transitions.

The 4-eV UV absorption band of CaF₂ (Fig. 1) is also determined by several components, related to the V_k and H centres and to the hole component of self-trapped excitons [1–3, 10–15]. Absorption in all these complexes occurs at the intramolecular transition of quasimolecules F₂⁻ having different distances between the nuclei and their surroundings. The absorption leads to the disintegration of quasimolecules.

As in Ref. [11], the dynamics of the processes occurring in fluorite under simultaneous exposure to ionising and UV laser radiation can be described with the help of a system of kinetic equations for the population of the crystal states under consideration, which are treated as quasiparticles. In the case under study, the system contains the equations for the following states: free electrons (*n*) and holes (*p*), autolocalised holes (V_k centres), highly excited excitons (S*), self-trapped exciton pairs in the ground S₁ singlet and S₃ triplet states, bound interstitial fluorine atom (H centre), and free fluorine atom (H*), F centres in highly excited (F*) and the ground (F) states, anion vacancy (α centre) and interstitial fluorine ion (I centre).

The anion sublattices of CaF₂ and MgF₂ are similar. Therefore, the recombination processes in them are also identical and can be described in the same way as in the model for MgF₂ [11]. The main difference in this case is in the phototransformations of the absorbing centres. An analysis of the possible versions of the description of these processes within the framework of the chosen model led to the following system of kinetic equations (System No. 1) for the components under consideration.

The main difficulty in this case is to determine the effect of photodissociation of the hole component on the self-trapped exciton. If the laws of conservation of charge, number of atoms and lattice sites observed in the crystal are taken into account, this reaction may lead to the formation of a pair of F and H centres, a return to one of the ground states of self-trapped excitons, or to a recombination of the lattice to the ground state. Calculations based on the model proposed in this work show that the second of these versions is realised. In the system of equations, this return to the ground state of the self-trapped exciton after absorption of a photon is described by a transition from the S₁ state to the S₃ state, and vice versa. In all other respects, the situation is identical to that for MgF₂ [11].

System No. 1.

1.
$$\frac{dn}{dt} = W_1 + (K_{811}F^* + K_{911}F)I + [(\sigma_{41} + \sigma_{42})S^* + \sigma_{51}S_1 + \sigma_{61}S_3 + \sigma_8F^* + \sigma_9F]J - (K_{13}V_k + K_{17}H + K_{110}\alpha)n.$$
2.
$$\frac{dp}{dt} = W_1 + (\sigma_3V_k + \sigma_{42}S^* + \sigma_{10}\alpha)J - \frac{p}{\tau_2}.$$
3.
$$\frac{dV_k}{dt} = \frac{p}{\tau_2} + (\sigma_{41}S^* + \sigma_{51}S_1 + \sigma_{61}S_3)J - \left(\frac{1}{\tau_3} + K_{13}n + \sigma_3J\right)V_k.$$

4.
$$\frac{dS^*}{dt} = \beta J^2 + K_{13}nV_k - \left[\frac{1}{\tau_4} + \frac{1}{\tau_3} + K_4n + (\sigma_{41} + \sigma_{42})J\right]S^*.$$

5.
$$\frac{dS_1}{dt} = \frac{X_{45}S^*}{\tau_4} + \sigma_{62}S_3J - \left(\frac{1}{\tau_5} + \frac{1}{\tau_3} + K_5n + \sigma_{51}J + \sigma_{52}J\right)S_1 - K_{56}(S_1 - S_3)n.$$

6.
$$\frac{dS_3}{dt} = \frac{X_{46}S^*}{\tau_4} + \sigma_{52}S_1J - \left(\frac{1}{\tau_6} + \frac{1}{\tau_3} + K_6n + \sigma_{61}J + \sigma_{62}J\right)S_3 - K_{65}(S_3 - S_1)n.$$

7.
$$\frac{dH}{dt} = \frac{V_k}{\tau_3} + \frac{S^*}{\tau_3} + \frac{S_1}{\tau_3} + \frac{S_3}{\tau_3} + \frac{H^*}{\tau_{12}} - (K_{17}n + K_{78}F^* + K_{79}F + \sigma_7J)H.$$

8.
$$\frac{dF^*}{dt} = \frac{S^*}{\tau_3} + K_{110}\alpha n + (\sigma_{10}\alpha)J - \left(\frac{1}{\tau_8} + K_{89}n + K_{78}H + K_{811}I + \sigma_8J\right)F^*.$$

9.
$$\frac{dF}{dt} = \frac{S_1}{\tau_3} + \frac{S_3}{\tau_3} + \left(\frac{1}{\tau_8} + K_{89}n\right)F^* - (K_{79}H + K_{911}I + \sigma_9J)F.$$

10.
$$\frac{d\alpha}{dt} = \frac{V_k}{\tau_3} + (\sigma_8F^* + \sigma_9F)J - (K_{110}n + K_{1011}I + \sigma_{10}J)\alpha.$$

11.
$$\frac{dI}{dt} = K_{17}nH - (K_{811}F^* + K_{911}F + K_{1011}\alpha)I.$$

12.
$$\frac{dH^*}{dt} = \sigma_7HJ - \frac{H^*}{\tau_{12}}.$$

13.
$$n + F^* + F = p + V_k + H + H^*.$$

14.
$$H + I + H^* = F^* + F + \alpha.$$

The last two equations are a consequence of the requirement of the conservation of charge and the number of atoms in the lattice. The following notation has been used in System No. 1: W_1 is the rate of formation of electron–hole pairs under the action of an external ioniser; βJ^2 is the rate of formation of excitons due to two-photon absorption; β is the two-photon absorption coefficient; J is the intensity of laser radiation in units of photon $\text{cm}^{-2} \text{s}^{-1}$; σ_i is the absorption cross section of the *i*th component; σ_{i1} and σ_{i2} are the absorption cross sections for the electron (1) and hole (2) components of excitons at the laser radiation wavelength; K_{ij} are the rate constants of the reactions between the components *i* and *j* (the number of a component coincides with the number of its kinetic equation in the above system of equations); τ_i is the relaxation time; τ_{ij} is the relaxation time of *i*th component to the *j*th one; and X_{ij} are the yields of the corresponding reactions. Recall that the laser radiation has a wavelength of 248 nm and a photon energy $h\nu = 5$ eV.

In this case, the specific absorption of the sample is:

$$K = \beta J + \sigma_3 V_k (\sigma_{41} + \sigma_{42}) S^* + (\sigma_{51} + \sigma_{52}) S_1 + (\sigma_{61} + \sigma_{62}) S_3 + \sigma_7 H + \sigma_8 F + \sigma_9 F + \sigma_{10} \alpha. \quad (1)$$

We neglect the absorption by free carriers (n , p , H^*) as well as the absorption by I centres because it is weak in the UV spectral range. The optical density D was calculated as the integral over the sample thickness l :

$$D = \int_0^l K dl. \quad (2)$$

These relations were used for a final adjustment of the model.

3. Results of numerical experiments

The model was adjusted by simulating experiments with CaF_2 in which the absorption induced by an electron beam was measured [12–16]. Since the concept of the model is only at the initial stage of its formation, several details have been omitted for the time being. The rate constants of the reactions are rounded off, their temperature dependences are neglected, the fine structure of the absorption spectra is also neglected, and the initial concentrations of the components are assumed to be equal to zero. For these reasons, the model is applicable at present for a time interval of ~ 100 ns and for sample temperatures around 300 K. This narrows the range of experimental results that are suitable for adjustment of the model. The results obtained in Refs [13–16] were taken as the starting point.

Pure fluorite samples were irradiated in Refs [13, 14] by short 12-ns 0.28-MeV electron beam pulses at room temperature, and the time evolution of the absorption spectra was studied, in particular, in the region of 5 eV. For the electron-beam energy density $E = 0.1 \text{ J cm}^{-2}$, the induced optical density in the samples at 248 nm was about 0.1.

Fig. 2 shows the model time dependences of the optical density D and the contributions of the main absorbing components to it calculated under the conditions of our experiments. The contributions of the remaining complexes to the absorption under these conditions did not exceed 0.001. The distribution W_1 (in $\text{cm}^{-1} \text{ s}^{-1}$) over the sample thickness was written in the form

$$W_1 = \left(\frac{80E}{3E_g T} \right) \exp(-80x), \quad (3)$$

where E is taken in J cm^{-2} ; $E_g = 1.7 \times 10^{-18} \text{ J}$ is the band gap in fluorite; T is the duration of the electron beam pulse; and x is in centimeters. This expression correctly reflects the experimental dependence of the absorbed dose over the sample thickness for 280-keV electrons [17]. It follows from Fig. 2 that the absorption kinetics in a CaF_2 sample for $t > 100$ ns will be determined entirely by the kinetics of triplet self-trapped excitons.

The results of measurements of the KrF_2 laser radiation absorption induced by an electron beam, in particular in CaF_2 , are presented in Ref. [16]. A probe laser pulse was delayed relative to the electron beam pulse by about 20 ns, as shown in Fig. 3. The shape of the laser radiation pulse

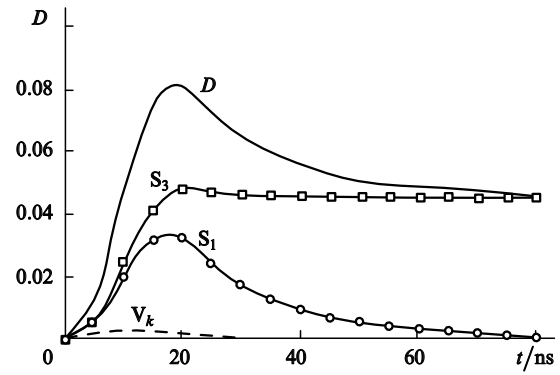


Figure 2. Calculated time dependences of the optical density D at 248 nm in CaF_2 under experimental conditions described in Ref. [15], and the contributions to D from V_k centres and self-trapped excitons in singlet (S_1) and triplet (S_3) states.

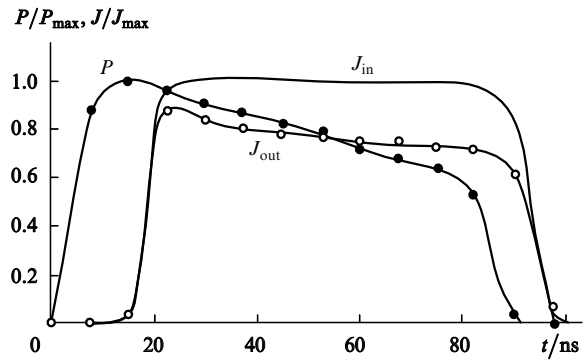


Figure 3. Shapes of the electron beam pulse P and the laser radiation pulse incident (J_{in}) on a CaF_2 sample irradiated by an electron beam, as well as the laser radiation pulse (J_{out}) transmitted through the sample.

was close to rectangular for a pulse duration of 80 ns, while its intensity was of about 3 MW cm^{-2} .

As in Refs [13, 14], the electron-beam energy was about 280 keV, so that the distribution of the quantity W_1 over the sample thickness was described in the model by formula (3). Fig. 4 shows the calculated time dependence of the concentration of the components under consideration in the surface layer of the fluorite sample for the electron-beam energy density of 0.4 J cm^{-2} . The specific power of the absorbed dose in this case was 400 MW cm^{-3} .

The shape of the laser radiation pulse passing through the sample is shown in Fig. 3. It is close to the shape of the experimental pulse [16]. Note the characteristic drop in the radiation intensity at the end of the pulse, indicating an increase in the absorption in the course of the pulse duration. This is a very important aspect that determines to a considerable extent the final structure of the equations in the model. In this case, the increase in the absorption is due to an increase in the concentration of long-lived H centres whose yield is determined by the constant τ_3 .

The increase in the absorption can also be explained by the production of long-lived H centres upon the photodissociation of self-trapped excitons, which, however, could not exceed 1%. If higher yields of long-lived H centres were assumed in this photoprocess, it would lead to a strong deformation of the shape of the output pulse for high intensities, which was not observed in real experiments. The results obtained in Ref. [4] also indicate that no absorbing

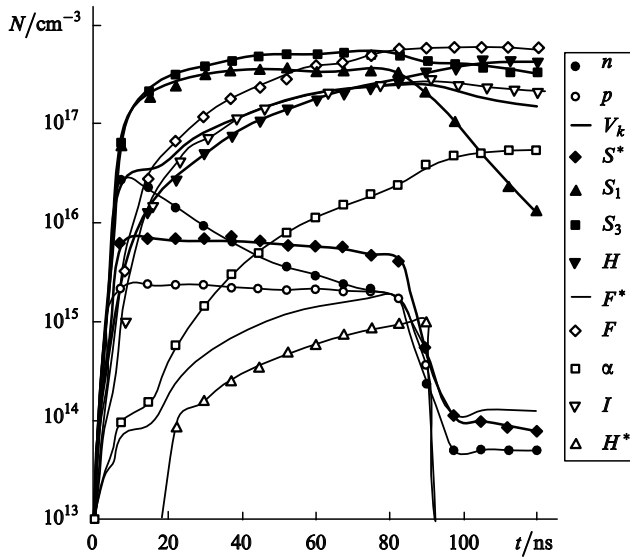


Figure 4. Time dependence of the components under the action of an electron beam and laser radiation with intensity 3 MW cm^{-2} on CaF₂.

centres were produced in pure fluorite irradiated by a KrF laser.

Fig. 5 shows the theoretical variation of D during the propagation of a pulse, as well as the components of this absorption related to the main absorbing colour centres. Note that the experimental value of D is about twice as large as the theoretical value. Both groups of results obtained in Refs [14, 15] and [16] for fixed values of the constants from System No. 1 were described with such a degree of accuracy.

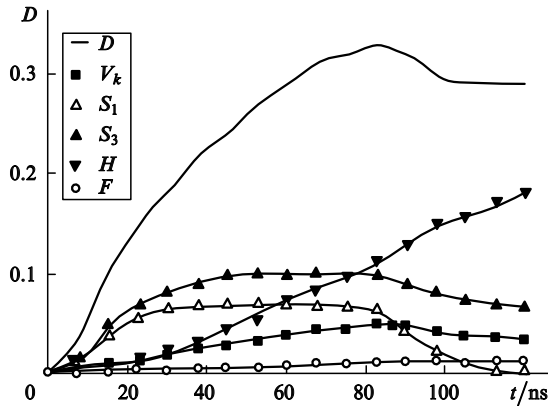


Figure 5. Time dependence of D at 248 nm in CaF₂, and the contribution to this absorption from the main components for a sample irradiated by a 0.4-J cm^{-2} electron beam.

The following values were used for these constants: $K_{13} = 10^{-7} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{17} = 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{110} = 10^{-7} \text{ cm}^{-3} \text{ s}^{-1}$, $K_4 = 5 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$, $K_5 = 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{56} = K_{65} = 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$, $K_6 = 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{78} = 10^{-10} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{79} = 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{89} = 10^{-7} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{811} = 10^{-10} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{911} = 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$, $K_{1011} = 10^{-10} \text{ cm}^{-3} \text{ s}^{-1}$, $X_{45} = X_{46} = 0.45$, $\tau_2 = 3 \times 10^{-11} \text{ s}$, $\tau_3 = 10^{-6} \text{ s}$, $\tau_4 = 10^{-10} \text{ s}$, $\tau_5 = 10^{-8} \text{ s}$, $\tau_6 = 10^{-4} \text{ s}$, $\tau_8 = 5 \times 10^{-10} \text{ s}$, $\tau_{12} = 3 \times 10^{-11} \text{ s}$, $\sigma_3 = \sigma_{42} = \sigma_{52} = \sigma_{62} = 10^{-17} \text{ cm}^2$, $\sigma_7 = 2 \times 10^{-17} \text{ cm}^2$, $\sigma_{41} = \sigma_8 = \sigma_{10} = 10^{-19} \text{ cm}^2$, $\sigma_{51} = \sigma_{61} = \sigma_9 = 10^{-18} \text{ cm}^2$. The rate constants K_{ij} of the reactions

were chosen in the same way as in Ref. [11] for the MgF₂ model. The relaxation times τ_i were based on the results of Refs [2, 12, 13–15]. The quantities τ_3 , σ_3 , σ_{i2} and σ_7 were selected during adjustment of the model. The absorption cross sections for the remaining complexes were estimated from the maxima.

The model proposed by us was later used for calculating the dependence of absorption in fluorite on the intensity of the KrF-laser radiation. For comparison, calculations were performed for $\beta = 0.002$ and 0.008 cm GW^{-1} . The second value of β is experimental and was obtained for a laser pulse duration of 0.7 ns [18]. In our calculations, the pulse duration was assumed to be equal to 80 ns.

It was found that the total absorption coefficient K on the quasi-stationary part of the pulse remained almost unchanged. The obtained dependences $K(J)$ and the quantities βJ are shown in Fig. 6. The values of K were chosen at the 40th nanosecond. One can see from Fig. 6 that nonlinear absorption of long laser pulses in CaF₂ is considerably higher than the two-photon absorption of 1-ps laser pulses. Similar relations between K and the absorption related to the components under consideration were observed for all values of $J > 0.1 \text{ GW cm}^{-2}$ and for different values of β . Note that the dependence $K(J)$ in this case differs significantly from that observed for MgF₂ [11].

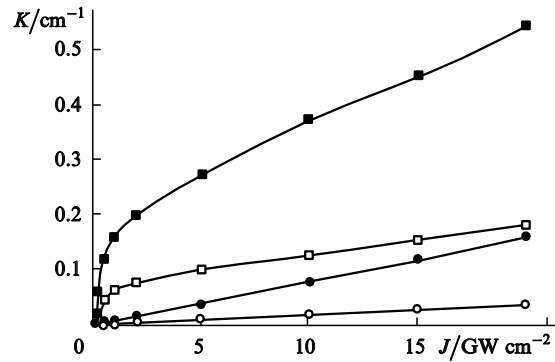


Figure 6. Theoretical dependences of the absorption K (squares) and βJ (circles) in CaF₂ samples for $\beta = 0.002$ (light circles) and 0.008 cm GW^{-1} (dark circles) on the intensity of 80-ns pulses from a KrF laser.

Table 1 presents the theoretical value of K and the contributions from main absorbing components to this quantity for $J = 10 \text{ GW cm}^{-2}$ and $\beta = 0.002 \text{ cm GW}^{-1}$.

Table 1.

K/cm^{-1}	$\beta J/\text{cm}^{-1}$	V_k/cm^{-1}	S^*/cm^{-1}	S_1/cm^{-1}	S_3/cm^{-1}	H/cm^{-1}
0.13	0.02	0.068	0.02	0.0078	0.0078	0.0048

The main contribution to K comes from V_k centres. The time τ_2 of their formation was small [1, 2] (about 30 ps). Laser pulses longer than τ_2 can be called ‘long’ pulses. The results presented here indicate that the change in the crystal structure should be taken into account for a correct description of the interaction of powerful long UV laser pulses with fluorite.

4. Conclusions

We have presented above a model for numerical description of the interaction of ionising and UV laser radiation with CaF_2 . This model is based on the modern concepts about recombination processes occurring in ionic crystals after the formation of electron–hole pairs in them. These processes are described by a system of kinetic equations for 12 states of the anion sublattice of fluorite. The effect of UV laser radiation is also taken into account in the equations.

The model has explained the enhancement of nonlinear absorption of long laser pulses in CaF_2 . The ‘long’ pulses in the our case are the pulses whose duration exceeds the time of formation of V_k centres.

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