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Various configurations of F-H pairs in CaF_2 crystals

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The spectral and kinetic parameters of electron-pulse-initiated transient absorption and luminescence of nominally pure CaF_2 crystals were studied using pulsed spectrometry with nanosecond time resolution. The effect of temperature on the formation of defects was studied. It was established that on increasing the temperature F-H pairs and unknown defects are created. Laser-induced change is studied by optical absorption and luminescence due to F-H pairs generated by an electron pulse in CaF_2.

Fluorite crystals / Point defects / Frenkel pairs / Separated F-H pairs

Introduction

The studies of radiation-stimulated formation and accumulation of defects in CaF_2 crystals are motivated by the prospect of applications in construction materials for high-power UV and VUV-radiation beam transfer from sources of coherent and incoherent types. Irradiation of CaF_2 crystals by ionizing radiation at temperatures at or below room temperature leads to the formation of self-trapped excitons (STE), which consist of a close Frenkel pair of F and H centers [1]. The F center occupies the lattice position of an anion while the H center is oriented roughly along the <111> axis. Several configurations can be distinguished, depending on the distance from the position of the vacancy at the anion site to the interstitial fluorine. A theoretical analysis of the energy required to generate various configurations of STE was carried out in [2]. In order to describe the structure of these excitations a geometric factor was introduced. As the temperature increases, the efficiency of close pair creation decreases, while the efficiency of the creation of spatially separated pairs increases [3]. It has also been established that with increasing temperature F-H pairs and unknown defects are created. The aim of the present paper was to contribute to clarify the picture of the unknown defects. With this objective, we decided to investigate the spectral and kinetic characteristics of optical absorption and luminescence in CaF_2 by pulse cascade excitation spectroscopy. Irradiation of a specimen with an electron pulse creates F-H pairs and subsequent irradiation with a laser pulse excites these F-H pairs from the lowest electronic state (*s*-like) to higher states (*p*-like).

Experimental technique

The pulsed measurement method used here is similar to that described in [3]. The study was performed on crystals grown by the Stockbarger method. The undoped samples were transparent to 125 nm and had no absorption bands caused by the presence of oxygen or lead impurities; the introduction of sodium and yttrium shifted the transmission limits into the visible region. The electron accelerator used as ionizing irradiation source had the following parameters: maximal energy of electrons 0.28 MeV, time resolution 7 ns, pulse-width at half-maximum 12 ns, repetition rate about 10^{-3} Hz, and energy density of the pulse 0.1 J cm^{-2}. Light pulses were generated by a neodymium-doped glass laser. The measurements were carried out in the temperature range 300-600 K. The samples were thermostatically controlled during irradiation. The extrapolated electron range in CaF_2 is 0.26 mm. Dosimetry was carried out using the calorimetric method. 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. The luminescence spectra were corrected. Control was provided by measurements on samples cleaved along the same direction. The samples were cleaved from one block.

Results and discussion

Characteristic luminescence spectra of CaF_2 crystals measured at 500 K, 2 µs and 10 µs after the end of the fast electron pulse, are shown in Fig. 1 (curves 1 and

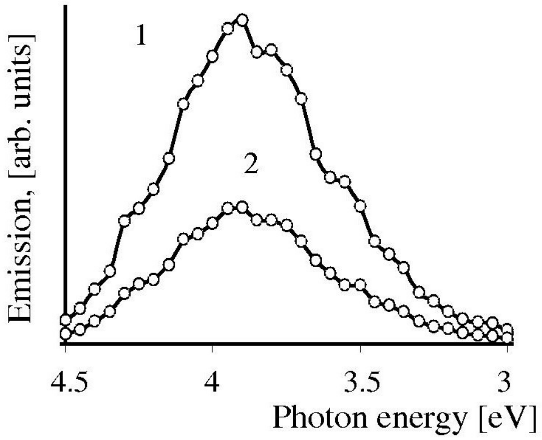

Fig. 1 Luminescence spectra of a CaF_2 crystal at 500 K measured 2 μs (1) and 10 μs (2) after the end of the fast electron pulse.

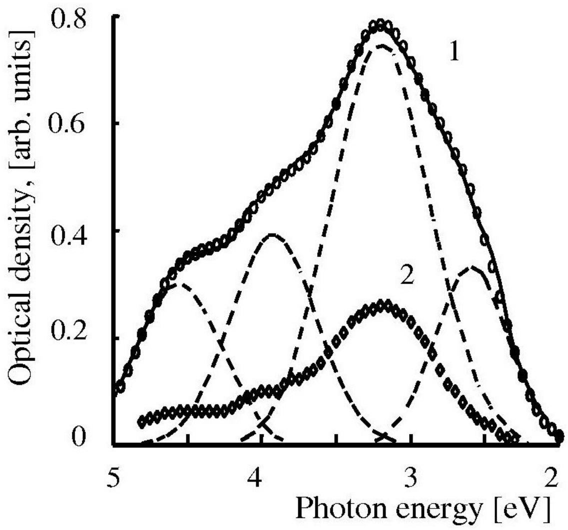

Fig. 2 Optical absorption spectra of a CaF_2 crystal at 500 K measured 10 ns (1) and 10 μs (2) after the end of the fast electron pulse. The dashed lines represent the best fit of 1.

2, respectively). The spectral position of the dominant luminescence band is only in approximate agreement with the parameters known for radiative transitions of STE in CaF_2 [1]. It follows from Fig. 1 that the luminescence spectrum has a complex structure. The decay of luminescence in the dominant band at 3.9 eV cannot be described by an exponential dependence. It has been established that the decay curves are composed of two parallel second-order reactions:

$$I(t) = I_0 \cdot (1 + \alpha \cdot t)^{-1/2} \tag{1}$$

Fig. 2 shows the optical absorption spectra at 500 K measured 10 ns and 10 μs after the end of the electron pulse. The dashed lines represent the best fit of spectrum 1 obtained by applying the Alentsev-Fok method. It follows that, in addition to the dominant H bands at 3.2 and 4.0 eV, the spectrum contains weak, unidentified bands with maxima at 2.5 eV and in the area of 4.6 eV.

At 10 ns after the end of the irradiation the absorption by color centers is dominant. Firstly, the characteristic lifetime of STE in CaF_2 crystals decreases with increasing temperature. Secondly, the efficiency of STE creation decreases with increasing temperature. In Arrhenius' coordinates this process can be described as the sum of two exponents with activation energy 0.01 eV in the 80-300 K region and 0.4 eV in the 300-400 K region [3].

Extrapolation of the data in [3] shows that the characteristic lifetime of STE at 500 K in CaF_2 crystals is less than 10 ns and cannot be resolved by our measuring system. Therefore, STE cannot be responsible for the time relaxation observed in the optical absorption (Fig. 2) and luminescence (Fig. 1) spectra recorded after high-temperature irradiation.

The absorption band with a maximum at 3.2 eV (Fig. 2) is close by its spectral position and half-width (0.83 eV at 500 K) to the known characteristics of F centers in CaF_2 crystals. The shift of the band maximum from 3.31 eV at 4 K up to 3.2 eV at 500 K is caused by thermal expansion of the crystal [4]. The close position of the maxima of the H and V_k bands in CaF_2 spectra (4.03 and 3.87 eV, respectively) does not allow drawing an unambiguous conclusion about the origin of the observed absorption in the 4 eV region. But since the extrapolated value of the lifetime of V_k centers is equal to ~10^{-8} s at 500 K [5] and the relaxation of the induced absorption and luminescence at the same temperature occurs in a microsecond time interval (Figs. 1-2), we can conclude that the band at 4.0 eV is due to H centers. The F and H centers are complementary defects. The shape of the F absorption band is close to the Gaussian form. The change of its half-width as a function of temperature is described by the following expression [4]:

$$H(T) = H(0) \cdot [\mathrm{cth}\,(\hbar\omega_0 / 2kT)]^{1/2}, \tag{2}$$

$$S_0 = [H(0) / \hbar\,\omega_0]^2 / 8\ln 2, \tag{3}$$

where $H(0) = 0.48$ eV is the half-width of the F-band at low temperature (4 K), $\hbar\omega_0 = 0.035$ eV is the effective phonon frequency, and $S_0 = 21$ is the Huang-Rhys effective factor. According to [4]:

$$\hbar\omega_0 = \lim_{T\to\infty} [H(0) / H(T)]^2 \cdot 2\,kT. \tag{4}$$

The best agreement between the experimental curve (Fig. 2) and data calculated by [4] is observed for $\hbar\omega_0 = 0.03$ eV and $S_0 = 46$. The Stokes shift for F centers luminescence in CaF_2 is:

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$$E_{\mathrm{abs}} - E_{\mathrm{lum}} = 2\,S_0 \cdot \hbar\omega_0. \tag{5}$$

From the estimations presented above it follows that luminescence of F centers in CaF_2 should be observed in the spectral range 700-800 nm [6]. However, this has not been found until now.

The temperature dependence of the efficiency of color center creation in the CaF_2 crystal is presented in Fig. 3. In Arrhenius coordinates the dependence of the efficiency of F center creation (curve 1) shows a straight line with the activation energy of the process $E_a = 0.4$ eV [3], which is in good agreement with the activation energy for migration of anion vacancies. The efficiency of the creation of unknown centers also increases with increasing irradiation temperature (curve 2). Curve 3 was obtained from curve 2 by taking F band temperature broadening into account. This curve presents a maximum for the irradiation temperature 500 K.

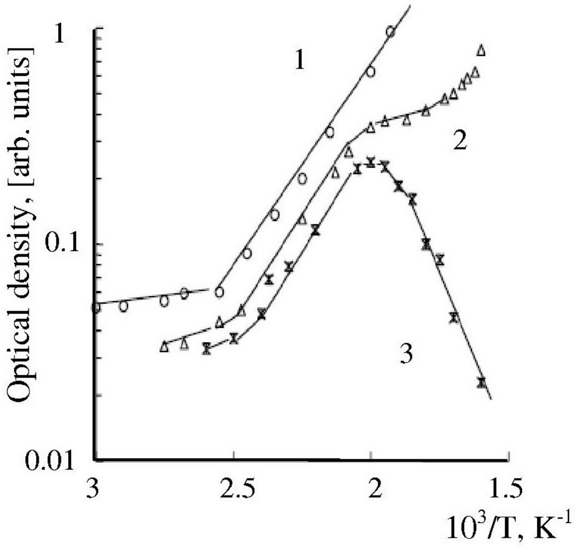

Fig. 3 Temperature dependence of the efficiency of the creation of F centers (1) and unknown centers (2) (absorption band at 2.5 eV) in CaF_2 crystals. Curve 3 was obtained from curve 2 taking into account temperature broadening of the F band at 3.2 eV.

A kinetic analysis of the curves was carried out in order to define the reaction rate constant, assuming that the relaxation of the induced absorption is described by second- or third-order reactions:

$$k_2 = 1/t_i \cdot (D_0 - D_i) \cdot (D_0 \cdot D_i), \quad (6)$$
$$k_3 = 1/2t_i \cdot [(D_i)^{-2} - (D_0)^{-2}], \quad (7)$$

where k is the reaction rate constant; and D_0 and D_i the optical density measured at the end of the fast electron pulse and at the time t_i, respectively.

The best adjustment of experimental and calculated data was made assuming that destruction of defects occurs by at least two parallel second-order reactions:

$$D(t) = D_0 \cdot (1 + \alpha \cdot t)^{-1}. \quad (8)$$

The two-stage process of the destruction of F centers in CaF_2 crystals has been ascribed to a recombination with various hole centers.

The decay curves of the induced absorption relaxation of the unknown centers in CaF_2 were also found to be composed of two second-order reaction stages.

During studies of the temperature dependence of the absorption decay, the characteristic half-decay times of the F centers were calculated. In Arrhenius coordinates this dependence presents a straight line with the activation energy of the process $E_a = 0.4$ eV, which coincides with the activation energy for migration of anion vacancies.

The nature of the defects responsible for the absorption bands with the maxima at 2.5 and 4.6 eV (Fig. 2) is unknown. However, absorption in the given spectral regions has earlier been observed for low-temperature irradiation of pure CaF_2 crystals [7], but it was not identified. An absorption band at 4.6 eV was observed for low-temperature irradiation of doped CaF_2 crystals [8]. We assume that in pure CaF_2 crystals absorption in an energy range higher than that corresponding to the absorption by V_k and H color centers (3.87 and 4.03 eV, respectively [7]) is caused by the formation of hole defects with a complex structure (such as X_3^- or di-H centers).

The defects responsible for the occurrence of absorption bands with maxima at 2.5 and 4.6 eV (Fig. 2) are not only primary products of the radiolysis but also complementary defects. These conclusions are based on the following facts:

1. The concentration of residual impurities in radiation-stable CaF_2 does not exceed 10^{-4} mol.%. An estimate of the concentration of F centers and unknown defects was made from Smakula's formula taking temperature broadening of the F band into account and assuming the oscillator strength of the corresponding transitions to be equal to 0.8. According to the estimates of [3] the concentration of F centers and unknown defects reaches 10^{17}-10^{18} cm^{-3} for the irradiation densities used in this work.
2. Using the cascade-excitation technique it was revealed that optical irradiation with the second harmonic (532 nm) of a neodymium-doped glass laser results in irreversible destruction of the optical absorption of the unknown defects (Fig. 4a), accompanied by the appearance of optical absorption by F centers (Fig. 4b). It is clear from these results that photoexcitation of the unknown defects responsible for the 2.5 eV band converts them to more distant pairs that induce optical absorption at 3.2 eV.
3. An indirect evidence of the electronic nature of the 2.5 eV band is the experimental fact that its optical destruction at 300 K is accompanied by the appearance of luminescence scintillation (Fig. 4c), the spectral and kinetic characteristics of which are identical to the STE luminescence parameters for pure CaF_2 crystals [1]. Since only pairs with greater

separation remain 2 μs after an electron pulse, it is clear that these unknown defects are converted to close pairs (STE).

4. As noted above, the temperature dependencies of the efficiencies of the formation of F centers and unknown defects are qualitatively similar (Fig. 3). The bands at 2.5 and 4.6 eV are characterized by similar values of the decay coefficients for induced absorption.

5. The theoretical analysis [2] of the adiabatic potential curve connecting various configurations of STE in CaF_2 crystals shows that, in comparison with the ground state of the electron at the vacancy, the adiabatic potential for the excited states has the even platter. This suggests that the system presents a high probability of conversion between various configurations of STE [9]. In [10] it is shown that optical excitation of STE in CaF_2 at 80 K can lead to their transformation into pairs of separated defects. The formation of STE by optical stimulation in the absorption band of separated defects was observed in SrF_2 at 6 K [9].

Hence, it is possible to assume that irradiation of CaF_2 crystals with a nanosecond electron pulse is able to create states of defects intermediate between STE and separated F and H centers that are connected by the same potential surfaces for motion of F-H pair hole nucleus.

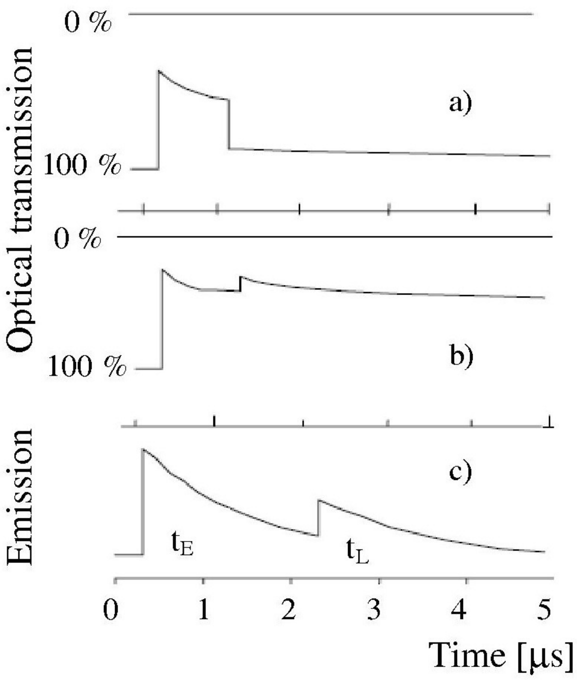

Fig. 4 Oscilloscope traces for optical transmission (a, b) and luminescence (c) of CaF_2 crystals induced by an electron pulse (at t_E) and by a subsequent laser pulse (at t_L), measured at 2.5 eV / 500 K (a), 3.2 eV / 500 K (b) and 4.4 eV / 300 K (c).

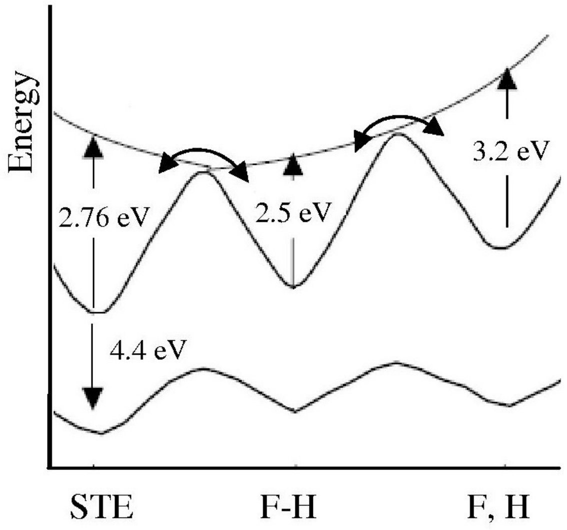

Fig. 5 A schematic configuration of coordinate curves for the hopping motion of an interstitial fluorine atom that is part of a Frenkel pair.

Conclusion

The experimental results described above show that excitation of electrons localized at the vacancy of a Frenkel pair causes migration of the F_2^- molecular ion. The motion is regarded as hopping of interstitial fluorine atoms.

Fig. 5 shows schematic adiabatic potential surfaces for the migration of defects. Irradiation of a specimen with an electron pulse creates F-H pairs and subsequent irradiation with a laser pulse excites the F-H pairs in the lowest electronic state to higher states. The absence of an electron at the vacancy will induce an attractive potential. Upon excitation to a higher state hopping motion will occur following the adiabatic potential curve, converting the F-H pairs to separated F and H centers. The fact that luminescence due to STE is emitted by excitation of separated pairs may indicate that branching into various configurations of F-H pairs occurs at the cross points of the configuration coordinate curves for the lowest and higher excited states.

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