

Optical Study of Photochromic Center in Yttrium – Doped CaF_2 Crystals

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Abstract – Optical spectroscopy with nanosecond resolution has been used to study of the creating of radiation – induced defects in yttrium – doped CaF_2 crystals under the influence of a pulse accelerated electrons. It is shown that the formation of a photochromic color centers in $\text{CaF}_2 – \text{YF}_3$ crystals occurs by thermally activated diffusions of the interstitials. It is established of the energy of activation of process the formation of photochromic color centers is 0,8 eV. A model of the formation of the photochromic defects is proposed

1. Introduction

The actuality of study of radiation stimulated processes of defects formation and accumulation in doped CaF_2 crystals is caused by prospect of their application as active environments for optical quantum generators, materials for optical memories, thermo – luminescence dosimetry and solid – state electric batteries.

Under an ionizing irradiation at room temperature in CaF_2 crystals with an yttrium impurity or the rare earths (Ce, Gd, La, Tb, Lu) thermally stable are the photochromic color centers (PC), representing a complex (a trivalent ion of an impurity – anion vacancy) on which are located one or two electrons. The photochromic effect will consist in a change of coloration of crystals colored by ionizing radiation at an irradiation of a ultra – violet light. Absorption of the UV light by the PC transfers an electron from a complex to an isolated impurity ion. The process is reversed by absorption of visible light, or thermal energy. However, the mechanism of formation photochromic defects has been investigated insufficiently.

The purpose of work is research by a method of pulse spectroscopy with nanosecond resolution of spectral – kinetic characteristics of an optical absorption induced by an accelerated electrons pulse in CaF_2 crystals, doped by an impurity yttrium.

The samples of CaF_2 crystals with the various contents of an impurity yttrium (0,03 – 1M%) were grown by a Stockbarger method. As a source ionizing irradiation was the electron accelerator with the parameters: the maximal electron energy is 0,28 MeV, the time resolution is 7 ns, the pulse width at half – maximum is 12 ns, and the energy density is 0,1 $\text{J}\cdot\text{cm}^{-2}$. Measurements are carry out in temperature range of 80 – 500 K. Initial purity of $\text{CaF}_2 – \text{YF}_3$ crystals was monitored as follows. First, purity was controlled on transmission spectra of the unirradiated samples. Well – known, that presence of "biographic" [2] impurity

of sodium or yttrium shifts the transmissions limits into the visible region in fluorite crystals, and lead and oxygen leads to occurrence of selective bands in vacuum ultraviolet (VUV) region of a spectrum. Second, purity was controlled on absorption spectra of the crystals by low – temperature irradiation. Presence of impurity of sodium or oxygen causes appearance in visible region of a spectrum of well investigated absorption bands of the F_A color centers.

2. Low – temperature irradiation

Figure 1 shows the spectrum of optical absorption of $\text{CaF}_2 – \text{YF}_3$ crystal, measured 10 ns after the end of an irradiation pulse. The centers that was responsible for induced absorption have been various thermally stability. A relaxation of unstable absorption in the dominant bands on ~2,8 and 4,1 eV it is well described by exponential dependence with a time constant of 40 μs .

The spectral and kinetic characteristics of unstable absorption are close to the well – known parameters of the self – trapped excitons (STE) [3].

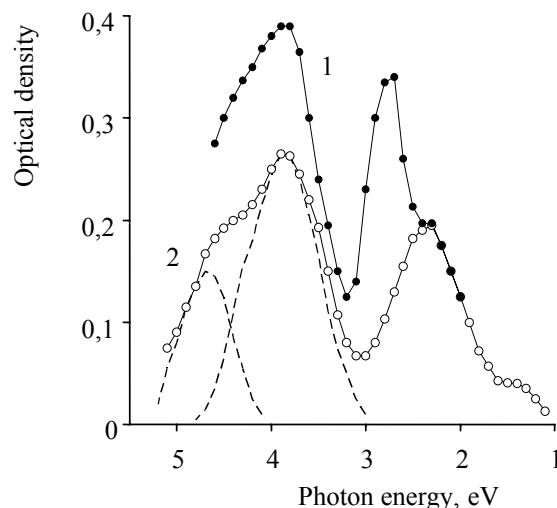


Fig. 1. The optical absorption spectrum $\text{CaF}_2\text{-}0,3\text{M}\%\text{YF}_3$, measured for 10 ns (1) and 1 ms (2) after the end of irradiation pulse at 80 K

The electron excitations effectively interact with the defects of lattice caused by the introduction of an yttrium impurity in CaF_2 crystals. Presence of the additional channel of a relaxation of electron excitation results in a reduction of the creation efficiency of STE in doped crystals, in comparison with pure CaF_2 .

Quantitative estimates are made from the amplitudes of the optical density measured at the time of the pulse ends at the maximum (2,76 eV) of an electronic component of the STE absorption [3]. The stable absorption was not taken into account. The characteristic dependences of STE creations efficiency and accumulation of the color centers in $\text{CaF}_2 - \text{YF}_3$ crystals are shown in Fig. 2.

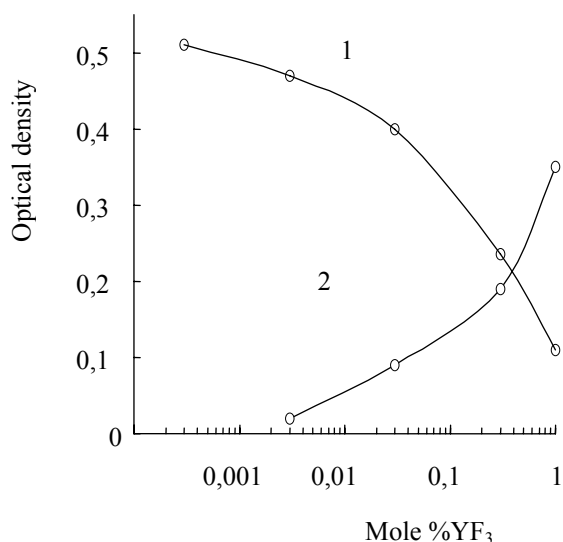


Fig. 2. Change of the creation efficiency of STE (1) and the color centers (2) in $\text{CaF}_2 - \text{YF}_3$ crystals at 80 K. Absorption of STE is measured at 2,76 eV, and the color centers – at 2,33 eV

With increase of the time after the end of an irradiation there is a change of structure of the induced absorption spectrum (Fig. 1, curve 2). For time 1 ms after the end of irradiation pulse in a spectrum are the bands at 1,65, 2,3, 3,9 and 4,6 eV caused by the creation of the color centers which are thermally stable, but optically unstable. It is necessary to note, that optical absorption of the F centers perturbed with of oxygen or sodium impurity, it is not revealed, that testifies about quality of researched $\text{CaF}_2 - \text{YF}_3$ crystals.

The structure of absorption spectra of the color centers, and, hence, type of impurity – associated color centers generated by radiation, does not depend on concentration (0,03 – 1M%) of an yttrium impurity entered into CaF_2 crystals (Fig. 3).

The absorption band at 3,9 eV (Fig. 1, curve 2) on the spectral position and the with half – width band 0,94 eV is close to known characteristics of the V_k color centers (${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ optical σ – transition) in CaF_2 crystals [4]. Optical π – transition ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_g^+$ should be at 1,65 eV. Spin – orbital splitting is not enough for fluorine ions (0,03 eV) and transitions from the state ${}^2\Sigma_u^+$ in state ${}^2\Pi_{1/2g}$ and ${}^2\Pi_{3/2g}$ are not spectral resolved.

On low – energy recession of a band at 2,3 eV the peak near 1,5 eV is really allocated. However, its intensity should be much lower as force oscillator for

the forbidden transition ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_g^+$ of the V_k color center by two orders of magnitude is less [4], than for the resolved transition in UV region.

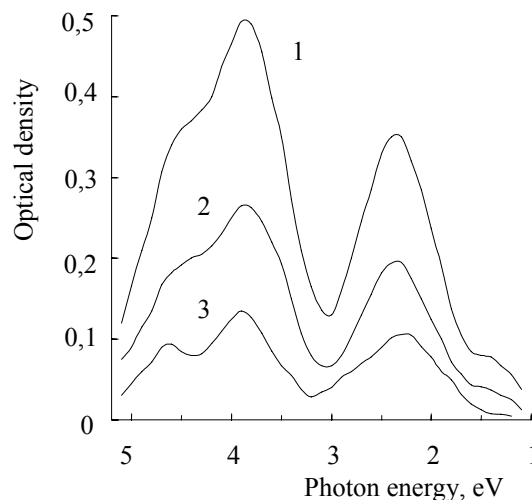


Fig. 3. The optical absorption spectrum of $\text{CaF}_2 - \text{YF}_3$ crystals, measured at 80 K for 1 ms after the end of irradiation pulse: 1- M% YF_3 ; 2 – 0,3M% YF_3 ; 3 – 0,03M% YF_3

The nature of the centers which responsible for an 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 an irradiation of pure CaF_2 crystals as in spectra of stable absorption at the low – temperature irradiation (4 K) [4] and as in spectra short – lived absorption at the high – temperature (500 K) an irradiation [5].

It is possible to conclude, that the defects which responsible for absorption at 4,6 eV are formed in the lattice undisturbed by an impurity. We assume, that in $\text{CaF}_2 - \text{YF}_3$ crystals absorption in more high – energy range of a spectrum, than absorption of the V_k and H color centers (3,87 and 4,03 eV respectively [4]) is caused by the formation of hole defects with a complex structure (such as the X_3^- or di – H centers).

The nature of the centers that was responsible for an absorption band at 2,3 eV and with half – width 0,8 eV is unknown. With using of cascade excitation technique it is revealed that at liquid nitrogen temperature the optical illumination with the second harmonic (532 nm) from neodymium – doped glass laser results in irreversible destruction of the color centers in $\text{CaF}_2 - \text{YF}_3$ crystals. As the indirect evidence of the electronic nature of the band at 2,3 eV are the experimental fact, that its optical destruction is accompanied by an appearance of luminescence flash in $\text{CaF}_2 - \text{YF}_3$ crystal [6] which is identical on spectral and kinetic characteristics to the parameters of STE luminescence in pure CaF_2 crystals [5].

3. High – temperature irradiation

The spectra of optical absorption of $\text{CaF}_2 - 0,03\text{M}\% \text{YF}_3$ crystal, measured at room temperature with a various delay concerning the end of a pulse of radiation are submitted in Fig. 4. As follows from the data of Fig. 4 that for time $4 \mu\text{s}$ after the end of an irradiation (curve 2b) dominates absorption of the color centers. The life – time of STE at room temperature is about $1 \mu\text{s}$ [5].

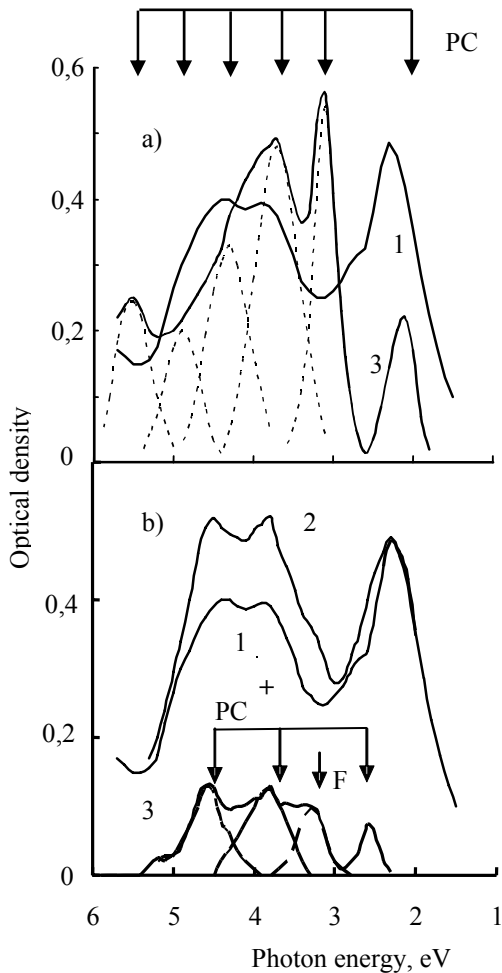


Fig. 4. The optical absorption spectrum of $\text{CaF}_2 - 0,03\text{M}\% \text{YF}_3$ crystal, measured at 295 K for $4 \mu\text{s}$ (2b), 0,1 s (1a, 1b) and 60 s (3a) after the end of irradiation pulse. (3 – difference of spectrum 2–1)

Comparison of the data submitted in Fig. 1 (curve 2) and Fig. 4 (curve 2b) shows that the spectra of optical absorption induced by a pulse electrons at various (80 and 295 K respectively) temperatures of an irradiation are qualitatively similar. However there are also essential differences: the intensity ratio of

absorption bands and also thermal stability of defects has changed. It is established, for example, that only about 50 % of the defects absorbing in region of V_k absorption band destructed at 150 K on exponential law with a time constant of 30 s. The activation energy of destruction process of thermally unstable hole centers coincides with migration energy of the V_k centers (0,33 eV) [4].

With an increase in time after the end of a radiation pulse from $4 \mu\text{s}$ up to 0,1 s the intensity of the induced absorption in UV region of a spectrum decreases, and on high – energy recession of a band 2,3 eV the additional maximum near 2,6 eV (Fig. 3, curve 1b) is shown.

Figure 4 presents the absorption spectrum (curve 3) received by subtraction of a curve 2 from a curve 1 is submitted. Comparison received a differentiated spectrum (curve 3) with the data of work [1] allows to conclude that in the time interval ($4 \mu\text{s} - 0,1 \text{ s}$) there is a destruction of the ionizing photochromic color centers (PC^+) causing the origin of bands with maxima at 4,6, 3,8 and 2,6 eV. Besides at the same time presence of the expressed maxima at 3,3 and 3,9 eV assumes there is destruction of the F centers when their recombination with the mobile V_k centers.

It is known, that force oscillator of transitions in the hole centers is much lower than ones in the electron color centers. The absorption of PC^+ band at 3,8 eV is blocked with a absorption of V_k band at 3,9 eV which intensity ones must be lower than intensity of a F band absorption.

With increase of time up to 60 s the originally induced spectrum of optical absorption (Fig. 4, curve 1a) is transformed in so – called "spectrum Smakula" [1] (Fig. 4, curve 3a) which is caused by formed PC (bands of absorption at 5,51, 3,70, 3,10 and 2,13 eV). Absorption bands with the maxima at 4,3 and 4,9 eV are allocated by us at decomposition.

It has been established, that kinetic curves of increase of an optical absorption of PC are well described by the assumption of the first order reaction. Measurements are executed on the fixed wave length of 400 nm. For example, the time of the formation of PC at 250 K is equal 600 s and at 295 K is near 2 s. The yield of PC increases with growth of temperature of an irradiation up to 270 K and at the further increase of temperature (400 K) – remains the constant.

The temperature dependence of characteristic times of PC formation in $\text{CaF}_2 - \text{YF}_3$ crystal is submitted in Fig. 5. In Arrhenius's coordinates this dependence looks like a direct line with the activation energy of the process $E_a = 0,8 \text{ eV}$ which will be coincided to activation energy of the interstitial migration (F_i^-) [7].

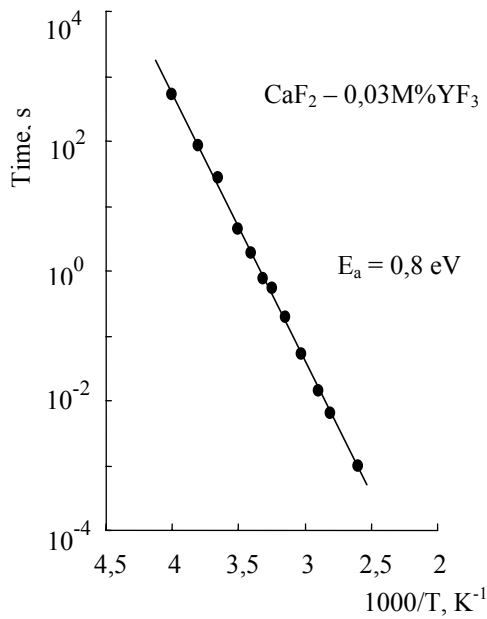


Fig. 5. Temperature dependence of the characteristic times of the formation of the photochromic color centers in $\text{CaF}_2\text{-YF}_3$ crystal

The obtained experimental data allow make a conclusion that the accumulation of PC in $\text{CaF}_2 - \text{YF}_3$ crystal occurs at the thermally activated diffusion of interstitials.

Earlier was considered [7] that at the impurity concentration 0,1 – 1M% both the local and not local ways of compensation of a excess charge of isolated ions basically take place. The formation of dimers from structural defects and the more complicated clusters occurs in case doping of an yttrium impurity in a concentration range (1 – 5M%).

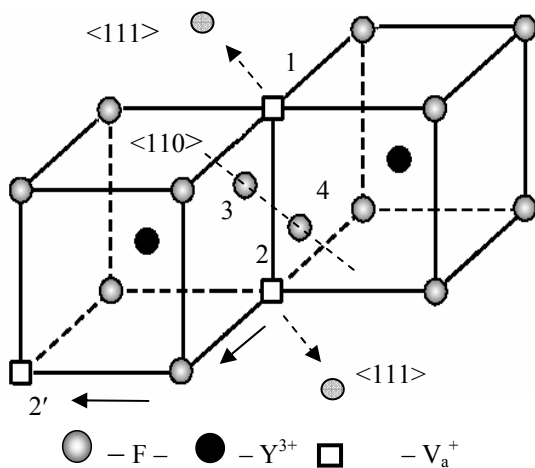


Fig. 6. Schematic representation of model of formation of the photochromic color centers in $\text{CaF}_2\text{-YF}_3$ crystal

We suppose that in case the diluted doped solutions take place the association of impurity – interstitials dipoles in the form of cluster such as 2:2:2 [8].

Figure 6 schematically shows a cluster that contains two interstitials 3 and 4 (compensators of a excess charge of an yttrium impurity) which do not occupy the cube – central positions in an anion cubes. As a result of the degeneration removal of 2p – levels of interstitials the interaction of an attraction is appearing. The distance between the adjacent interstitials 3 and 4 focused along $\langle 110 \rangle$ directions decreases up to 0,2 nm. The decrease distance results in the appearance of relaxed anions which are displaced from their site position into empty anion cubes along $\langle 111 \rangle$ directions [8]. In a defect cluster is a barrier for recombination of the interstitial with the vacancy.

As a working hypothesis the mechanism of the formation of PC in $\text{CaF}_2 - \text{YF}_3$ crystals can be assumed as follows. In case of localization of one or two electrons on an anion vacancies 1 and 2 oriented along $\langle 100 \rangle$ direction take place the formation of defects such as the F_2^+ or F_2 color centers in which nearest environment the ion of an yttrium impurity is located. The opportunity of formation of complex electronic color centers at optical or thermal destruction of PC is earlier observed in [9]. Thermally stimulated diffusion of interstitials results in a jump of anion vacancy from the position 2 to the position 2' in that way the axis of symmetry of both vacancies 1 and 2 becomes focused along the main diagonal of anion cube (i.e. in the $\langle 111 \rangle$ direction). In the center of a cube the ion of an impurity yttrium is located.

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