Transfer and Trapping of Electrons in the Crystals $CaF_2 - O^{2-}$ and $CaF_2 - Eu$ by the Low-Energy Impurity Excitation

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***Abstract*—Dipole centers $Eu^{3+} - F_i^-$ and $O^{2-} - V_a^+$ were investigated as the centers trapping electrons. It was investigated the ionic processes (orientation TDP) and the electronic ones induced by the laser excitation of sample at the low temperature in the electric field (electronic TDP). It was found that the parameters of electronic and ionic TDP peaks coincided. It was hypothesized that a thermal electron escaped due to the reorientation of the dipole centers.**

***Index Terms*—Alkali-earth crystals, dipole trapping centers, excimer-like bond, thermal depolarization (TDP).**

I. Introduction

A calcium fluoride crystal doped by the ions of Eu^{2+} is the scintillator (decay time ~940 ns, light output of NaI(Tl) bialkali pmt is 50%) [1], [2]. One of the important characteristics of scintillation materials is the small contribution of the long-time luminescence component. The interaction between luminescence centers and distant traps resulting in the tunnel recombinations increases the scintillation time. The experimental results on the alkali-halides found the interaction between centers that were excited not only by ionizing, but also one-photon intra-center excitation [3]–[5], [13]–[15].

In this work the transfer of electrons was investigated by the methods of the thermo- and photo-depolarization currents, thermal luminescence, and phosphorescence on the crystals $CaF_2 - O^{2-}$ and $CaF_2 - Eu$ excited in the long-wave bands of impurity absorption by radiation of the nitrogen laser.

II. Methodology

The crystals CaF_2 doped with 0,01 at mol. % O^{2-} and $CaF_2 - Eu^{2+}, Eu^{3+}$ (the total concentration of europium determined by the chemical analysis amounted about 0,3 mol. %, the concentration Eu^{2+} estimated from the activator absorption coefficient in the long-wave band accordingly [6] amounted $3,5 \times 10^{17}\ cm^{-3}$) were used. The crystals were grown by the Stockbarger method in a graphite crucible in vacuum.

Specimens of 1 cm^2 cross section and about 0.7 mm thickness were mounted in a vacuum cryostat. Indium-gallium eutectic electrodes $(10^{-1}\ cm - diameter)$ were used for the current measurements. The Ohmic type of the contacts was shown in the volt-ampere characteristic [7], [8]. The value of the field intensity did not exceed $10^4\ V/cm$. The nitrogen laser ($hv = 3,68\ eV$, $P = 10^3\ W/cm^2$ in impulse $t = 10^{-8}\ s$) was used for the excitation of luminescence. The photoelectronic multiplier was used for the luminescence measurements. The temperature control was carried out by the copper-constantan thermocouple.

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III. Results

A. Thermal Depolarization (TDP)

The ionic processes (orientation TDP) and the electronic ones induced by the laser excitation of the sample at the low temperature in the electric field (electronic TDP) were investigated.

Orientation TDP (OTDP): The electric field was switched on at room temperature. After cooling down to 80 K, the sample was shorted upon the electrometer. The experiments were performed at the constant heating rate. The obtained results are shown in Figs. 1(a) and 2(a).

The OTDP peak with maximum ~150 K and width on a half-height ~10 K took place in the Eu doped crystals.

The OTDP peak centered at ~200 K and width on a half-height ~25 K took place in the samples of $CaF_2 - O^{2-}$.

The exposure of the sample in the electric field at the low temperature (80 K) without any influences (for example irradiation) did not result in the TDP appearance.

Electronic TDP (ETDP): Electronic processes observed in TDP were investigated in the samples cooled down to 95 K. The external electric field was switched on at the low temperature and the sample was irradiated by the laser. At the irradiating the photocurrent was detected. After switching the electric field off the temperature dependence of ETDP current was recorded. The results are given in Figs. 1(a) and 2(a).

The low temperature peaks ETDP are coincided with the OTDP ones (~150 K for the Eu doped crystal and ~200 K for the oxygen doped one).

B. Photodepolarization (PhDP) in $CaF_2 - O^{2-}$

In the crystal being put in the electric field the photodepolariation (PhDP) stimulated by white light took place. The PhDP current depended on the temperature. The thermal dependence is shown on the Fig. 3.

C. Low Temperature Phosphorescence and the Thermal Luminescence (TL)

The low temperature phosphorescence in a minute interval (Fig. 4) in the investigated samples was obtained after the laser irradiation at 95 K and the subsequent cooling down to 80 K. The decay was followed by a hyperbolic law.

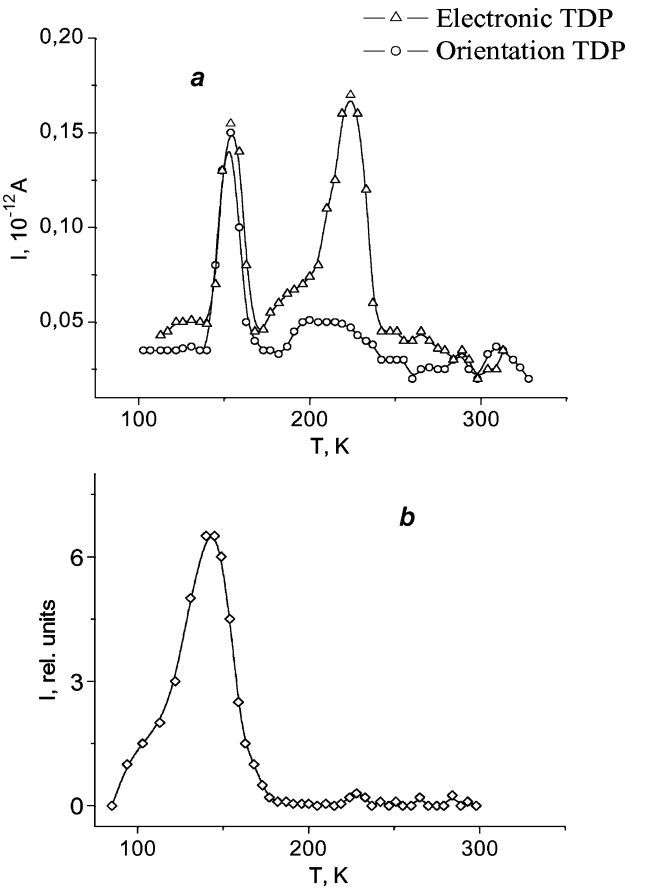

Fig. 1. Temperature dependences of $CaF_2 - Eu$. (a) Electronic and orientation TDP. (b) Thermal luminescence.

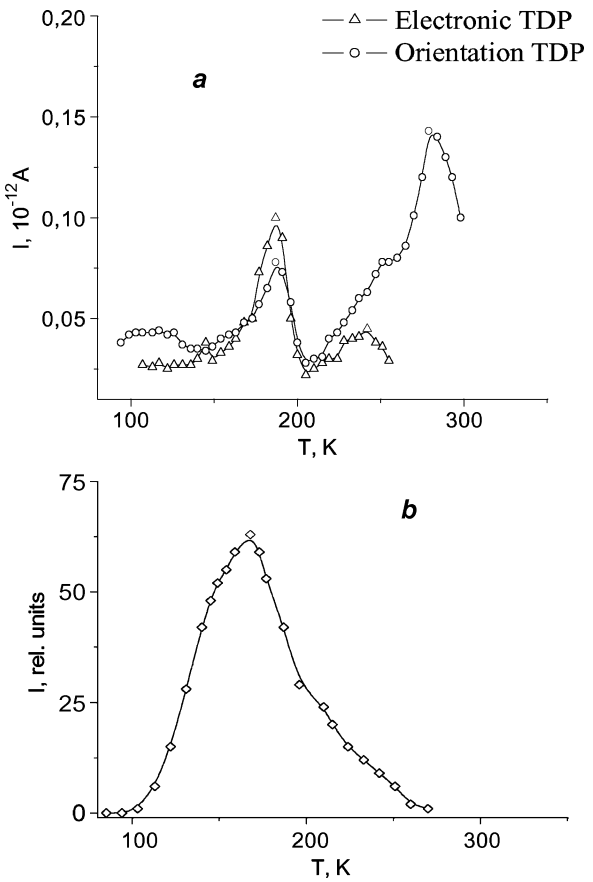

Fig. 2. Temperature dependences of $CaF_2 - O^{2-}$. (a) Electronic and orientation TDP. (b) Thermal luminescence.

The TL investigations were carried out after the laser excitation at 95 K. The irradiating time was about 10–20 minutes. The results are shown in Figs. 1(b) and 2(b).

The wide peak between 100 and 170 K, centered at ~140 K was found out for the Eu doped crystals.

In the oxygen doped samples the peak took place between 110 and 260 K. The TL maximum was found at ~160 K.

The spectra of the phosphorescence and TL in the calcium fluoride with europium and calcium fluoride with oxygen were in the green region with the maximum about 510 nm.

IV. Discussion

The OTDP is connected with reorientation of dipoles that had been orientated at the high temperature (room temperature). The ionic current resulting in the formation of the near-electrodes charge also contributes to the polarization. In the process of heating the depolarization of the crystal occurs as a result of the ionic and reorientation motion that is manifested in the appearance of the TDP peaks in different temperature regions.

It was found that a polarization occurred also with the excitation of the electronic subsystem of the crystals by the laser irradiation in the electric field at the low temperature.

The localization of the electrons on the traps in the anode layer results in the crystal polarization (the mechanism of free electrons appearance as a result of the intracenter impurity excitation was suggested in the papers [3]–[5], [7], [9], [10], [13]–[15]).[1] Therefore, the OTDP and ETDP processes have the different nature. So, the appearance of the free electrons was registered with the ETDP, but the reorientation of dipoles was registered with the OTDP.

The centers, which supply the electrons by the intracenter excitation in the investigated processes, are determined by the spectral distribution of the phosphorescence and TL. The spectra of the relaxation luminescence in the investigated crystals coincide with the luminescence spectrum of oxygen-vacancy centers.

And so we can conclude that the suppliers of the electrons are the oxygen-vacancy centers for both types of crystals. It is known [7], [10], that the nitrogen laser irradiation is in the long-wave decay region of the oxygen-vacancy centers excitation band. The escaping of the electrons into the conduction band takes place due to the releasing of the electrons not from the directly excited states of the luminescence centers $(O^{2-} - V_a^+)$ but from the trapping centers interacting with the excited centers.[2]

The filling of the electron traps by the low-energy excitation was observed in the luminescence experiments. The phosphorescence with a hyperbolic law of decay can be explained with the subband tunnel returning of electrons to the luminescence centers.

[1]The different capture centers correspond to the different ETDP peaks.

[2]That was investigated on the alkali-halide crystals. It was found that the transfer was occurring as a result of the interaction between distant defects. The interaction took place due to the recovering of the exciting ion and capture centers states that resulted in the formation of the excimer-like short-time molecular bond [3]–[5], [13]–[15]. At the time of the relaxation an electron "was flowing" into the trap with the formation of the capture center atomic state. That destroyed the excimer-like bond.

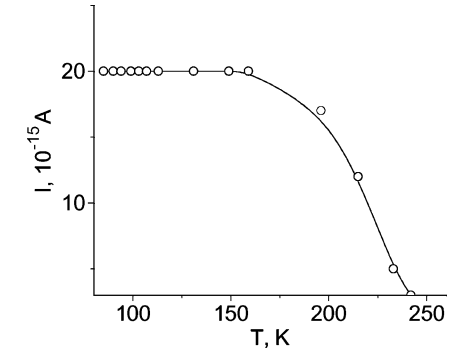

Fig. 3. Thermal dependence of photodepolarization in $CaF_2 - O^{2-}$.

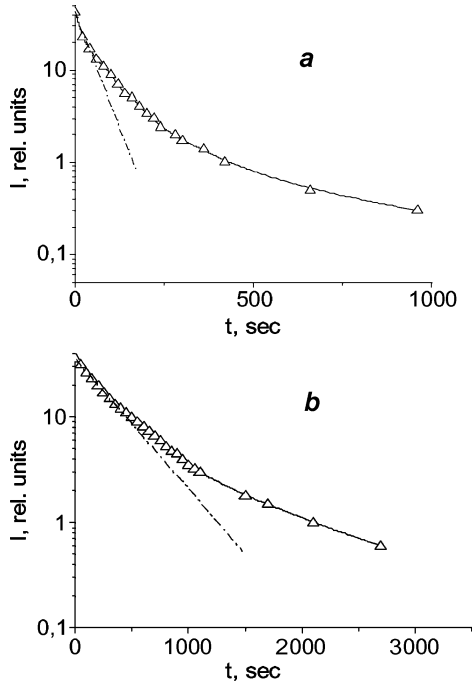

Fig. 4. Kinetic of phosphorescence decay of (a) $CaF_2 - Eu$ and (b) $CaF_2 - O^{2-}$.

The electrons being in traps, the probability of tunneling from that is negligible, were observed in the TL and ETDP measurements. The maxima of peaks ETDP and TL don't coincide because the relaxation processes are differed. After having been in the conduction band the electrons cause the ETDP. Both the electrons obtained with the photocurrent (after having been in free state) and the electrons trapped as a result of the subband transfer cause the TL. The experimental results let us hypothesize that the later electrons make the largest contribution into the TL (the maximum TL takes place in the low temperature range, where the investigated centers are stability).

The availability of dipoles in the investigated crystals was manifested with the OTDP peak ~150 K in the calcium fluoride with europium [Fig. 1(a)]. It is known [11], that the orientation TDP is due to the reorientation of the $Eu^{3+} - F_{int}$ dipoles.

The ETDP took place as a result of the low temperature laser irradiation of the crystal being located in the electric field. The parameters of the ETDP and OTDP peaks coincide.

The analogous picture took place in the calcium fluoride with oxygen. The ETDP and OTDP parameters of the peaks coincide. The observed ETDP on the calcium fluoride doped with oxygen with the maximum ~200 K [Fig. 2(a)] can be connected with the oxygen-vacancy centers trapping electrons [7]. It is known [12], the absorption of the F_H centers (oxygen-vacancy dipoles trapped an electron) is in visible region. The observed PhDP stimulated with white light can be connected with the deexcitation of the F_H centers (the photoelectrical signal in the F_H absorption region was registered in the [12]).

The temperature dependence of the PhDP is represented on the Fig. 3. The PhDP decay takes place in the region of the OTDP peak connected with the oxygen-vacancy dipoles. It is the evidence that the OTDP peak ~200 K belongs to the oxygen-vacancy dipoles.

V. Conclusions

The trapping centers corresponding with the low temperature peaks of the ETDP are dipole centers. The parameters of the OTDP and ETDP peaks coincide. This lets us assume that an electron trapped by the dipole center is released as a result of the thermal reorientation of the dipole. Thus the process of the ionic motion causes the electron releasing.

The energy parameters of the dipole centers aren't changed by the capturing electron. This fact is the evidence that the electron is trapped into the molecular dipole state but not into the single component of the center (e.g., F_H center—the F center perturbed by oxygen [12]).

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