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INFLUENCE OF THERMAL TREATMENT ON OPTICAL AND ELECTRICAL PROPERTIES OF CaF_2 WITH OXYGEN

Oxygen-vacancy centers were studied by luminescence, absorption and investigation of temperature dependence of ionic current methods. It has been found out, that quenching results in decrease of luminescence and absorption concerned with oxygen-vacancy centers. The upper bound of activation energy of vacancies mobility is considered.

Keywords: ionic current, absorption, luminescence, activation energy of mobility, fluoride calcium.

1. INTRODUCTION

Ions of oxygen contained in fluoride calcium must be charge-compensated by anionic vacancies. They form associates with oxygen in the equilibrium conditions; this results in local compensation of charge. The simplest associates are dipoles, which can be merged into more complicated associates (dimers, trimers etc). Oxygen-vacancy centers have property to emission. Thermal treatment modifies their structure; this results in change optical and electrical characteristics of crystals. Influence of the thermal treatment on ones is investigated in this paper.

2. METHODOLOGY

Crystals of CaF_2–O^{2-} used in these experiments were grown by Stockbarger method in a graphite crucible in vacuum. Oxygen concentration was ~ 10^{-2} mol. %, estimated by value of absorption in band at $h\nu_m = 6{,}7$ eV according to [1].

Indium-gallium eutectic electrodes (10^{-1} cm-diameter) were used. The Ohmic type of the contacts is shown in the volt-ampere characteristic. The study of temperature dependences of ionic currents were carried out on vacuum-processed samples. The value of field intensity didn't exceed 10^4 V/cm.

The nitric laser LGI-21 was used for excitation of luminescence. Its radiation was located at long-wave edge of excitation band of oxygen-vacancy's centers with $h\nu_m = 4{,}27$ eV found out in [2].

3. DATA AND RESULTS

3.1. Ionic current

The temperature dependence of ionic current in a coordinates lg$I$~$1/T$ was linear (Fig. 1*a*) in the range of temperature from 290 to 410 K for the samples not subjected to thermal treatment. Energy of thermoactivation process was (0,82±0,02) eV.

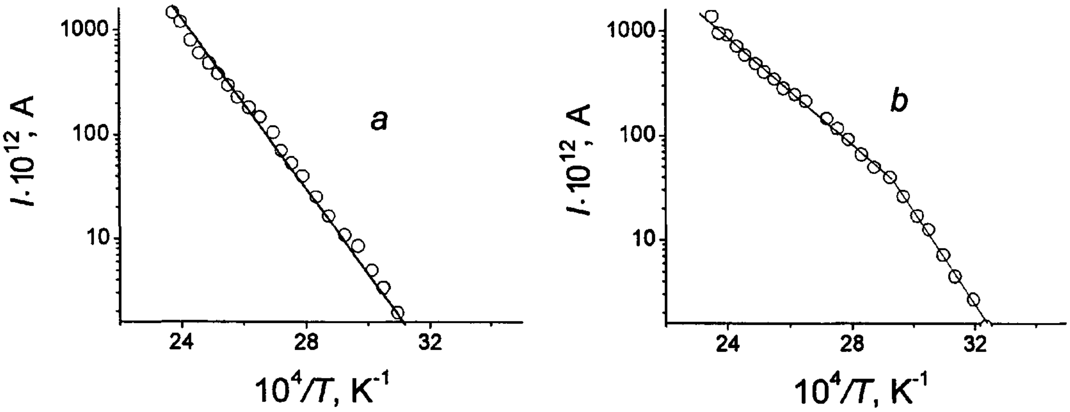

Fig. 1. Temperature dependences of ionic current in crystal CaF_2–O^{2-}: *a* – not subjected to thermal treatment, *b* – in third measurement cycle.

After dependence had been measured, the sample was hold at 430 K during 40–60 and then cooled down to room temperature during 15–40 min. The described consecutive actions made up one cycle.

In the subsequent cycles the behavior of temperature dependence was modified. Two rectilinear parts appeared on it (Fig. 1*b*). The low temperature region corresponded to values of activation energy, which were situated at interval 0,83–1,00 eV, depending on number of the cycle. The high temperature region corresponded to values of activation energy, which were situated at interval 0,51–0,6 eV. The consecutive thermal treatments decreased the slope of linear parts. The change of slope in all dependencies took place in 340 K. The current measured at room temperature significantly increased on the sample, which was subjected to thermal treatment. The main results are shown at Table 1.

Table 1

The values of activation energy for non-quenched sample (sample No. 1)

Type of thermal treatment	Number of cycle	Activation energy, low part, eV	Activation energy, upper part, eV
No quenching	1	0,81± 0,01	0,81± 0,01
	2	0,93± 0,03	0,65± 0,01
	3	0,89± 0,03	0,51± 0,01

The crystal was clouded (hazed) in the experiments when the sample first heated to 950 K was then cooled down slowly to room temperature during 24 hours. In that case, the temperature dependence was modified. Two straight parts appeared (Fig. 2). Activation energy of low-temperature part was (0,15±0,02) eV and that of high-temperature part was (0,57±0,02) eV. The change of slope of dependence took place in 350–370 K. The current measured at room temperature was decreased after thermal treatment more than tenfold.

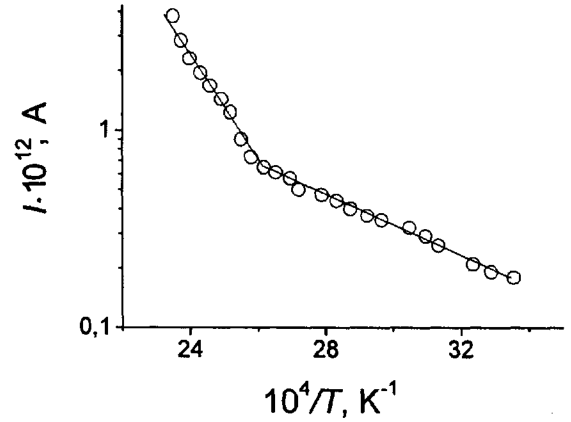

Fig. 2. Temperature dependence of current in crystal slowly cooled down to room temperature.

Experiments were carried out too, when sample was subjected to annealing at high temperature (950 K) during different time intervals with following quenching to room temperature., the temperature dependence of current in the sample quenched during 24 hours is shown on Fig. 3*a*. Two straight line parts appeared in the temperature dependence. The change of slope was noted approximately 280 K. In the sample, which was annealed during 3–4 hours (Fig. 3*b*), the change of slope was noted approximately 340 K. The values of activation energy are shown at Table 2.

Temperature dependence of ionic current in the crystal can be represented as:

$$I(T)=\frac{U}{T}\left(\sum_{i=1}^{n}C_i e^{-\frac{E_i^a+E_\mu^a}{k_B T}}+C_v e^{-\frac{E_\mu^a}{k_B T}}\right), \tag{1}$$

where U – electric field intensity; E_i^a – binding energy of vacancy in associate of i-type ($i=1$ corresponds to dipoles, $i=2$ corresponds to dimers etc); E_μ^a – activation energy of mobility of vacancy; C_v – parameter determined contribution of free vacancies in ionic current; C_i – parameter depending on concentration of associates of *i*-type, among others. The later determines their contribution to the value of ionic current.

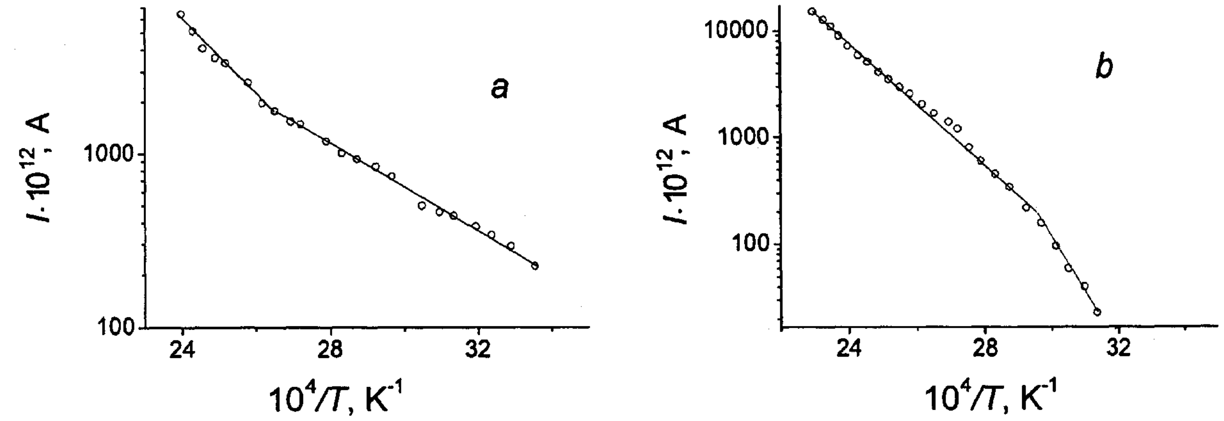

Fig. 3. Temperature dependences of current in quenched crystals CaF_2–O^{2-}: *a* – annealing during 24 hours; *b* – annealing during 3–4 hours.

Table 2

Activation energies for quenched samples

Number of sample	Activation energy, low part, eV	Activation energy, upper part, eV
Sample No. 3	0,25 ± 0,03	0,43 ± 0,02
Sample No. 4	0,87 ± 0,03	0,55 ± 0,01

The charge carriers mainly liberated from bound states can be a part of ionic current in the crystal, which has not been subjected to thermal treatments for a long time. The binding energies in the associates of different types are unequal. Binding energy of vacancies at dipoles is 0,89 eV, in quadrupoles – 1,01 eV (two ions of oxygen and two vacancies) according to [5], i.e. the more complex the structure of associate is the more strongly the vacancy is bound in it. Therefore, at the low temperature the contribution to current is the most probably from the simplest associates (dipoles). Accordingly, the ionic current can be present as follows:

$$I = \frac{U}{T}\left(C_1 e^{-\frac{E_1^a + E_\mu^a}{k_B T}} \right), \tag{2}$$

where E_1^a is binding energy of vacancy in dipole.

The subsequent modification of associates into more complex ones occurs after annealing at high temperature and following long cooling to room temperature. The milkiness (haziness) can be probably connected from this. We can suppose that binding energy of vacancies in such unions is higher than in the aforementioned associates. This is confirmed by the fact that annealing at 550 K and following quenching do not result in disappearance of milkiness. Consequently, the probability of destroyed of compound associates at room temperature is insignificantly. The milkiness in the investigated samples had a bulk nature. It is proved by impossibility of its removal by polishing samples' surface. The crystal gets limpidity after the annealing at high temperature (~ 950 K) and subsequent quenching to room temperature. In [4] the milkiness of crystals is also connected with the presence of the compound associates (precipitates).

The compound associates cannot make considerable contribution to ionic current in the crystals processed as described above. However, there are also a small number of free vacancies, which presence might cause low-level ionic current. Therefore, low-temperature part of Fig. 3 can be presented as

$$I = \frac{U}{T} C_v e^{-\frac{E_a^\mu}{k_B T}}. \tag{3}$$

The value of corresponding activation energy can be compared to activation energy of mobility of free vacancies. Earlier, the activation energy of mobility was estimated at 0,51 eV [3]. Yet formation of F_{2h} centers in fluoride calcium at 150 K [6] and the results of research [2] related to motion of vacancies at the 150 K are the evidence of considerable mobility. The lowest value of activation energy of ionic conductivity was known from [7] (0,07 eV), found in the crystals of CaF_2 – CaO. Thus, we can assume that the activation energy of mobility in the crystals of fluoride calcium at least doesn't exceed the value 0,15 eV.

3.2. Optical measurements

The availability of oxygen in investigated crystals is shown by excitation of characteristic broadband luminescence with $h\nu_m$ about 2,5 eV. Quenching of the sample from 1100 K to room temperature resulted in decrease of the luminescence, which did not restore during long-term storage at room temperature. The time of storage in the aforementioned experiments was two months. The restoring of luminescence occurred after heating up of the crystal. Luminescence is more intense than a higher the temperature of heating. The sample is heated in the stove for the obtaining of temperature dependence of luminescence restoring. The measuring of luminescence is carried out at the room temperature after five-minutes holding at the given temperature. The temperature dependence of luminescence increment of inverse temperature at semi-logarithmic coordinates is shown at Fig. 4. The energy of thermoactivation process of luminescence restoring was (0,29 ± 0,02) eV, as calculated from the given dependence.

The quenching of sample influences also upon decrease of absorption pertaining to oxygen-vacancy dipoles. Absorption was measured at 200 nm on the long-wave part of band with maximum 6,7 eV. As a result of the quenching the absorption reduced by 20 %.

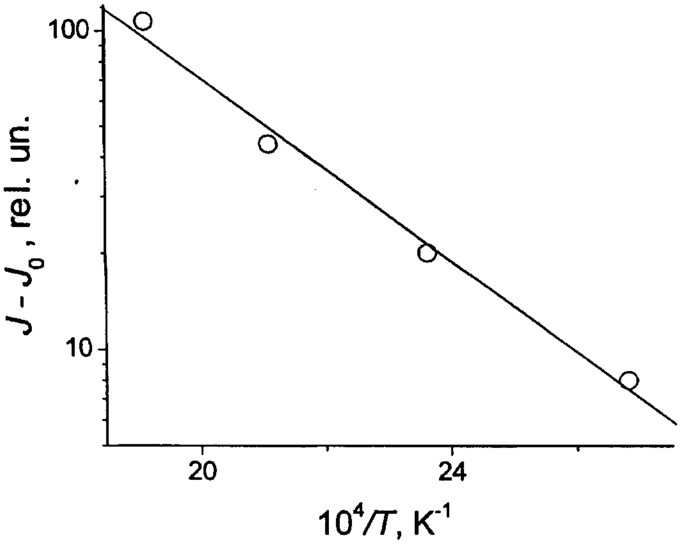

Fig. 4. The value of increment of luminescence subject to temperature of heating of crystal CaF_2–O^{2-}.

The shown results are evidence, that the high-temperature annealing destroys oxygen-vacancy's dipoles dividing them on oxygen's ion O^{2-} and anionic vacancy. The vacancies are mobile at room temperature, and we might expect the centers of luminescence to be restored during storage of a sample. However, as demonstrated by experiments, the activation energy of 0,29 eV is required to make it happen

As the experiments used a long-stored sample, that we can suppose, that local compensation of charge in such crystal did occur, but in order to form the centers of luminescence, the energy for rebuilding the components of the centers was required.

4. CONCLUSIONS

The following results are got in this work.

(i) Quenching of CaF_2 – O^{2-} crystals from 1100 K results in destruction of luminescent oxygen-vacancy dipoles. The activation energy of 0,29 eV is required for restoring luminescence.

(ii) The activation energy of mobility of vacancies in fluoride calcium doesn't exceed 0,15 eV.

REFERENCES

1. V.A. Arkhangelskaya, V.M. Reiterov, L.M. Trofimova, Impurity absorption of alkaline-halogen fluorite crystals in vacuum UV spectra, Zh. Prikl. Spectroscopii, **32**(1), 103–109 (1980).
2. V.V. Pologrudov, E.E. Penzina, K.K. Kheder, Electron transfer under photoexcitation of Oxygen-Vacancy Centers in CaF_2, SPIE Proceedings, in this volume.
3. W. Bollmann, H. Henniger, Concentration and mobility of fluorine ion vacancies in CaF_2, Phys. Stat. Sol. (a), **11**, 367–371 (1972).
4. P.W.M. Jacobs, S.H Ong, Thermal depolarization in crystals of calcium fluorite doped with oxygen, J. Chem. Phys., **41**(3), 437–441 (1980).
5. W. Bollmann, Absorption, ionic conductivity, and thermal depolarization of oxygen-containing CaF_2 crystals, Cryst. Lattice Defects, **7**(1), 139–148 (1977).
6. R. Rauch and G. Schwotzer, Disturbed color centers in oxygen doped alkaline earth fluoride crystals after X-ray irradiation at 77 and 295 K, Phys. Stat. Sol. (a), **74**(1), 123–132 (1982).
7. P. Asadi, On the existence of a spontaneous polarization in fluorite single crystals doped with lime, Phys. Stat. Sol., **16**, K55-K59 (1966).

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