

Ionic Conductivity in the Crystals of Calcium Fluoride with Oxygen

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Abstract – The temperature dependences of ionic current in crystals $\text{CaF}_2\text{-O}$ were investigated. It has been found that the temperature dependence after thermal treatment can be represented in the form of two exponents with different indexes. The activation enthalpies were estimated, and one of them is related to the enthalpy of mobility for the anionic vacancies, and the other to the binding energy of oxygen-vacancies dipoles.

1. Introduction

The oxygen ions, replacing ions of fluorine, in the calcium fluoride, must be charge compensated. Compensation occurs by means of the positively charged anionic vacancies. In the thermodynamic-equilibrium state, the vacancies with oxygen ions form the associates (dipoles, quadrupoles, etc.), i.e. a local compensation for charge exists.

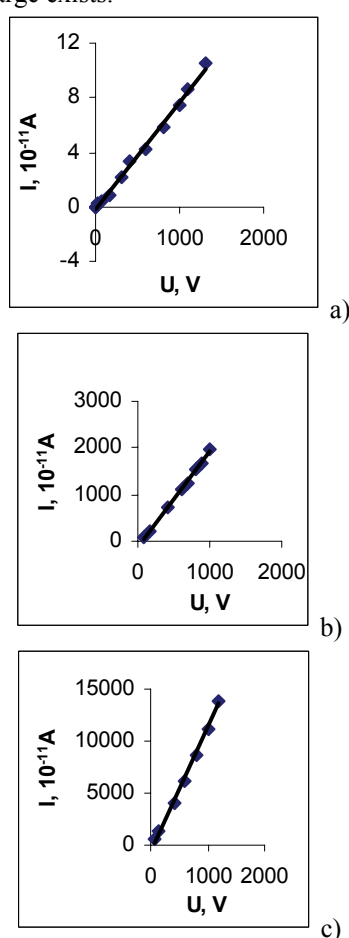


Fig. 1. Ionic current as a function of the applied electric field at various temperatures (a – at the room temperature, b – at 370 K, c – at 400 K)

2. Experimental method

The volt-ampere method was used to measure conductivity, i.e. the ionic current through the crystals was measured.

The $\text{CaF}_2\text{-O}$ crystals investigated in this work, were grown by Stockbarger method in a graphite crucible in vacuum. Electrodes from the indium-gallium eutectic of a diameter of approximately 10^{-1} cm were used. The ohmic nature of the contacts is shown in the volt-ampere characteristic curves (Fig. 1).

Measurements were made for the samples in vacuum. The maximum voltage applied to the electrodes was < 1000 V, and the thickness of samples was about 1 mm. The temperature was measured by the aid of a copper-constantan thermocouple.

The following successive procedures we called one cycle: the measuring of temperature dependence, holding the crystal in the electric field at high temperature and cooling the crystal to the room temperature.

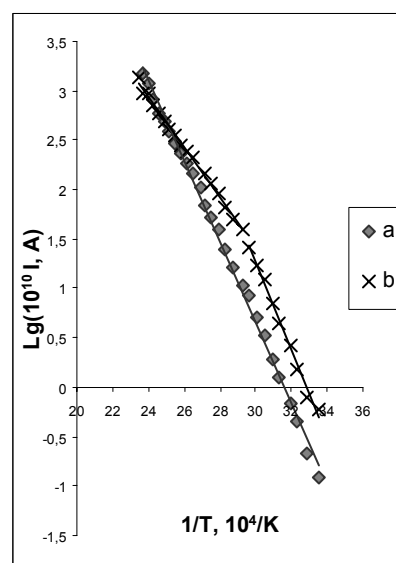


Fig. 2. Temperature dependences of current of the non-quenched sample (sample 1) (a – first cycle, b – third cycle)

3. Experimental results

The temperature dependence of current takes the form represented in Fig. 2(a). The dependence in coordinates $\text{lg}I \sim 1/T$ is linear. Energy of thermal activation process, determined according to the slope of the straight line (Fig. 2(a)), is equal to 0,82 eV. After measuring of the dependence, the sample held at temperature 430 K for 40–60 minutes and then quenched

to room temperature during 15–40 minutes. These procedures represent one cycle.

In the subsequent cycles, the form of temperature dependence is modified. Two straight parts appear in it (Fig. 3 (b)). The low-temperature part corresponds to the values of activation energy lying at the interval 0,83–1,00 eV, depending on the number of cycle, and to the upper part – 0,51–0,66 eV (Table 1). The change in the slope in all dependences is observed at about 340 K.

The investigated samples were initially annealed at temperature 1100–1200 K for 3,5 hour and then quenched to room temperature. In the temperature dependence of quenched samples, the appearance of two linear parts was also observed, for which a change in the slope occurs in the region 340–350 K, and the values of the activation energy for the upper and lower parts are equal to 0,55 and 0,87 eV, respectively (Fig. 3).

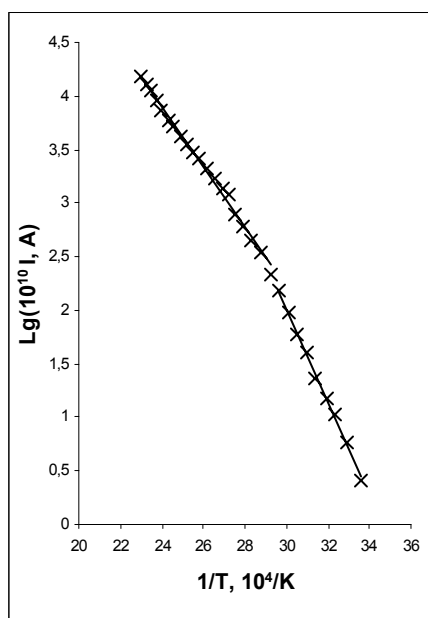


Fig. 3 Temperature dependence of current of the quenched sample (sample 3)

It is necessary to note that the current in the sample, recorded at room temperature, which subjected to the thermal treatment in the first cycle, substantially increases.

4. Discussion

In the samples, which had not subjected to the thermal treatments, non-equilibrium charge carriers are absent, and in the ion current only the charges liberated from the bound states can participate. This process is described by exponential dependence:

$$I = \frac{C}{T} e^{-\frac{E}{kT}}, \quad (1)$$

where $E = E_a + E_\mu$ – the energy of the activation of whole process, E_μ – enthalpy of mobility of vacancies,

and E_a – binding energy of associates, C – parameter, depending on the concentration of associates and on the frequency factors of the processes of releasing of vacancies and their motion.

Table 1. The values of activation energy

Sample	Comment	Number of cycle	Activation energy, lower part, eV	Activation energy, upper part, eV
1	non-quenched	1	0,870± 0,012	0,870± 0,012
		2	1,010± 0,030	0,660± 0,012
		3	0,860± 0,037	0,500± 0,015
2	non-quenched	1	0,810± 0,010	0,810± 0,010
		2	0,930± 0,034	0,650± 0,013
		3	0,890± 0,028	0,510± 0,010
3	quenched	1	0,870± 0,020	0,550± 0,010

In the subsequent cycles, both the charges, liberated from the bound states, and the non-equilibrium charges, arisen as a result of the previous thermal treatments, are involved in the current. This fact explains the considerable increase at room temperature in the current after the first cycle of measurements. Thus, for the subsequent cycles, the dependence of current on the temperature can be represented as a summation of the two components:

$$I = \frac{C}{T} e^{-\frac{E_a + E_\mu}{kT}} + \frac{\tilde{C}}{T} e^{-\frac{E_\mu}{kT}}. \quad (2)$$

This fact is reflected in the modification of temperature dependence after the thermal treatment of the crystal (Fig. 2, 3). Temperature dependence consists of two linear parts, and the slope of the lower part of dependence increases. The modification of dependence occurs due to the non-equilibrium charge carriers, which are responsible for the appearance of the second term in eq. 2. At high temperatures, when associates are dissociated, only the motion of free vacancies determines the ionic current.

The slope of the high-temperature part in different cycles is unequal. The decrease is more significant, as the number of cycle is higher. The minimum value, which has been obtained, corresponds to energy 0,51 eV. This value coincides with the value of the enthalpy of mobility of anionic vacancies, obtained by Bollmann [1].

The binding energy of vacancies in the associates can be estimated using the obtained value of the enthalpy of mobility of vacancies. It was found to lie within the limits of 0,31–0,36 eV. It can be supposed from the luminescence characteristics of our crystals that the investigated associates are dipoles.

References

- [1] W. Bollmann; phys. stat. sol. (a) 40, 49 (1977).