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EFFECT OF LATTICE OXYGEN ON THERMAL AND ELECTRICAL PROPERTIES OF FLUORITE

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UDC 536.21+537.311+537.22

The electrical conductivity, thermal conductivity, and thermo-emf of CaF_2 crystals with an oxygen impurity are measured. Values of the defect transfer parameter are obtained. The existence of thermal diffusion of oxygen-vacancy complexes in fluorite is proposed.

One of the greatest difficulties in synthesizing fluorite crystals is elimination of oxygen, which is always present in the original ingredients. This problem arises because of the direct connection between optical properties of CaF_2 and O^{2-} concentration. In particular, the presence of oxygen produces unsatisfactory radiation stability in the crystals, low transparency in the ultraviolet, existence of light-scattering phases, etc. At the same time, in growth of CaF_2 crystals activated by rare earth metals for use as volume registration devices oxygen plays an important role, since it ensures stability of the nonequilibrium transition of the rare earth ion from the trivalent to the bivalent state [1]. Thus, it is of practical importance to study means for determination and control of oxygen content in fluorite specimens.

In contrast to univalent cation impurities which are able to produce both vacancies and interstitial ions (depending on the mode of solution in the fluorite lattice), the presence of O^{2-} leads only to vacancies [1]. Thus, the coincidence of kinetic defect parameters in oxygen-containing crystals and specimens of CaF_2 + MeF is additional and independent confirmation of the vacancy nature of the defects produced by a univalent metal impurity (as in the case of BaF_2 [2]). Interest in the anion impurity in anti-Frankel systems is caused by the fact that in this case conditions exist for thermal diffusion of the impurity ion or its complexes.

The present study considers the electrical conductivity, thermal conductivity, and thermo-emf of a number of oxygen-containing CaF_2 specimens. The measurement method is described in [4, 5]. The specimens were produced by the Stokebarger method in a graphite crucible. Doping with oxygen was effected by admission of a weak air flow through the vacuum crystallization chamber over the course of the entire crystal-growth process. As a result, the transmission spectra of the crystals (Fig. 1) show intense absorption bands at ~155 nm and ~205 nm, connected with the presence of O_2 [3]. For comparison, Fig. 1 also shows the transmission spectrum of pure CaF_2. In both specimens (Nos. 1 and 6, Fig. 2a) the oxygen content was determined to an accuracy of 20% by the vacuum fusion method (No. 1, 0.22 mole % O^{2-}; No. 6, 0.64 mole % O^{2-}).

Results of conductivity measurements on several $CaF_2 + O_2$ specimens (Nos. 1-6, Fig. 2a) reveal that the temperature dependences $\sigma = f(1/T)$ are similar to each other and to analogous functions for crystals of CaF_2 + NaF (No. 7, Fig. 2a). On the curves $\sigma = f(1/T)$ one can distinguish segments of natural conductivity (high-temperature region), dissociation (middle region), and association (low-temperature region). The slopes of these segments characterize the activation energies, which, within the limits of experimental error, coincide with the following values for CaF_2 + NaF [4]: in the dissociation region $h_- = (0.5 \pm 0.03)$ eV, in the association region $(h_- + (^1/_2)h_{a-}) = (0.7 \pm 0.05)$ eV. Hence, the bonding energy of the O^{2-}-vacancy h_{a-} complex is

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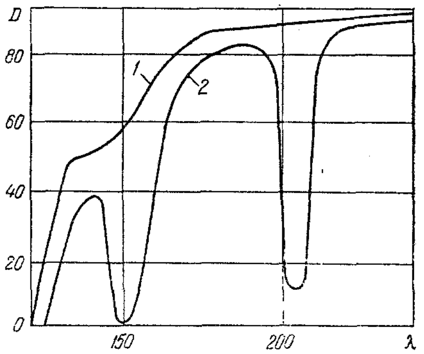

Fig. 1. Transmission spectra of pure (1) and oxygen-containing (2) CaF_2.

equal to (0.4 ± 0.1) eV. If we then commence from the known oxygen concentrations and use the conductivity values to determine the anion vacancy mobility, the values obtained are almost 30 times smaller than those found for CaF_2 + NaF specimens [4] (the divergence with the data of [6] is still greater). At the same time, measurements on alkali halide crystals [7] indicate that carrier mobility is weakly dependent on the type of impurity. This same opinion was also maintained in [8], where anion vacancy mobilities in SrF_2 + NaF and SrF_2 + SrO were taken to be identical. Assuming that the kinetic vacancy motion parameters coincide for Na^+- and O^{2-}-doped crystals, by preceding in the opposite direction and using the vacancy mobility value u_- in CaF_2 + NaF in the dissociation region, we can find the electrically active oxygen concentration. These concentrations prove to be equal to 10^{-2}, $2.7 \cdot 10^{-2}$; $3.2 \cdot 10^{-2}$; $4.1 \cdot 10^{-2}$; $5.9 \cdot 10^{-2}$; and $1.18 \cdot 10^{-1}$ mole % O^{2-} for specimens No. 1-6, respectively. Use of these values in analysis of concentration isotherms [9] over the entire experimental temperature interval for u_- gives the following expression:

$$u_- = \frac{45}{T} \exp\left[-\frac{(0.5 \pm 0.15)}{kT}\right] \text{cm}^2/\text{V} \cdot \text{sec}. \tag{1}$$

The bonding energy v_{a^-} of the oxygen-vacancy complex can be written in the form

$$v_{a^-} = (0.75 \pm 0.4) - (10 \pm 6)\,kT\ \text{eV}. \tag{2}$$

The difference between the known concentration and that determined from the conductivity for specimens Nos. 1 and 6 is evidently caused by differing methods of O^{2-} disposition in the fluorite. An important role is played in CaF_2 crystal growth by pyrohydrolysis [10], as a result of which centers are formed corresponding to displacement of a fluorine ion by hydroxyl groups [11]. The replacement of F^- by OH^- does not lead to the appearance of mobile vacancies and, consequently, does not affect conductivity. The existence of oxygen in a nonlattice form in the light-scattering phase of the crystals is also possible. Consequently, the concentration c_σ of electrically active oxygen will differ from the total O_2 content in the specimen. Comparison of data for specimens Nos. 1 and 6 indicates the relatively small portion (from 5 to 30%) of oxygen-vacancy centers in the oxygen-containing impurity.

This conclusion was confirmed by measurements of thermal resistance W, which are shown for two specimens (No. 6 and a pure CaF_2 crystal) in Fig. 2b. The value of W of No. 6 varies linearly with temperature, preserving the slope characteristic of pure CaF_2, i.e., the additional thermal resistance caused by the impurity is independent of temperature. Also, it should be proportional to impurity concentration [12]. Measurements on alkali halide crystals doped by bivalent cations [13] led to the conclusion that for similar radii of dopant and original ions (O^{2-} — 1.36 Å; F^- — 1.33 Å) the additional thermal resistance shows properties intrinsic to isotopic phonon scattering. For oxygen-vacancy complexes the value of the additional thermal resistance of the isotopic sort is equal to $W_i = 6.7 \cdot 10^{-3}\, c_\lambda$ m·deg/W (for hydroxyl centers W_i is still smaller). Comparing the experimental and calculated values of W_i, we obtain an estimate of the "isotopic" oxygen-impurity content c_λ, which proves to be higher than c_σ (for specimens Nos. 3 and 6, $c_\lambda = 0.1$, 0.6 mole %; $c_\sigma = 3.2 \cdot 10^{-2}$, $1.8 \cdot 10^{-1}$ mole %). The ratios c_λ / c_σ lie within the limits 5 to 30%, as determined by comparison of c_σ with vacuum fusion data, i.e., the value of c_λ is probably a reasonable estimate of total oxygen content in the fluorite crystals. The highest concentration of electrically active oxygen-vacancy centers in the specimens studied was $c_\sigma \simeq 0.2$ mole % < $c_\lambda \simeq 0.6$ mole %. However, the conductivity curves show no transitions into the precipitation region [2]. It is probable that the limiting solubility was not reached in the experiments. At the same time, a portion of the oxygen-containing impurity is not in a state transformable to the electrically active form.

Results of thermoelectric measurements on specimens Nos. 3, 6, and 7 are presented in Fig. 2c. For analysis of the change in α observed on transition from CaF_2 + NaF to CaF_2 + O_2 we write the

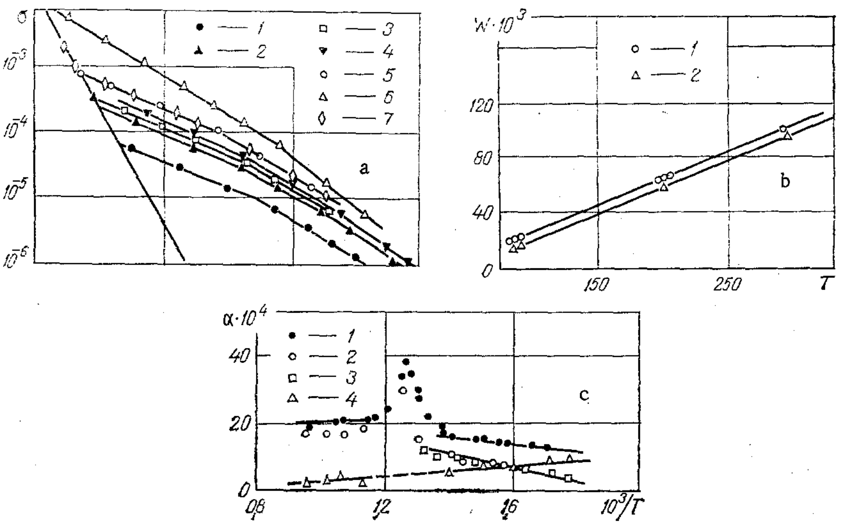

Fig. 2. Temperature dependence of thermal and electrical parameters of fluorite: a) conductivity of CaF_2 with O_2 impurity (1-6, Nos. 1-6) and NaF (7, No. 7): b) thermal resistance of CaF_2 (1, No. 6: 2, pure); c) thermo-emf of CaF_2 (1, No. 7; 2, No. 3; 3, No. 6; 4 [α (No. 7) — α (No. 2)]).

thermo-emf coefficient of the vacancy-saturated coefficients with anti-Frankel defects in the form [4]

$$\alpha = \frac{\varepsilon_-}{eT} + \frac{\tau_c Q_c}{lT} + \frac{k}{e}\ln\frac{eN_{X^-}u_-}{\sigma} - \frac{s_e}{e}, \tag{3}$$

where in contrast to the normal representation of α in impure crystals the quantity $\tau_c Q_c$ [14] is used, characterizing the effect on thermo-emf of migration of oxygen-vacancy complexes with corrected transfer number τ_c (τ_c positive for complex motion in the direction of motion of positively charged particles in an electric field) and heat of transfer $Q_c = Q_{O^{2-}} + Q_- + h_{a^-}$. The decrease of α in oxygen-containing crystals in comparison to Na-doped crystals with similar conductivity values can be ascribed to changes in the conditions for occurrence of reactions at the electrodes (parameter S_e), since the oxygen evidently replaces fluorine ions more active in electrical exchange. If the heterogeneous component of the thermo-emf remains unchanged, and the energy and kinetic parameters of the vacancies are identical in the CAF_2 + NaF and $CaF_2 + O_2$ specimens, then the deciding role will be played by diffusion of complexes. With a vacancy mechanism of oxygen ion displacement $Q_c < 0$ (complexes migrate along the temperature gradient) [9]. With increase in temperature the number of complexes drops, i.e., the difference [α(No. 7) — α(No. 2)] should decrease (Fig. 2c). According to Wirtz [9] $Q_- \simeq h_- \simeq 0.5$ eV, and $h_{a^-} \simeq (0.4\text{-}0.7)$ eV. Consequently, taking $Q_{O^{2-}} \simeq Q_-$ we have $Q_c \simeq 2Q_- + h_{a^-} \simeq -0.5$ eV, and in the impurity conductivity region $e\tau_c \simeq 1$. It appears that the value of τ_c obtained is too high, so that the oxygen impurity also affects the occurrence of the heterogeneous reaction.

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NOTATION

σ, conductivity, $\Omega^{-1} \cdot cm^{-1}$; h_-, vacancy mobility activation enthalpy, eV; h_{a^-}, oxygen-vacancy complex association enthalpy, eV; T, temperature, °K; W, thermal resistance, m·deg/W; u_-, anion vacancy mobility, $cm^2/V \cdot sec$; v_{a^-}, oxygen-vacancy complex binding energy, eV; c, concentration, mole %; α, thermo-emf coefficient, V/deg; e, electronic charge; ε_-, anion vacancy transfer energy; k, Boltzmann's constant; s_e, heterogeneous reaction parameter; τ_c, corrected transfer number; Q, anion vacancy transfer heat; $Q_{O^{2-}}$, oxygen ion transfer heat; Q_c, complex transfer heat; D, transmission, %; N_{X^-}, anion density in fluorite lattice.

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METHOD AND APPARATUS FOR ACCURATE MEASUREMENT OF TEMPERATURE OF A HOT PLATE BY A COMPENSATION THERMOSENSOR

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A method is described for accurate temperature measurement by a contact thermosensor, based on eliminating heat loss through the sensor during measurement. The error in measurement of the temperature of heated thermally "thin" plates comprises 1.6°K.

The technique of thermophysical experimentation is simplified significantly when the specimen to be investigated is chosen in the form of thermally "thin" plates or cylinders. However, as a rule, accurate measurements of temperature then present great difficulty. In a number of cases accurate temperature measurements on thin plates may be performed by radiation pyrometry methods which do not require a knowledge of the material's emissivity [1, 2]. However, the area in which such techniques may be employed is limited to optically opaque bodies and requires special experimental conditions.

Contact methods of measurement provide highly accurate information if special measures are taken to eliminate the disturbing influence of the thermoprobe on the ribbon temperature field.

The appropriate corrections may be calculated, for example, with the formula presented in [3].

For the case where the thermoprobe can be approximated by a bar, the formula relating the actual temperature of the ribbon t_0 before contact of the thermoprobe with that after contact t_e, as measured by the thermoprobe, is written in the form

$$t_0 = t_e\left[1+\sqrt{\frac{\lambda\alpha h_0}{\lambda_0\alpha_0 R}}\cdot\frac{K_0(\nu)}{K_1(\nu)}\right], \tag{1}$$

where $K_0(\nu)$ and $K_1(\nu)$ are modified Bessel functions of the second kind of zero and first orders.

The parameter

$$\nu^2 = \frac{2\alpha_0}{h_0\lambda_0}R^2; \tag{2}$$

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