THE STUDY OF ION TRANSFER IN STRONTIUM FLUORIDE BY THE THERMO-emf METHOD

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The results are given of measurements of the thermo-emf and of the reducibility of pure and impure strontium fluoride on the basis of which characteristics of ion transfer are obtained.

Measuring thermoelectric potentials is one of the most important methods of studying ion transfer under the influence of a temperature gradient, since it enables us to determine in ion-conducting materials the main characteristics of this process — the values of the transfer heat. Here what is of special interest is establishing the mutual connection between the values of the transfer heats and the parameters found as a result of other independent measurements. Among them, following [1], are the amounts of the activation mobility energies calculated from the conductivity. In the present study we give data on research into the temperature dependences of the thermo-emf coefficient and electric conductivity of SrF_2 and SrF_2 with impurities NaF_1YF_3, and LuF_3 in the range 550-1100°K. The measurements were made in accordance with the methods described in [2].

The researches which have been carried out showed that, as in CaF_2 [2-4], we observe in SrF_2 with YF_3 and LuF_3 impurity a breakdown in the increase in conductivity with increase in the content of the

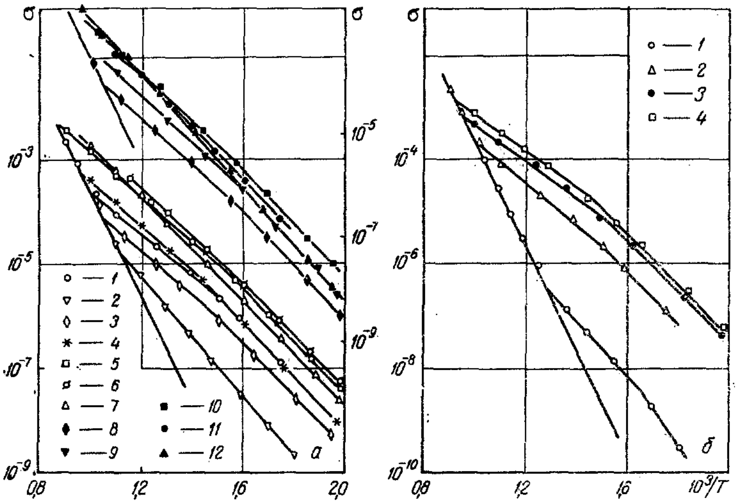

Fig. 1. Conductivity of SrF_2 samples versus temperature. a): 1) pure, 2) 0.001 M% YF_3; 3) 0.03 M% YF_3; 4) 0.1 M% YF_3; 5) 0.5 M% YF_3; 6) 1 M% YF_3; 7) 3 M%; 8) 0.03 M% LuF_3; 9) 0.1 M% LuF_3; 10) 0.5 M% LuF_3; 11) 1 M% LuF_3; 12) 3 M% LuF_3 (right-hand scale for 8-12); b): pure (1, 2) and admixture (3, 4) samples of SrF_2.

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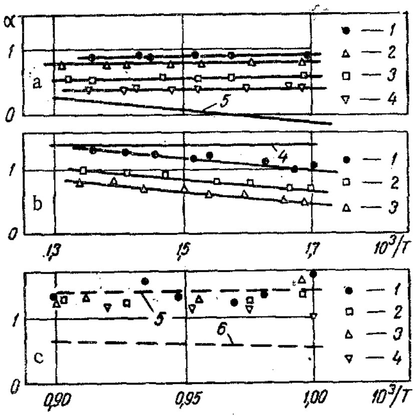

Fig. 2. Thermal emf α of SrF_2 crystals: a, 1) 0.5 M% YF_3; 2) 0.5 M% YF_3 LuF_3; 3, 0.03 M% YF_3; 4, 0.001 M% YF_3; 5, calculated value G_i/kT; b) 1 and 2, pure samples; 3, 1 m% NaF; 4, calculated value G_i/kT; c) 1 and 2, pure sample; 3, 0.001 M% YF_3; 4, 0.03 M% YF_3; 5, and 6, extrapolated values of $G_v/kT—G_i/kT$ and for low-temperature region.

impurity (Fig. 1a). However, this breakdown occurs at higher concentrations of the impurity (0.5 M and higher) than in the case of CaF_2. If we assume, as in [4, 5], that in strontium fluoride, by analogy with CaF_2, the characteristic defects are the anti-Frenkel defects, then the introduction of YF_3 and LuF_3 will lead to the formation of interstitial fluorine ions, and the introduction of NaF will lead to the formation of anion vacancies. Then the result observed is probably caused by more favorable conditions of fluorine ion distribution in the octahedral interstices in the SrF_2 because there is less lattice deformation in the places where the impurity centers are located; apart from geometrical reasons (increase in the lattice constant and cation radii) an important part in this may be played by the increase (compared with Ca^{2+}) in the polarizability of the Sr^{2+} ions. A consideration of the isotherms $[c/\sigma = f(\sigma)]$ makes it possible to describe the mobility of the interstitial anions by means of the expression $u_i = B/T \exp(-0.92/kT)$, $cm^2 \cdot v^{-1} \cdot sec^{-1}$, where $B = 9.2 \cdot 10^3$ ($SrF_2 + LuF_3$) and $B = 6.6 \cdot 10^3$ ($SrF_2 + YF_3$). For the binding energy of the complex Lu^{3+} we have the value 2.77 kcal/mole. The analysis of the SrF_2 specimens with added NaF, the content of which in the crystals grown differed greatly from the content in the initial material (shown in Fig. 1b), was carried out on the basis of the conductivity curves $\sigma T = f(1/T)$. Treating the region of these curves in front of the sector of intrinsic conductivity σ_0 as a region of impurity depletion, we obtain the activation energy of the vacancy mobility $v_V = 17.7$ kcal/mole, and the binding energy of the Na^+-vacancy F^- 11.5 kcal/mole. The magnitude of the defect-formation energy ΔE_f, calculated from σ_0 on the assumption that φ is constant ($\varphi \sim 1$) for various different T [4], is 50.7 kcal/mole.

The results of the thermoelectric measurements are given in Fig. 2a, b, c. In the region of impurity conductivity for specimens with YF_3 and LuF_3 a linear increase is observed in the thermo-emf coefficient α with an increase in ln σ (Fig. 2a), and for specimens with added NaF and "pure" specimens a linear decrease (Fig. 2b) in accordance with the following relationships [2]:

$$e\alpha T - kT \ln \frac{\sigma}{\sigma_0} = -G_i \quad (SrF_2 + YF_3 \text{ or } LuF_3),$$

$$e\alpha T + kT \ln \frac{\sigma}{\sigma_0} = G_V \quad (SrF_2 + NaF).$$

For the integral heat of transfer $q = G_i + G_V = \varepsilon_V^* + \varepsilon_i^* + \Delta E_f$ we obtain 20.7—18.4 kcal/mole, which does not contradict the data on conductivity. Assuming that the heat of transfer of the vacancies is $\varepsilon_V^* = -v_V$, and the heat of transfer of the interstices is $|\varepsilon_i^*| \ll v_i$ [1], we find for $q \approx \Delta E_f - v_V = 33$ kcal/mole. In the region of intrinsic conductivity (Fig. 2c, but here values of G_V and G_i are introduced which are extrapolated from the low temperature region) the quantity α is determined by means of the expression $e\alpha T = G_V - q\varphi / 1 + \varphi$. This fact that the experimentally observed values of α are close to G_V indicates that $\varphi < 1$.

NOTATION

σ, conductivity, $ohm^{-1} \cdot cm^{-1}$; c, admixture concentration, M%; u_i, mobility of interstitial anions, $cm^2 \cdot V^{-1} \cdot sec^{-1}$; σ_0, intrinsic conductivity, $ohm^{-1} \cdot cm^{-1}$; v_i, activation energy of vacancies mobility, kcal/mol; ΔE_f, energy of defect formation, kcal/mole; φ, ratio of interstitial mobility of anions to vacancies mobility; T, absolute temperature, °K; α, thermo-emf coefficient, mV/deg; k, Boltzmann constant, kcal/deg; e, electron charge; G_i, generalized interstitial heat of transfer, kcal/mole; G_V, generalized vacant heat of transfer, kcal/mole; q, integral heat of transfer, kcal/mole; ε_i^*, heat of transfer of interstitial, kcal/mole; v_i, energy of activation of interstitial mobility, kcal/mole; ε_V^*, vacant heat of transfer, kcal/mole.

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