INFLUENCE OF HIGH YTTRIUM CONCENTRATIONS ON THE ELECTRICAL PROPERTIES OF CaF₂ CRYSTALS

EMIL MARIANI*, MATEJ ŠVANTNER*, Bratislava

PAVEL PAVLOVIČ FIODOROV**, BORIS PAVLOVIČ SOBOLEV**, Moscow

In this paper our measurements of dc electric conductivity of CaF₂ : Y³⁺ crystals with the Y³⁺ concentration ranging from 0.1 mol % to 5 mol % are reported. The measured results are compared with a simple association theory and its applicability to the concentrations in question is discussed. The discrepancies from the theory are explained by the presence of oxygen in samples with an YF₃ amount up to 2 mol % and by the formation of large complexes at higher yttrium concentrations, respectively.

ВЛИЯНИЕ БОЛЬШИХ КОНЦЕНТРАЦИЙ ИТТРИЯ НА ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА КРИСТАЛЛОВ CaF₂

В работе приводятся результаты измерений электропроводимости кристаллов CaF₂ : Y³⁺ при постоянном напряжении в области концентраций Y³⁺ 0,1—5 моль.%. Проводится сравнение полученных результатов с теорией простых ассоциаций. Отклонения от теории объясняются присутствием кислорода в образцах, содержащих до 2 моль.% YF₃ или же образованием больших комплексов при более высоких концентрациях иттрия.

I. THEORY

It was proved in many experimental works that the anti-Frenkel defects represent a dominant type of disorder in alkaline fluorides [1—9]. These materials possess the ability to dissolve large amounts of rare earths and yttrium. Their solubility ranges from 30 to 50 mo % at melting temperature [10]. The presence of trivalent impurities substitutionally built into the cationic sublattice increases the concentration of defects. The general relation for the anti-Frenkel type defects

$$x_v = x_0^2 = 2 \exp \left[-g_f/kT \right] \tag{1}$$

in the case of doping by Y³⁺ ions yields

$$x_i = \frac{1}{2} y + \frac{1}{2} [y^2 + 4 \exp \left(-g_f/kT \right)]^{1/2} \tag{2}$$

$$x_v = -\frac{1}{2} y + \frac{1}{2} [y^2 + 4 \exp \left(-g_f/kT \right)]^{1/2} \tag{3}$$

where x_i, x_v, y are molar fractions of the interstitials F$_i^-$, F⁻ ion vacancies, Y³⁺ ions substitutionally built into the cationic sublattice, respectively. The Gibbs free energy of the anti-Frenkel pair formation is denoted as g_f, k is the Boltzmann constant, and T is the temperature. When considering the interaction among defects the relation

$$x_i x_v / x_c = (1/z) \exp \left(-g_a/kT \right) \tag{4}$$

is to be added. It expresses the association between substitutional Y³⁺ ions and F$_i^-$ interstitials. In the case of CaF₂, $z = 6$ is the coordination number of associated complexes, x_c is their molar fraction, and g_a is the Gibbs free energy of complex formation. The last relation is valid for Y³⁺ — F$_i^-$ complexes in the closest neighbourhood, which are formed at low concentrations of Y³⁺. Then the interstitial F$_i^-$ ions are of the cubic symmetry. In the works [12, 13] for higher concentrations the existence of two types of interstitials shifted from the cubic centre is assumed. These interstitials form the basic units for the construction of complexes consisting of more than two defects.

There are two knees in the dependence of dc electrical conductivity on temperature in CaF₂ : Y³⁺ [15, 16]. One is at the transition from intrinsic to impurity conductivity, the other is at the Y³⁺ — F$_i^-$ pairs dissociation. For concentrations of molar fractions $y \leq 3 \times 10^{-4}$ the following relations were found for electric conductivity [14]:

$$\sigma T = 3.45 \times 10^9 y^{1/2} \times \exp \left(-14\,620/T \right) \, \Omega^{-1} \text{cm}^{-1} \text{K for the association, and } \sigma T = 1.32 \times 10^8 y \exp \left(-10\,680/T \right) \, \Omega^{-1} \text{cm}^{-1} \text{K for the dissociation region, respectively.}$$

The transition between the regions is a function of the Y³⁺ concentration. With an increasing concentration it shifts to higher temperatures and the width of the dissociation region decreases.

There are few experimental works devoted to alkaline earts fluorides doped by higher concentrations of trivalent impurities. Therefore, we present in this paper the influence of yttrium — within a wide concentration range — on the electric conductivity of CaF₂ crystals.

II. EXPERIMENTAL

The CaF₂ : Y³⁺ single crystals were synthesized by the Stockbarger method. A slow temperature reduction (1.1 deg/min) was used in tempering. The resulting single crystals with a diameter of 5 mm to 10 mm were cut by a diamond saw and smoothed with abrasive paper. On the smoothed and cleaned samples either colloid

* Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta, CS-899 30 BRATISLAVA.
** Institute of Crystallography, Academy of Sciences of the USSR, Lenin prospect, MOSCOW.

graphite Dag 580 electrodes were vapor deposited, respectively.

The dc electrical conductivity measurements were performed in vacuum within the temperature range from 293 K to 973 K. The temperature was measured by two Pt-PtRh thermocouples. The conductivity measurements were carried out by using a Va-J-51 electrometer.

III. RESULTS

The dependence of dc electrical conductivity on temperature and concentration was measured in two groups of samples: crystals with concentrations 0.1 to 1 mol % Y^{3+} (prepared at the Institute of Physics of the Slovak Academy of Sciences in Bratislava), and those with concentrations 1 to 5 mol % Y^{3+} (prepared in the Institute of Crystallography, Moscow). In Fig. 1 the dependence of the conductivity of CaF_2 crystals with an Y^+ amount up to 1 mol % are plotted. With a higher doping the values of conductivity also increase. At the curve 0.3 mol % of Y^{3+} at the temperature 490 K a region with a lower activation energy is observed caused probably by the presence of O^{2-} ions. A similar increase in conductivity was observed in $BaF_2 : O^{2-}$ by Barsis and Taylor [8].

The courses of electric conductivity at concentrations 1 to 5 mol % of Y^{3+} are plotted in Fig. 2. They are all smooth (no knees). The increase of conductivity with
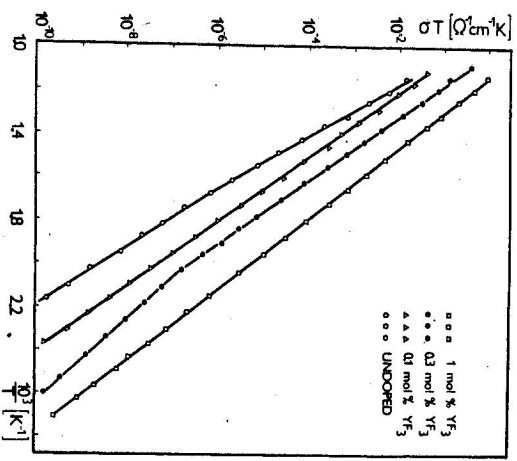

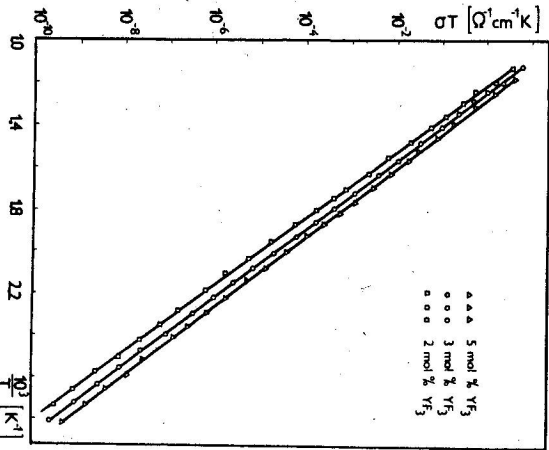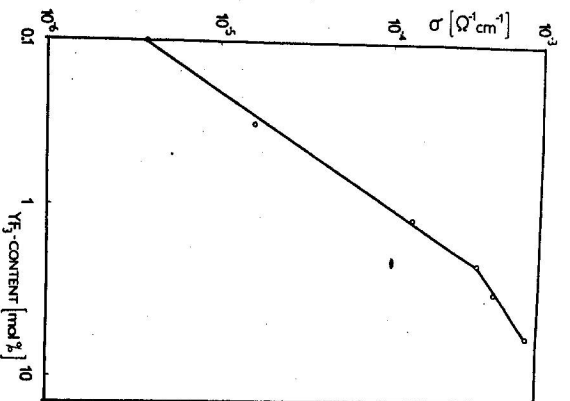
Fig. 1. dc conductivity of CaF_2 crystals doped by YF_3.

□ □ □ 1 mol % YF_3
• • • 0.3 mol % YF_3
▲ ▲ ▲ 0.1 mol % YF_3
○ ○ ○ UNDOPED

Fig. 2. dc conductivity of CaF_2 crystals doped by YF_3.

▲ ▲ ▲ 5 mol % YF_3
○ ○ ○ 3 mol % YF_3
□ □ □ 2 mol % YF_3

a higher concentration remains, though it is not so fast as at lower concentrations. This is illustrated in Fig. 3, where the conductivity isotherm at 769 K for all concentrations is shown.

Fig. 3. dc conductivity of CaF_2 versus YF_3 concentration at 769 K

IV. DISCUSSION

Etzel and Maurer [16] provide that large values of x_i/x_0 we have

$$y = L\sigma^2 + F\sigma .\qquad(5)$$

For a given temperature L and F are constants, from which the mobility of interstitials and the association constant can be determined. Such an analysis of results was done by Ure [5] at temperatures over 963 K. In our temperature and concentration regions the relation (5) is not valid.

In our further considerations we assume the validity of a simple association theory for high Y^{3+} concentrations. We have employed the results derived by Boltzmann and Reimann [14] in the way of extrapolating to higher concentrations. These results were compared with the measured ones.

At temperature 769 K the simple association theory yields for the concentration of free interstitial charge carriers

$$x_d = (y/z)^{1/2} \exp (s_a/2k) \exp (-h_a/2kT) ,\qquad(6)$$

where $s_a = 4.42 \times k$ and $h_a = 0.68$ eV are entropy and enthalpy of association, respectively. The contribution of interstitials to conductivity at 0.1 mol % is

$\sigma_i = n_i v_i e = x_i N v_i e = 1.12 \times 10^{-4} \, \Omega^{-1} \text{cm}^{-1}$. N denotes the molecular density of CaF_2, v_i is the mobility of interstitials F_i^-, e is the charge of an electron. The contribution of thermally created vacancies is $\sigma_v = 1.19 \times 10^{-7} \, \Omega^{-1} \text{cm}^{-1}$. The total conductivity $\sigma = \sigma_i + \sigma_v$ is thus given mainly by the contribution of interstitials. Our measured value $\sigma_{exp} = 3.9 \times 10^{-6} \, \Omega^{-1} \text{cm}^{-1}$ is substantially lower then it follows from the simple association theory. On the other hand, the conductivity increases faster than predicted by the theory.

The presence of oxygen may be one of the reasons for a fast conductivity increase. In the sample it increases the concentration of free anionic vacancies and, consequently, the conductivity. The increase of conductivity at a given temperature will depend not only on the concentration of Y^{3+} dopants but also of the unknown concentration of oxygen. For a high degree of association between Y^{3+} and F_i^- even a small change of oxygen concentration yields a concentration of vacancies comparable with the concentration of F_i^- interstitials.

The lower values of the measured conductivity present another discrepancy from the theory, which confirms a higher degree of association than predicted by the theory. The electrostatic interaction between defect with opposite charges lead at higher concentrations to a clustering of defects into larger complexes than dipoles. These complexes differ only in the number of construction units. We suppose that the knee at the conductivity isotherm at a concentration 2 mol % of Y^{3+} (Fig. 3) is due to the loss of free interstitials and vacancies, which are built into the large complexes.

V. CONCLUSION

The measurements of electrical conductivity of alkaline earth fluorides doped by high concentrations of rare earths and yttrium are difficult to interpret. The association — dissociation transition is shifted to higher temperatures causing the performance of measurements in the association conductivity region. Moreover some discrepancies from the $\sigma \sim y$ and $\sigma \sim y^{1/2}$ dependences occur. These facts confirm that at high concentrations the simple association theory due to Lidiard [17] cannot be mechanically applied.

When this theory was applied for the investigated concentration larger conductivity values than the measured ones were found. Furthermore, the conductivity increases with the concentrations faster than predicted by the theory. This has led us to the conclusion that conductivity is determined not only by the ions created by the Y^{3+} dopants compensation but also by some other free carriers of charge. At a high degree of association of Y^{3+} and F_i^- ions a small dose of O^{2-} can provide a concentration of vacancies comparable to that of free F_i^-.

The results obtained are rather complicated because the defects at the considered concentration may agglomerate into larger complexes. In this manner the conductivity isotherm knee at 2 mol % of Y^{3+} is interpreted.

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