

LOW-TEMPERATURE ASSOCIATION OF NaCl + BiCl₃ CRYSTALS

MÁRIA HARTMANOVÁ*, EMIL MARIANT*, Bratislava

The temperature treatment of NaCl + *x*. BiCl₃ crystals by annealing before the measurement of electrical conductivity causes an increase in the number of substitutionally incorporated Bi³⁺ ions as shown in the present paper. The treatment enables to observe the low-temperature association, i.e. the formation of Bi³⁺ □_k □_k complexes, the existence of which followed from theoretical considerations.

It is shown that the regions of low-temperature associations of the measured crystals have some properties which are in agreement with the association regions for the divalent impurities — vacancies, e.g. a similarity of expressions for the concentration of vacancies. The presence of oxygen in the form of BiO⁺ centres in the samples with a higher amount of bismuth causes an anomaly in the course of the low-temperature association and the extrinsic conductivity region on the whole.

I. INTRODUCTION

The presence of trivalent impurities in alkali halide crystals itself suggests the possibility of at least two association processes — i. e. the existence of at least two kinds of complexes in the ground state.

Theoretical considerations carried out for the case of NaCl + *x*. BiCl₃ [1] have shown that the existence of Bi³⁺ □_k □_k (I) and Bi³⁺ □_k □_k (II) complexes is well founded. This theoretical assumption was partly confirmed also by experimental results [1]. However, the used temperature range over which the association was investigated, but above all the small solubility of bismuth in NaCl were the reasons why only the region of the formation of complexes I was observed experimentally.

Therefore, the aim of the present paper is to confirm the possibility of the existence of complexes II and thus to complement the results published in [1].

* Fyzikálny ústav SAV, 899 30 BRATISLAVA, Dúbravská cesta.

II. EXPERIMENTAL

The size of samples used for measuring the electrical conductivity (0.005, 0.01, 0.1, 0.5 and 1 mol % BiCl_3 in the melt) was approximately $0.6 \times 0.6 \times 0.1$ cm³. The graphite electrodes were coated on the face surfaces. The measurements were carried out in the temperature region of 25–150 °C in vacuum. The measuring electrodes were made of nickel with Pt foils on the surface. The measured sample was put between them. The electrodes were held by quartz and teflon insulators. Heating was provided by a resistance furnace. The temperature was measured by a copper-constantan thermocouple which was placed in the lower electrode. The electrically isolated „cold“ junction of the thermocouple was kept at 0 °C by putting it in a vessel with mercury. This vessel was placed in a Dewar flask with a mixture of ice and water. A Tesla MR 30 digital voltmeter as indicator of temperature was used.

All samples used for measuring the conductivity were submitted to the same temperature treatment — they were annealed at 650 °C for 1 hour in an inert atmosphere and quenched.

The description of the preparation of $\text{NaCl} + x \cdot \text{BiCl}_3$ crystals can be found in [2].

III. RESULTS

Fig. 1 shows the results of the measurements of the electrical conductivity σ in dependence on the temperature in the range of 25–150 °C. The curves 1–5 were measured on crystals without any temperature pre-treatment (as cleaved) and with a different concentration of Bi^{3+} ions added into the melt. The course of σ in the region of the low-temperature extrinsic conductivity can be attributed to an association process between the impurity cations and cation vacancies in agreement with cases of the divalent impurity doping.

The results of measurements of the same dependence as in Fig. 1 can be seen in Fig. 2. The only difference consists in the annealing of the used samples immediately before the measurement of conductivity. It is evident from Fig. 2 that the region of low-temperature extrinsic conductivity for crystals treated in such a way consists of two parts. This fact supports the possibility of the existence of two association processes — i.e. the formation of complexes I and II as it resulted from the theoretical considerations in [1].

The influence of the consideration gradient on the region of low-temperature extrinsic conductivity, especially for crystals with a higher concentration of Bi^{3+} ions, can be seen in Fig. 3.

All used samples were cleaved from the middle parts (m) of grown crystals.

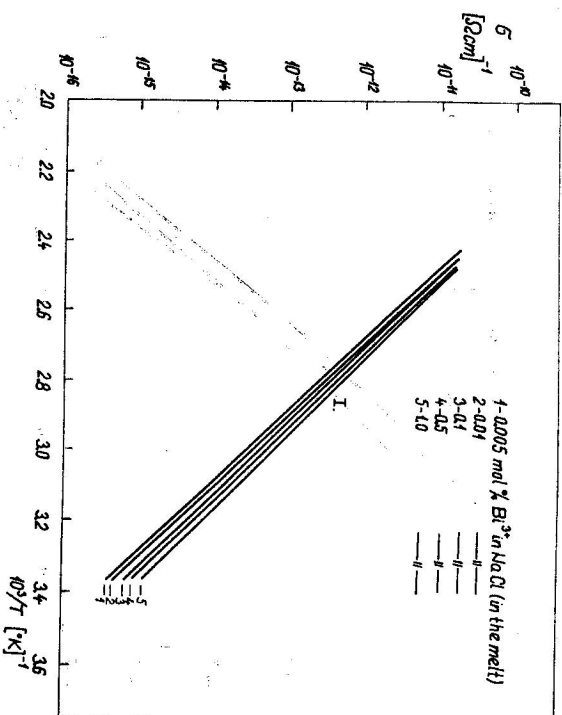


Fig. 1. The temperature and concentration dependences of the electrical conductivity σ for $\text{NaCl} + x \cdot \text{BiCl}_3$ crystals (as cleaved).

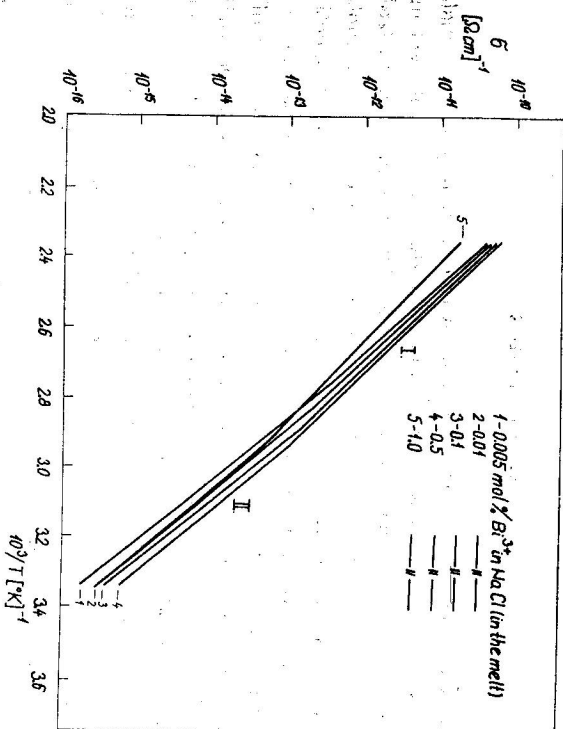


Fig. 2. The temperature and concentration dependences of the electrical conductivity σ for $\text{NaCl} + x \cdot \text{BiCl}_3$ crystals (after annealing).

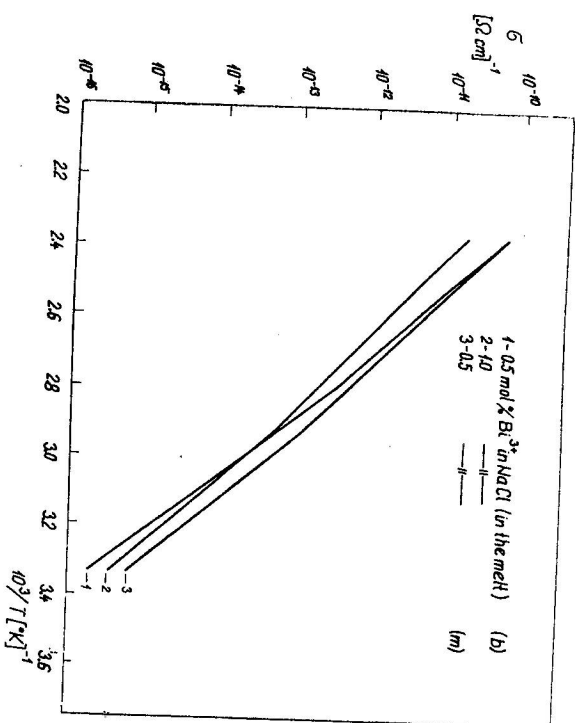


Fig. 3. The influence of the concentration gradient in the crystal on the low-temperature region of the extrinsic conductivity σ .

IV. DISCUSSION

The aim of the present paper is to confirm the possibility of the existence of complexes II and in this way to complement the results published in [1], as mentioned already in the introduction. Therefore we shall concentrate in the following on the region of the low-temperature extrinsic conductivity and the low-temperature association of $\text{NaCl} + x \cdot \text{BiCl}_3$ crystals, respectively.

The substitutionally incorporated Bi^{3+} ion has a double excess charge with respect to the lattice. In such a case we can suppose the existence of two association processes, i.e. the formation of two kinds of complexes $\text{Bi}^{3+} \square_k^-$ denoted as I, and $\text{Bi}^{3+} \square_k^- \square_k^-$ denoted as II, at corresponding lower temperatures, as it resulted from theoretical considerations in [1].

The measurements carried out in crystals without any temperature pre-treatment (as cleaved) have confirmed, however, the existence of the association process I only (Fig. 1). On the basis of theoretical considerations and measurement results from the point of view of the small solubility of Bi^{3+} in NaCl we could assume the formation of complexes I, i.e. $\text{Bi}^{3+} \square_k^-$ only. From the theoretical point of view the sufficient amount of substitutionally incorporated impurity ions should help to discover the other association

process, i.e. the formation of $\text{Bi}^{3+} \square_k^- \square_k^-$ complexes. This assumption was supported also by the observed accidental occurrence of the association region II for crystals without any temperature pre-treatment (as cleaved) at the highest concentrations in dependence on the concentration gradient in the crystal.

We supposed therefore that it would be possible to obtain (first of all at higher concentrations) an increase in the number of substitutionally incorporated ions in crystals doped with trivalent impurities, similarly as in the case of divalent ions, by means of annealing at higher temperatures.

It is seen from Fig. 2 that the association region on plots of $\log \sigma$ vs $1/T$ for the annealed samples actually consists of two parts — I and II. In the following we shall deal in greater detail with the low-temperature association II.

In the low-temperature region, where free trivalent cations do not exist any more (they are partially all bound with vacancies in the form of complexes as long as the solid solution is sufficiently dilute) we can write

$$x_{\text{Bi}} = 0, \quad x_1 = x_{\text{I}} \quad (1)$$

(x_{Bi} — the concentration of free trivalent cations, x_1 — the concentration of free vacancies and x_{I} — the concentration of $\text{Bi}^{3+} \square_k^-$ complexes). The $\text{Bi}^{3+} \square_k^-$ (I) complex has still an excess charge against the lattice. Therefore the next vacancy can preferentially stay close to the $\text{Bi}^{3+} \square_k^-$ and form a $\text{Bi}^{3+} \square_k^- \square_k^-$ complex (II). This process can be described by the equilibrium



Applying the mass action law to the process (2) we obtain the following equation

$$\frac{x_{\text{I}} x_{\text{I}}}{x_{\text{II}}} = K_{\text{II}} \exp \left(-\frac{W_{\text{II}}}{kT} \right), \quad (3)$$

where x_{I} is the concentration of $\text{Bi}^{3+} \square_k^- \square_k^-$ complexes, K_{II} is the constant for the association process (2) and W_{II} is the association energy of the complex II, kT has its usual meaning.

Besides, also the following balance equations are valid

$$\begin{aligned} c &= x_{\text{Bi}} + x_{\text{I}} + x_{\text{II}} \\ x_1 &= 2x_{\text{Bi}} + x_{\text{I}} \end{aligned} \quad (4)$$

(c — the total concentration of bismuth ions in the lattice).

Starting from eqs. (3), (4) and at the same time considering (1), we obtain the following system of equations

$$c = x_1 + x_{II}$$

$$x_{II}^2/x_{II} = \Phi_{II}$$

(Φ_{II} — the right-hand side of eq. (3)). The concentration of free cation vacancies, which is decisive for the behaviour of the association region and the extrinsic conductivity region on the whole, can be determined by the solution of the equation

$$x_1^2 + x_1 \Phi_{II} - \Phi_{II} c = 0 \quad (6)$$

resulting from (5). Hence

$$x_1 = \frac{\Phi_{II}}{2} \left[\left(1 + \frac{4c}{\Phi_{II}} \right)^{1/2} - 1 \right]. \quad (7)$$

The similarity of the expressions for the concentration of vacancies — (7) and the association of vacancies with divalent cations [3] is not surprising because $\text{Bi}^{3+} \square_k \square_k$ complexes are neutral with respect to the lattice.

The influence of the concentration gradient on the low-temperature region of extrinsic conductivity, as represented in Fig. 3, is perceptible in high doping concentrations only. It is evident that the sample cleaved from the region of the highest impurity concentration (bottom of the crystal — b) has a similar behaviour as was observed for 1 mol % BiCl_3 (Fig. 3).

The anomaly in the behaviour of samples with a high concentration of Bi^{3+} as compared with a lower Bi^{3+} amount (Figs. 2 and 3) can be attributed to the presence of oxygen in these crystals. The bismuth is considerably hygroscopic and from the chemical point of view produces relatively stable BiO^+ centres, as confirmed by the results of the optical absorption and the dielectric losses as well [1, 2]. The presence of oxygen in crystals with a high Bi^{3+} concentration (first of all 1 mol % BiCl_3 in the melt) and thus the presence of a higher number of BiO^+ centres, causes on the one hand a decrease in the concentration of Bi^{3+} ions, which can be free or bound with vacancies, on the other hand a decrease in the number of impurity vacancies needed to maintain the electrical neutrality of the crystal. This is shown as an anomaly on the plots of $\log \sigma$ vs $1/T$ — a decrease of the absolute value of conductivity and in the gradually disappearing formation region of complexes II.

V. CONCLUSION

In the conclusion we can summarize the obtained results as follows.

Two association processes which can be attributed to the formation of $\text{Bi}^{3+} \square_k$ and $\text{Bi}^{3+} \square_k \square_k$ complexes on the ground of theoretical considera-

tions are observed in the region of the extrinsic conductivity in samples with a temperature treatment before the measuring of the conductivity.

The appearing of the low-temperature association (the formation of $\text{Bi}^{3+} \square_k \square_k$ complexes) on the plots of $\log \sigma$ vs $1/T$ requires a higher concentration of substitutionally incorporated Bi^{3+} ions. The region of low-temperature association shows in consequence of the neutrality of $\text{Bi}^{3+} \square_k \square_k$ complexes against the lattice, some properties in agreement with the association region for divalent impurity — vacancy, for example a similar structure of expressions for the concentration of free vacancies. The anomaly in the course of $\log \sigma$ vs $1/T$ observed for samples with a higher bismuth amount (i.e. 1 mol % BiCl_3 and 0.5 mol % BiCl_3 (b), respectively) is due to the presence of oxygen in the form of BiO^+ centres in these samples. The presence of a higher number of stable BiO^+ centres causes both the decrease in the absolute value of conductivity in consequence of the decrease in the impurity vacancies and the decrease in the concentration of Bi^{3+} ions and thus the gradual disappearance of the region of low-temperature association, i.e. the formation of $\text{Bi}^{3+} \square_k \square_k$ complexes, observable by means of conductivity measurements.

REFERENCES

- [1] Hartmanová M., Lébl M., Mariani E., Crystal Lattice Defects (to be published).
- [2] Hartmanová M., Mariani E., Lébl M., Czech. J. Phys. B 22 (1972), 623.
- [3] see for example Lidiard A. B., Handbuch der Physik 20 (1957), 246.

Received February 26th, 1973