

PREPARATION OF HIGH PURITY NaCl AND DETERMINATION OF ITS PURITY FROM ELECTRICAL PROPERTIES

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The commonly used „very pure“ NaCl crystals contain a relatively large amount of heterovalent cation impurities, particularly calcium (10^{-4} mol %). We have shown from the temperature dependence of the conductivity and of the dielectric losses that this is still a large amount and its influence on various physical properties has to be considered. We demonstrate further that with a new method of purification single crystals may be grown with a cation impurity content lower by about 2 orders of magnitude ($4 \cdot 2 - 7$) $\times 10^{-6}$ mol % and that from the temperature dependence of the conductivity and dielectric losses the purity of the material used may be estimated.

INTRODUCTION

In experimental studies of electrical properties of solids one starts generally with some relatively „very pure“ material, and adds to it a known amount of the impurity the influence of which is to be investigated. We shall demonstrate, as an example, the influence of calcium on various physical properties of NaCl, to which it is admixed at various concentrations.

The choice of calcium as the studied impurity is intentional, as all the so called pure crystals of NaCl contain a natural impurity „background“, in which calcium prevails. This impurity „background“ cannot be reduced by physical methods such as zone melting or multiple recrystallization, since the separation coefficient of calcium at low concentrations in NaCl is ≈ 1 . [1, 2]. Even a 40 times repeated zone melting failed to reduce noticeably the original calcium content. It may appear at first sight that this „impurity background“ ($\approx 10^{-4}$ mol %) cannot influence the results of doping by other bivalent cations. It is apparent from Fig. 1 that this is not the case; here the temperature dependences of the conductivity are plotted for NaCl crystals doped with

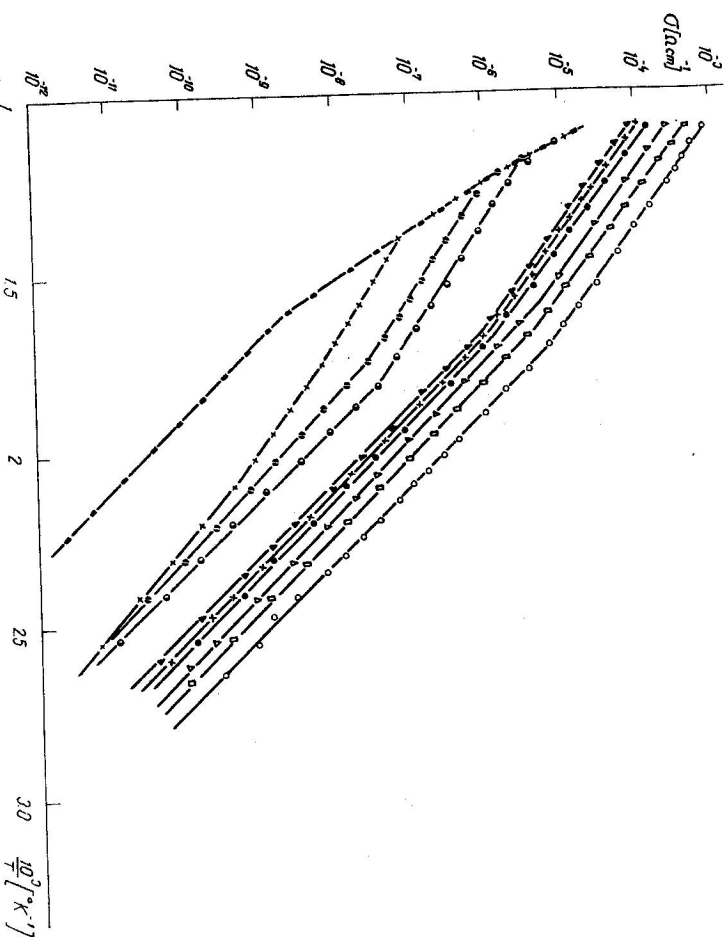


Fig. 1. Temperature dependence of the conductivity of NaCl crystals with various concentrations of CaCl_2 : O — 1 mol % CaCl_2 (in the melt), \square — 0.2 mol %, \triangle — 0.1 mol %, \bullet — 0.04 mol %, \times — 0.02 mol %, \blacktriangle — 0.01 mol %, \bullet — standard purity, specially refined NaCl, \circ — NaCl prepared by the new method of selective extraction of CaCl_2 , \blacksquare — natural NaCl

different concentrations of calcium. The conductivity of a standard-purity crystal is higher by 4 orders of magnitude than that of an ideally pure crystal, while the plots of $\ln \sigma$ vs $1/T$ lie in the middle between the conductivities of the ideally pure and maximum-doped (1 mol % CaCl_2 in the melt) crystals. The ideal dependence is approached by that of the natural crystal of NaCl, although the latter contains the same amount of Ca as standard-purity crystals. During the long storage (millions of years) the calcium has obviously precipitated, and such samples have to be heated to high temperatures in order to restore the substitutional dispersion of the impurity [3].

The preparation of pure substances is accompanied by the difficult problem of determining the purity of the materials used. The optico-chemical methods

are not sufficiently sensitive, the sensitivity limit being about 10^{-4} mol % in the case of Ca^{++} . Apart from that, by these methods it cannot be distinguished whether the impurity is substituted in the lattice or precipitated.

In the following we describe an attempt to apply physical methods in estimating the concentrations of bivalent cation impurities dispersed substitutionally in the lattices of crystals, which have been purified in various ways. These estimates are based on measurements of the temperature dependences of the conductivity and of the dielectric losses.

PREPARATION OF MATERIAL

Several methods exist for the preparation of high-purity material for the growth of NaCl crystals, however, none is suitable for production of larger amounts [4]. In our case the extraction method was used, which has the advantage that it enables one to produce a larger quantity of identical very

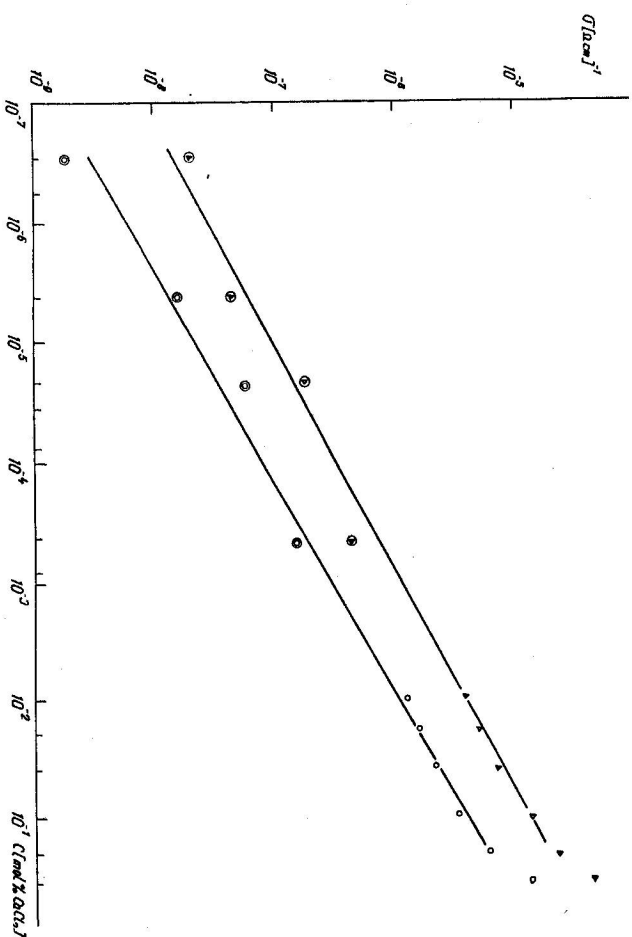


Fig. 2. Isothermal dependence of the conductivity on the CaCl_2 concentration, at temperatures $\triangle - 103/T = 1.48$; $\circ - 103/T = 1.68$.

Table 1

measured by means of UVISPEK	calculated from eq (3)	10^3 at $T = 1.48$	σ [$\Omega \text{ cm}$] $^{-1}$ at $\frac{10^3}{T} = 1.63$
0.2		2.5×10^{-5}	6×10^{-6}
0.08-0.1		1.4×10^{-5}	3.5×10^{-6}
0.04		7.1×10^{-6}	2.1×10^{-6}
0.02		5.1×10^{-6}	1.6×10^{-6}
0.01		4.1×10^{-6}	1.4×10^{-6}
	4.53×10^{-4}	4.0×10^{-7}	1.5×10^{-7} standard purity
	2.1×10^{-5}	1.9×10^{-7}	5.9×10^{-8} specially refined
	4.21×10^{-6}	4.2×10^{-8}	1.6×10^{-8} purified by the described method
	2.92×10^{-7}	2.0×10^{-8}	1.9×10^{-9} natural crystal

pure material. This is very important in the case where a series of crystals is needed for physical investigation.

The extraction was preceded by precipitation of impurities in the form of hydroxides in a medium of higher pH value. After filtration the solution specially prepared for the selective separation of calcium is extracted first with a solution of oxine in chloroform, and then with a solution of dithizone in the same solvent. The dithizone extraction starts in a medium with higher pH, which is subsequently reduced. Crystallization from the extracted solution is performed in a special evaporator [5]. The material thus obtained, free from cation impurities but containing remainders of organic agents and solvents, is placed in a quartz ampoule, which has been previously prepared for crystal growing by the Stockbarger method. In the case of doped crystals the respective amount of impurity (CaCl_2 in our case) is added to this refined material. The filled ampoule is placed in a refining furnace. The molten material is then refined by a halogenating agent, in our case by phosgene, following the method described in [6]. After the refining the ampoule is sealed off under constant flow of the refining gas. Then the single crystal is grown in a different furnace. The organic remainders are pyrolyzed at that temperature and the pyrolytic carbon is expelled to the crystal surface by the crystallization pressure. Infrared absorption measurements on such crystals, even 1.5 cm thick, do not indicate any trace of the band at 2.8μ , which is ascribed to the presence of OH $^-$ ions.

The sample preparation and the measurements of temperature dependences

of the conductivity and dielectric losses were performed in an inert atmosphere using the equipment described in previous papers [3].

RESULTS OF MEASUREMENTS

In Fig. 1 the temperature dependence of the conductivity of pure NaCl crystals is plotted, which were grown from materials obtained by various methods of refinement, and of crystals doped with various concentrations of CaCl_2 . The same dependence is also plotted as obtained from the natural crystal.

In Fig. 2 the isotherms $\ln \sigma$ vs $\ln c$ are shown at two different temperatures.

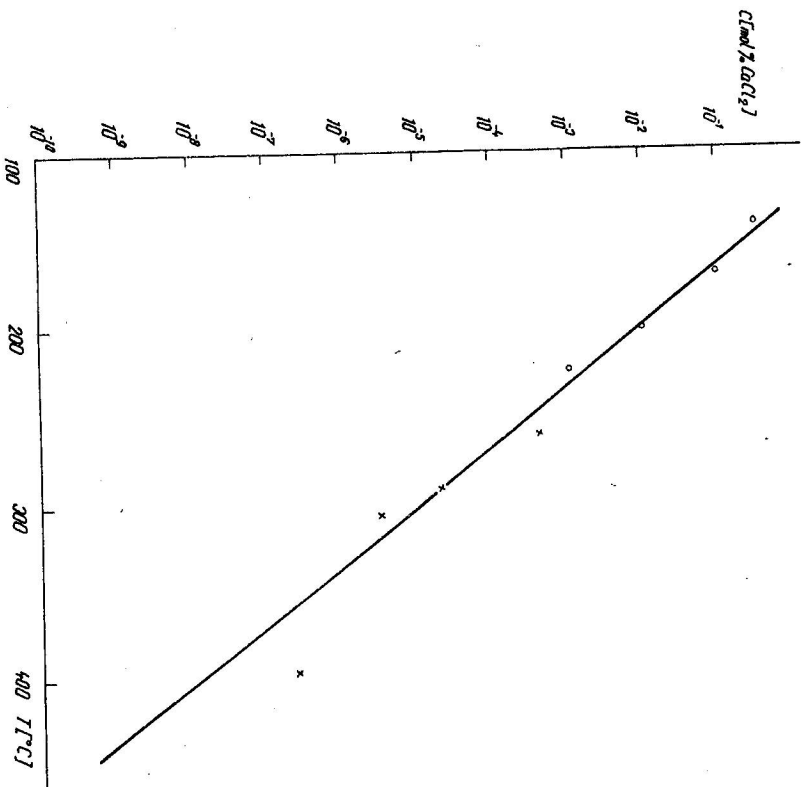


Fig. 3. Dependence of the temperature of relaxation maximum on the concentration of CaCl_2 in NaCl crystals.

At higher doping levels the concentration c of the impurity was determined by the atomic absorption method (UVISPEK), Tab. 1. In „pure“ crystals, grown from refined materials, the estimated cation impurity concentration was calculated from equation (3) (7); the alternatives are the extrapolation of the conductivity isotherms of Fig. 2 from higher c values, or of concentration-dependence of the temperatures of maximum dielectric losses (to be analyzed below).

Fig. 3 shows the dependences of the impurity concentration on the temperature of maximum dielectric loss, as found from the temperature dependence of losses.

Fig. 4 shows typical temperature dependences of the dielectric losses in a standard-quality NaCl crystal and in one prepared by the method described above.

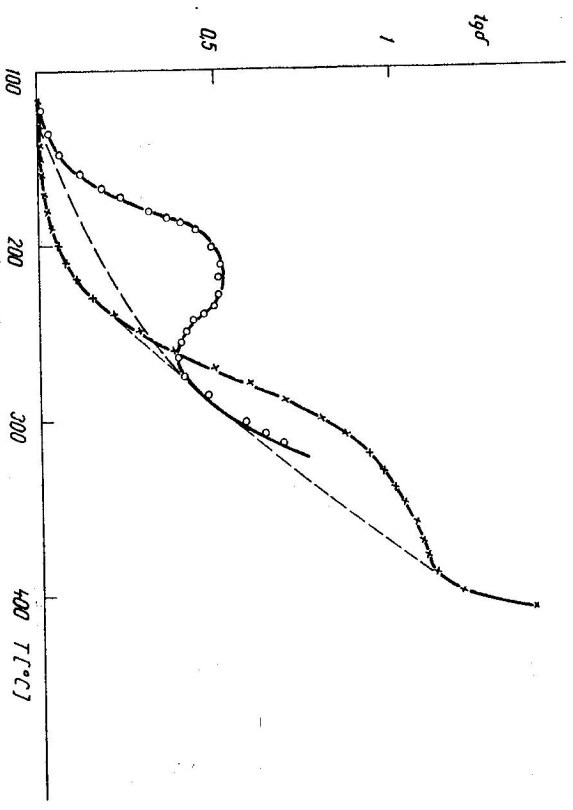


Fig. 4. Temperature dependence of the dielectric losses at elevated temperatures; \times — „pure crystal“; \circ — specially refined by the presently described method.

DISCUSSION

In a real ionic crystal, as NaCl in our case, the heterovalent impurities at low concentrations are built-in substitutionally. The electrical neutrality can

be preserved only if a corresponding number of compensating vacancies is formed. The ionic conductivity is caused by migrations of vacancies; thus if their concentration is determined by the concentration of substitutional impurities, the latter may be determined in a first approximation from the conductivity. The mentioned assumption is fulfilled in a certain region of temperatures (the region of impurity conduction). In this region the number of thermal vacancies may be neglected, and if also the possibility of aggregation of the vacancies and impurities is negligible, the neutrality condition yields

$$x_1 = c, \quad (1)$$

where x_1 is the molar ratio of free cation vacancies and c is the molar ratio of substitutional bivalent cation impurities.

For a direct determination of the concentration C the temperature will be used at which the extrapolations of the two linear parts (corresponding to the intrinsic and impurity conductivity, respectively) of the temperature dependence of conductivity meet (Fig. 1) Tab. 2. At this temperature the

Table 2

$\frac{10^3}{T}$	concentration		
	calculated from eq. (3)	calculated from conductivity measurement	calculated from relaxation measurement
1 1.3	4.53×10^{-4}	3.4×10^{-4}	1.9×10^{-4} standard purity
2 1.26	2.1×10^{-5}	7.0×10^{-5}	7.0×10^{-5} specially refined
3 1.41	4.21×10^{-6}	7.0×10^{-6}	7.0×10^{-6} purified by the described method
4 1.63	2.92×10^{-7}	2.0×10^{-7}	1.9×10^{-8} natural crystal

concentrations of vacancies formed as a result of thermal vibrations and of those resulting from the impurity charge concentration are just equal. The value of the former may be calculated from the formula [7]

$$x_1 = c = \exp\left(\frac{S_i}{2k}\right) \exp\left(-\frac{h_i}{2kT}\right), \quad (2)$$

where S_i and h_i are the entropy and enthalpy of the defect formation, k is the Boltzmann constant.

In the case of NaCl this formula obtains the following form (8) which will be used for the calculation of the concentration of bivalent impurities:

The equation for the temperature dependence of the conductivity has also an exponential form

$$x_1 = 5.3 \exp\left(-11.7 \frac{10^3}{T}\right). \quad (3)$$

E is the activation energy.

At low impurity concentrations it may be assumed, in the first approximation, that the dependence of the conductivity upon the impurity concentration is linear, i. e. that the conductivity increases proportionally with the increasing impurity content

$$\sigma \propto c \text{ for } T = \text{const.}$$

This assumption neglects the aggregation of vacancies with bivalent cations. As can be seen in Fig. 2, the concentrations calculated from equation (3) and those determined by extrapolation of the conductivity isotherms (Fig. 2) do not differ much.

In order to confirm the preceding estimates of the cation impurity concentrations we have also analyzed the temperature dependence of the dielectric losses. The results of measurements of $\tan \delta$ vs temperature (Fig. 4) reveal large relaxation peaks, which we assume to be due to the existence of space charge on the surfaces of the dielectric [9]. The temperatures at which these peaks are observed depend only on the concentration of free vacancies. As they occur at relatively high temperatures, where the conductivity is controlled by the vacancies resulting from the charge compensation, the positions of the peaks are correlated with the purity of the sample. The plot of the impurity concentrations, as obtained by optico-chemical methods, against the temperatures at which the relaxation maxima are found, yields a linear dependence (Fig. 3). Extrapolating this dependence towards lower concentrations we have determined the values of concentration corresponding to the positions of relaxation peaks in the pure samples. These values agree well with the values determined from the conductivity measurements and from equation (3), Tab. 2.

CONCLUSION

In the present paper we have attempted to show that definite conclusions about the purity of materials used for NaCl crystals growing, or, respectively,

about the merits of the methods used to refine the materials, may be inferred from the physical properties of the crystals (the conductivity and dielectric losses as functions of the temperature).

The concentration of cation impurities has been determined by two independent methods. At high doping levels the concentrations were determined by the method of atomic absorption. In accordance with equation (3) an extrapolation was made and the content of substitutional cation impurities estimated down to very low concentrations, indicated in Table 2.

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