

# THE INVESTIGATION OF AGGREGATION PROCESSES IN QUENCHED NaCl:SrCl<sub>2</sub> CRYSTALS BY DIELECTRIC LOSS MEASUREMENTS

By

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It is a well-known fact that bivalent cation impurities connected with cation vacancies form dipoles in alkali halides. This dipole formation results in dielectric losses. By ageing the crystals at elevated temperatures the dielectric loss values decrease because of the production of dipole aggregates. Since the physical properties of the crystals are much influenced by the changes of the impurity distribution, investigations into the aggregation processes became recently more important [1, 2, 3]. The general characteristics of the disappearance (aggregation) of dipoles in crystals containing small amounts of impurities appear to be identical for every system. The dipole decay is a third-order kinetic process, i.e. three single dipoles form one aggregate (one trimer). If, however, the concentration of divalent cation impurities is high enough, aggregates already exist in the crystal practically at any heat treatment, consequently the dipole decay which may be expected during the ageing process will presumably not follow a third order kinetics. The impurity content of the NaCl:SrCl<sub>2</sub> crystals used in the experiments to be described was large enough ( $1.6 \times 10^{-2}$  mol%) to enable the investigation of this case. Specially grown crystals were used free of any anion or OH<sup>-</sup> content whose eventual presence might present difficulties in the interpretation of the results [4].

Two types of samples were used; one group consisted of crystals whose impurity content was at normal temperature in a thermodynamically stable i.e. in a precipitated state (aged crystals), whereas the samples of the second group were quenched, consequently their impurity content became precipitated only to a small degree, corresponding to a thermodynamically unstable state. This crystal type is suitable for ageing experiments.

The dielectric loss in alkali halides consists of two parts: conductivity loss, which is connected with free vacancies, and of losses due to dipole reorientation. These two loss components can be separated, since their temperature dependence is different. If the conductivity loss is subtracted from the total loss, the dielectric loss obtained is proportional with the number of dipoles. In our  $\text{tg } \delta$  versus  $T$  (= dielectric loss-temperature) curves one maximum was observed at approximately 90 °C for the fixed frequency  $\omega = 10^4$  Hz.

Subtracting the conductivity loss from this maximal value resulted in the  $\operatorname{tg} \delta$  value proportional to the number of dipoles. Objects of our investigation was to determine the dependence of the number of dipoles on the quenching temperature and the time of heat treatment at this temperature. The quenching was carried out in a low heat-capacity furnace in an inert gas atmosphere at a cooling rate of 100 °C/min from  $T_q$  to room temperature. The size of the samples was  $10 \times 10 \times 1 \text{ mm}^3$ , quenching did not change the dislocation density of the crystals.

### Experimental results

Figure 1 depicts the change of the  $\operatorname{tg} \delta = \varepsilon''$  values, proportional to the number of dipoles for both sample types. The  $\operatorname{tg} \delta$  values of the aged samples increase nearly exponentially up to 450 °C to become stable above this temperature (curve 1, Fig. 1). The time of heat treatment at the quenching temperature was 10 hours. Repeated quenching (ageing) of already quenched samples resulted in a minimum (curve 2, Fig. 1). In these experiments the time of heat treatment at the quenching temperature was 10 hours. While the first case seems to be an evidence of the dissolution of the precipitates, the second may be explained by a local precipitation at the quenching temperature  $T_q = 300 \text{ °C}$ .

The dielectric loss dependence on the time of heat treatment at various temperatures is depicted in Figs 2 and 3. The dielectric loss presents an exponential function of the time of heat treatment for the aged crystals as well as for the pre-quenched samples, for this latter case it takes for example the form (Fig. 3):

$$\varepsilon''(t) = \varepsilon''_{\min} + (\varepsilon''_{\max} - \varepsilon''_{\min}) \cdot e^{-t/\tau}.$$

The fact that for both sample types the time dependence of the loss values is represented by an exponential function leads to the conclusion that both the impurity dissolution (aged samples, Fig. 2) and the precipitation (pre-quenched samples, Fig. 3) can be accounted for by the same mechanism. The logarithm of the  $\tau$  value versus the reciprocal temperature as calculated from the curves give straight lines. The activation energy calculated from the slopes, is  $1.5 \pm 0.05 \text{ eV}$  for aged samples, and  $0.65 \pm 0.05 \text{ eV}$  for pre-quenched crystals.

Hence, our experimental results opposite to weakly contaminated samples, follow first rather than third order kinetics. Accordingly the number of dipoles proportional to the dielectric loss value increases or else decreases by diffusing away from a fixed number of sources or diffusing to a fixed number of sinks. The sinks or sources consist most probably of aggregates of much more than three dipoles. The actual existence of such aggregates, in both the aged and the pre-quenched samples is also indicated by the conductivity

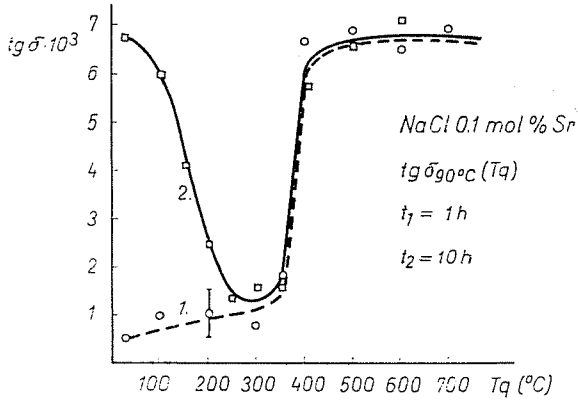


Fig. 1. Quenching temperature dependence of  $\text{tg } \delta$ . 1: "aged" sample, 2: "pre-quenched" sample

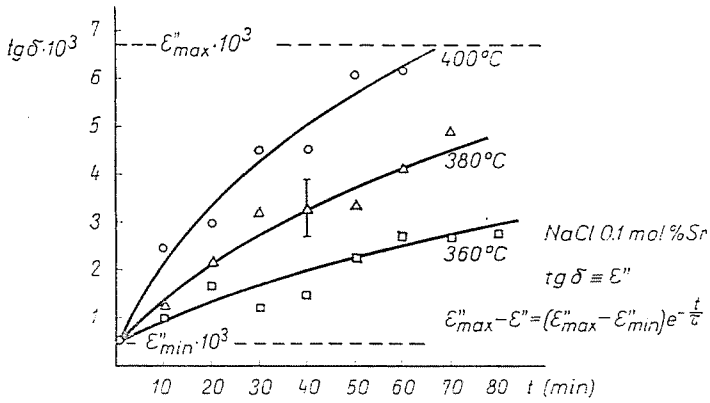


Fig. 2. Time of heat treatment dependence of  $\text{tg } \delta$  of "aged crystals" at various heat treatment temperatures

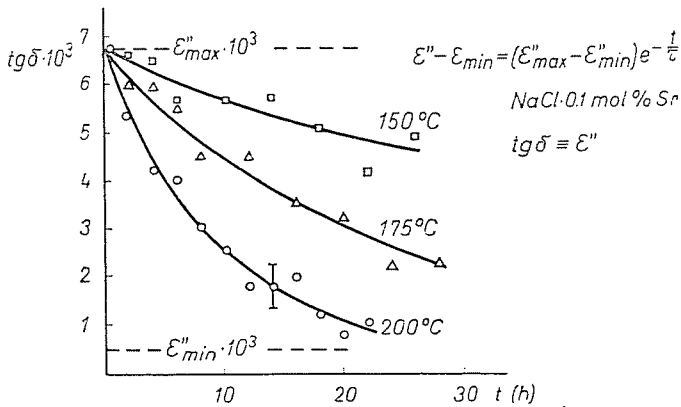


Fig. 3. Time of heat treatment dependence of  $\text{tg } \delta$  of "pre-quenched" crystals at various heat treatment temperatures

( $\log \sigma T$  vs.  $1/T$ ) curves of the same samples. The curves contain in every case a precipitation stage as seen in Fig. 4. Curves 1 and 2 refer to the changes of conductivity of "aged" and pre-quenched crystals respectively. Pre-quenching is seen from Curve 2 not to cancel the precipitation state in Stage IV.

The activation energies corresponding to the values 0.65 eV and 1.5 eV may be explained in the following way. The slopes of Stage IV (precipitation), association Stage (Spection III.) and dissociation Stage yield 1.2, 1 and 0.78 eV, respectively. It seems to be generally accepted that the energy of migration of the cation vacancies  $E_m = 0.78$  eV. The value 1 eV can be resolved into the form  $E_m + E_a/2$  where  $E_a$  is the binding energy of a dipole. Furthermore the value 1.2 eV can be resolved into the form  $E_m + E_s/2$  where the energy of dissolution  $E_s$  of an impurity atom is  $E_s = E_{s_1} + E_a$  [5], here  $E_{s_1}$  represents the energy necessary to tear away one dipole from the aggregate. From these values  $E_a = 0.44$  eV and  $E_s = 0.84$  eV. Taking  $E_s = E_{s_1} + E_a$  into consideration we obtain for  $E_{s_1}$  the more interesting term of our investigation, the value 0.4 eV, an energy required to tear off one dipole from the aggregate or else, released when a dipole becomes attached to the aggregate. These dipoles do not remain, however, in the surroundings of the aggregates, but diffuse away in the crystal with an energy of diffusion 1 eV ( $= E_{ma}$ ) [6]. The sum of

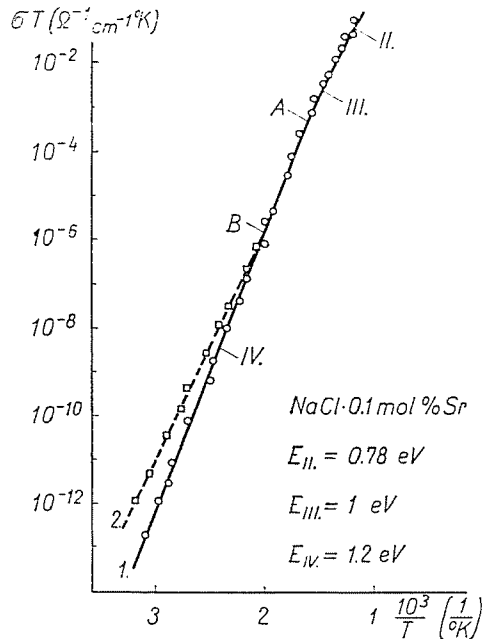


Fig. 4. Electrical conductivity curves of NaCl: Sr single crystals. 1: "aged" sample, 2: "pre-quenched" sample. The letter A denotes the end of the precipitation range, and B indicates that "pre-quenching" does not discontinue the precipitation state

these two energies  $E_{s_1} + E_{m_a} = 1.4$  eV appears to be in good agreement within experimental error with the energy of activation obtained from the kinetical curves, hence the described mechanism should also be in agreement with the experimental results. The kinetical curves obtained with pre-quenched samples (Fig. 3) yielded an activation energy of 0.65 eV. The sum  $-E_{s_1} + E_{m_a}$  ( $= 0.6$  eV) is in good agreement with this result, i.e. any aggregation of the dipole takes up the energy of diffusion  $E_{m_a} = 1$  eV, whereas by joining the aggregate energy  $E_{s_1} = 0.4$  eV is released. In conclusion, the discussed dissolution and precipitation processes are governed by equation

$$E = E_{m_a} \pm E_{s_1}$$

where  $E_{s_1}$  is the binding energy characterizing the attachment of a dipole to an aggregate, whereas  $E_{m_a}$  is the energy of diffusion of a dipole.

### Summary

The aggregation processes of the  $\text{Sr}^{2+}$  ion-vacancy dipoles of NaCl single crystals strongly doped with  $\text{Sr}^{2+}$  have been investigated by means of electrical conductivity and dielectric loss measurements. According to the kinetical curves obtained it was found that the dipole decay due to heat treatment followed first, rather than third-order kinetics. The electrical conductivity curves were used to determine the binding energy of the dipoles in the aggregates.

### References

1. HARTMANOVÁ, M.: Phys. stat. sol. (a) **7**, 303 (1971)
2. WILLIAMS, G. P. Jr.—MORTON, I. W.: Phys. stat. sol. (a) **17**, 305 (1973)
3. FRÖHLICH, F.—HENSEL, G.: Phys. stat. sol. **24**, 535 (1967)
4. VOSZKA, R.: Fizikai Szemle, **XX**, 6, 1, 1970.
5. CAPPELLETTI, R.—FIESCHI, R.: Crystal Lattice Defects I, No. 1. 69 (1969)
6. SÜPITZ, P. and TELTOW, I.: Phys. stat. sol. **23**, 9 (1967)

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