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Anion grain-boundary diffusion in sodium chloride

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The grain-boundary diffusion of ^{131}I in Harshaw pure and Ca-doped NaCl was investigated in the temperature range between 430 and 560°C. The Arrhenius plot of the grain-boundary diffusivity parameter $D\delta$ displays a marked dip at around 510°C. It is proposed that this dip is due to a phase transformation occurring at the grain boundary, possibly calcium segregation.

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While enhanced anion grain-boundary diffusion in alkali halides has been established,¹ enhanced cation grain-boundary diffusion was disputed until recently.² Since no enhancement mechanism has been established for either ion, however, further experimentation is indicated. Thus, the present study on the possible influence of the grain-boundary charge on the anion grain-boundary diffusion in sodium chloride was undertaken. Iodine was chosen as the anion because its enhancement is the largest of all halogens.¹ No evidence for space-charge-controlled grain-boundary diffusion was found. The data to be presented show a diffusion anomaly, however, which is tentatively ascribed to a first-order phase transformation taking place at the grain boundary.

Undoped and doped sodium chloride bicrystals containing a planar symmetric 45° [100] tilt grain boundary were grown by the Kyropoulos technique³ from Harshaw material in nominally 99.996% argon gettered with 87% Zr-13% Ti. The total impurity content of the starting material is typically below 15 ppm. A spectroscopic analysis indicated that, except for the dopant, no additional impurities were introduced during the growth process. Calcium chloride was used as a dopant. Chemical analysis indicated that the variations of the dopant concentrations were less than 4% throughout the ingot.

The iodine diffusion was investigated in the temperature range between 430 and 560°C. Bicrystals with a vapor-deposited layer of Na ^{131}I were annealed and sectioned using a microtome technique. Throughout the experimentation, particularly during the anneal, care was taken to eliminate water as well as possible. The quality of the data taken may be judged from the fact that single-crystal iodine penetration plots, run for checking purposes, were Gaussian over at least four orders of magnitude in time reduced iodine activity. The bicrystal penetration plots were distinctly non-Gaussian and autophotomicrographs of all diffused samples indicated pronounced grain-boundary diffusion. The time-reduced iodine activity varied linearly with the distance in the tail portion of the penetration plot

over at least 1.5 orders of magnitude. Therefore, Fisher's analysis was applied to extract values of the grain-boundary diffusion parameter ($D^{(b)}\delta$), $D^{(b)}$ is the grain-boundary diffusivity, δ is the "width" of the grain boundary.

Figure 1 shows the key result of this study, an Arrhenius plot of the iodine grain-boundary diffusion parameter for undoped and CaCl₂-doped (142 ± 5 ppm) sodium chloride. All samples of one kind of bicrystal

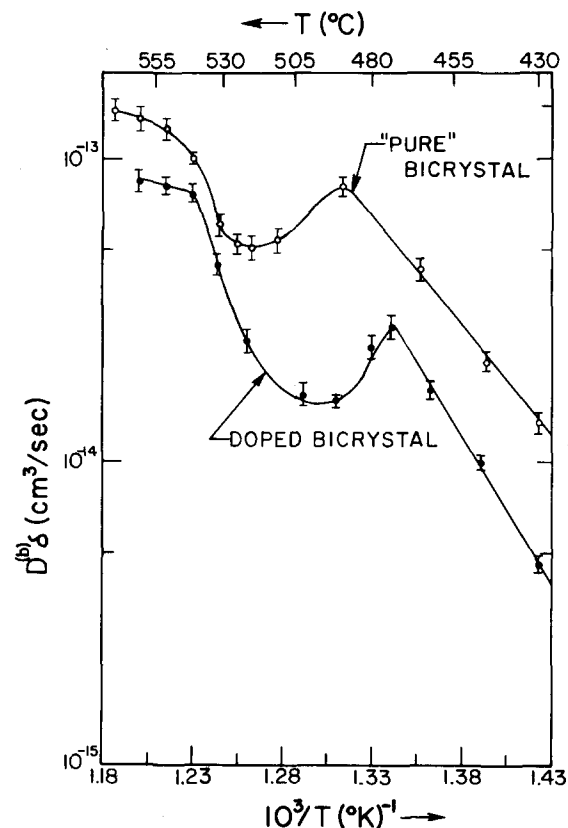


FIG. 1. Arrhenius plot of the grain-boundary diffusion parameter ($D^{(b)}\delta$) for ^{131}I diffusion along 45° [100] tilt grain boundaries in "pure" and CaCl₂-doped (145 ± 5 ppm) NaCl.

were cleaved from the same boule and treated identically so that both the dip in the Arrhenius plot as well as the shift with dopant concentration evident in Fig. 1 are significant. These two features will thus be discussed briefly in the following.

The grain-boundary diffusivity is given by

$$D^{(b)} = (\gamma\lambda^2f)^{(b)} p_f^{(b)} p_m^{(b)}, \quad (1)$$

where the product $(\gamma\lambda^2f)^{(b)}$ contains a geometrical factor γ , the jump length λ , and the correlation factor f , all characteristic of the grain-boundary diffusion. The probability of defect formation, $p_f^{(b)}$, is given by the free enthalpy of defect formation at the boundary, $g_f^{(b)}$, and $p_f^{(b)} = \exp(-g_f^{(b)}/kT)$. The jump probability, $p_m^{(b)}$, depends on both the attack frequency, $\nu^{(b)}$, as well as the free enthalpy of defect motion "along" the grain boundary, $p_m^{(b)} = \nu^{(b)} \exp(-g_m^{(b)}/kT)$. In ruling out drastic variations of the widths of the grain boundary, δ , as well as of the factors in parentheses in Eq. (1) the dip in the Arrhenius plot of $(D^{(b)}\delta)$ in Fig. 1 is determined by the probabilities $p_f^{(b)}$ or $p_m^{(b)}$.

It has been observed that the enhancement of the anion grain-boundary diffusion in alkali halides is proportional to the polarizability of the halogen ion.¹ Therefore, it might be suspected that the probability of defect motion depends on the space charge.^{4,5} In this case $g_m^{(b)}$ is approximated by

$$g_m^{(b)} = g_0^{(b)} - \alpha \left(\frac{\partial \phi}{\partial x} \right)^2, \quad (2)$$

where $g_0^{(b)}$ contains the base contribution, independent of the space charge arising from the potential ϕ . The quantity α denotes the polarizability of the halogen ion. The coordinate x will be directed perpendicularly to the grain boundary for a continuum model. For a real discontinuous boundary, components "along" the direction of defect proportion will exist, however. To first order Eqs. (1) and (2) yield

$$D^{(b)} \propto \alpha$$

as has actually been observed.¹ While the space-charge concept thus reproduces satisfactorily the experimen-

tal observations concerning the grain-boundary diffusion of different halogens, it cannot account for the dip in Fig. 1. Even if the isoelectric temperature T_i of the grain boundary is about equal to the temperature at which the dip is observed,⁶ the condition $\partial \phi / \partial x |_{T=T_i} = 0$ yields only an inflection point in the Arrhenius plot at $T = T_i$.

Turning to other possible variations of the probabilities, $p_m^{(b)}$ and $p_f^{(b)}$, leading to the dip in Fig. 1, we observe that an abrupt change of any property of a solid in a narrow temperature range usually signals a phase transformation. It may thus be argued very generally that the strong variation of the quantity $(D^{(b)}\delta)$ shown in Fig. 1 is the result of a first-order phase transformation occurring at the grain boundary. Such a transformation would be nucleation controlled which would explain the shift of the dip towards lower temperatures as the dopant concentration is increased if it is assumed that the phase transformation consists of the segregation of a Ca-rich phase. Unfortunately, there does not exist at present enough information to further characterize the phase transformation envisioned. Grain-boundary segregation is likely,⁷ however, as it is known that this can occur at solute concentrations substantial below the bulk solute solubility.⁸

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