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Cation Grain-Boundary Diffusion in Sodium Chloride

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ured with the apparatus described in an earlier paper.¹ The measurements were carried out at a wavelength of 10.6 μ , using a CO₂ laser beam diameter of 0.2 cm. The average power flowing through the sample was 0.2 W. The temperature of the sample was varied from 20° to 45°C.

The single crystal material was obtained from Nuclear Elements Corporation. The sample was a parallelepiped with its long axis in the [110] direction, and the other two axes in the [001] and [110] directions. The dimensions in the three directions were 2.545, 0.289, and 0.306 cm respectively. The (110) and ($\bar{1}\bar{1}0$) faces, 0.289 \times 0.306 cm², were polished flat and parallel.

To determine δ , the transmission of coherent radiation through the sample was monitored as a function of temperature. With changing temperature, the optical length of the sample varied so that the phase difference of the light reflected from its entrance and exit surfaces varied as well, producing interference maxima and minima in the transmission. From the temperature change ΔT which corresponds to a phase difference $\Delta\psi$ one obtains¹

$$\delta = (1/n) (dn/dT) = [(\Delta\psi/\Delta T) (\lambda_0/4\pi ln)] - \gamma, \quad (1)$$

where λ_0 is the wavelength of the radiation in vacuum, l is the length of the sample, n its index of refraction, and γ the expansion coefficient of the material.

For cadmium telluride:

$$n = 2.64 \pm 0.02 \quad \text{at } 10.6 \mu,$$

$$\gamma = (5.5 \pm 0.4) \times 10^{-6} (^\circ\text{C})^{-1}.$$

The index of refraction was calculated from the paper of Lorimor and Spitzer,² and the coefficient of expansion was obtained from the work of Ladd.³ The error in the expansion coefficient was estimated from the spread in the data given by Ladd.

The experiment we performed yielded

$$\Delta T = 1.718 \pm 0.010^\circ\text{C} \quad \text{for } \Delta\psi = 2\pi.$$

From these values and the other parameters mentioned earlier, we obtain⁴ from Eq. 1

$$\delta = (4.02 \pm 0.05) \times 10^{-5} (^\circ\text{C})^{-1}.$$

The absorption coefficient was measured calorimetrically. This was achieved by sending the laser beam through the sample to a calorimeter where the full beam was absorbed. The rate of temperature rise of the sample and of the calorimeter gave a measure of the power absorbed by them,

$$W = C_p \Delta T g / \Delta t. \quad (2)$$

In Eq. (2) W is the power absorbed, and C_p is the specific heat of the material of weight g in which the temperature rises ΔT over a period of time Δt . Then, for small α

$$\alpha = (W_s / IW_s) [2n / (n^2 + 1)], \quad (3)$$

where W_s and W_e refer to the power absorbed by the sample and by the calorimeter, respectively. The dissipation in the sample and the calorimeter are measured simultaneously. The factor $2n / (n^2 + 1)$ is a correction which has to be used because the samples were not antireflection coated. This factor (valid for $\alpha \ll 1$) is the ratio of the energy transmitted by the sample (W_s) to the energy flowing through it. The ratio is smaller than one because less energy is transmitted than flows through the sample. This is due to the standing waves set up by the reflecting ends.

The specific heat of CdTe at room temperature was determined with a Perkin-Elmer differential scanning calorimeter, Model DSC-1B. A value of $C_p = 0.044 \pm 0.004$ cal/(g $^\circ\text{C}$) was obtained.

The absorption coefficient⁴ of 10.6- μ laser radiation in the sample was found to be $0.0072 \pm 0.0014\%$ cm⁻¹.

An attempt was made to measure the electro-optic coefficient of the sample. However, it was found that, though the specimen had a resistivity of $4 \times 10^6 \Omega \cdot \text{cm}$ in a 0.6 V/cm field, the resistance dropped several orders-of-magnitude at the higher fields needed

to get a measureable electro-optic effect. These fields could not be maintained across the sample because of the power dissipated and consequent thermal runaway.

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¹ R. B. Weil, J. Appl. Phys. **40**, 2857 (1969).

² O. G. Lorimor and W. G. Spitzer, J. Appl. Phys. **36**, 1841 (1965).

³ L. L. Ladd, Infrared Phys. **6**, 145 (1966).

⁴ Preliminary data, presented by J. Kiefer and A. Yariv in a post deadline paper at the 1969 IEEE Conference on Laser Engineering and Applications, are in general agreement with these results.

Cation Grain-Boundary Diffusion in Sodium Chloride

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While the phenomenon of enhanced grain-boundary¹ and dislocation-pipe² diffusion in metals is well established there are conflicting reports on the enhanced diffusion along structural defects in alkali halides.³⁻¹² Generally, some degree of enhancement of either the cation or anion diffusion is observed in sintered poly- and bi-crystals^{3,6,7} but not in recrystallized samples¹² indicating that the observed enhancement might be due to internal voids. Therefore, a study was initiated of the diffusion in high-grade sodium chloride bicrystals. In this note the results of cation diffusion experiments in such bicrystals containing low- and high-angle [100] tilt grain boundaries are reported.

Sodium chloride bicrystals containing planar symmetric tilt grain boundaries with tilt angles varying between 10° and 45° were grown by the Kyropoulos method¹³ from Harshaw material in nominally 99.996% argon gettered with 87 at.% Zr-13 at.% Ti. The total impurity content of the starting materials is typically below 15 ppm.¹⁴ A spectroscopic analysis of the bicrystals grown indicated that no additional impurities were introduced during

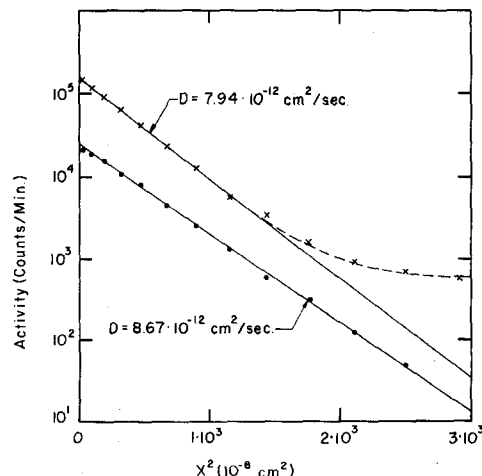


Fig. 1. Penetration plots of ²²Na⁺ in NaCl bicrystals containing a 45° [100] symmetric tilt grain boundary annealed for 32 h at 500°C., vapor deposition method 1 (no NaOH added); × × × × vapor deposition method 2 (with NaOH added).

the growth process. Diffusion samples were prepared by cleaving symmetric portions from the boule, preannealing them for 24 h at 700°C, and vapor depositing a thin layer of NaCl containing ^{22}Na on one side. The samples were diffusion annealed in vacuum ($\approx 10^{-6}$ Torr), they were sectioned with a Spencer Model 860 Microtome after cleaving off the sides to eliminate surface diffusion and evaporation and recondensation effects.

The cation diffusion in bicrystals containing tilt grain boundaries of 10°, 30°, and 45° tilt angle was investigated in the temperature range between 300° and 550°C. Bicrystals deposited with radioactive NaCl which was crystallized in the vapor deposition crucible out of a solution of NaCl in 1N HCl (method 1) displayed no enhanced grain boundary diffusion. However, if the acid NaCl solution was neutralized with NaOH before drying and phenolphthalein was used as an indicator (method 2) enhanced grain-boundary diffusion was observed.

Figure 1 shows a comparison of the penetration plots of two essentially identical 45° tilt bicrystals typical of all tilt grain-boundaries investigated. They were processed identically with the exception of the vapor deposition method. In order to increase the effect of the neutralization on the grain-boundary diffusion an excess of NaOH was added to the solution after neutralizing it. The penetration profile of the bicrystal sample vapor deposited according to method 1 is Gaussian and shows no indication of enhanced grain-boundary diffusion. The cation diffusion constant calculated from the slope is in good agreement with previous bulk diffusion data.^{15,16} On the contrary, the penetration profile of the bicrystal sample vapor deposited according to method 2 displays a "tail" characteristic for diffusion enhancement by structural defects. An autoradiographic analysis showed that the high diffusivity path is the tilt grain boundary. The difference of the slopes of the linear sections of the two profiles is due to differences in sample alignment and uncertainties of the thickness of the first section.

The lack of evidence of enhanced intrinsic cation grain boundary diffusion is in agreement with results reported in Refs. 3, 8, and 12. It disagrees with other reports.^{9,11} As no information concerning experimental details is given in Refs. 9–11 a comparison is difficult. Considering the influence of the vapor deposition method on the enhancement of the grain-boundary diffusion reported in this note one might speculate that the discrepancy is due to impurities.

Since the color change of phenolphthalein occurs at $8.3 \leq pH \leq 10$ it is concluded that the observed enhancement of the cation tilt grain-boundary diffusion occurs only if an excess of OH^- ions is present in the vapor deposited layer. Consequently, this diffusion enhancement may be compared to the enhancement of the electrical conductivity of $\alpha\text{-Al}_2\text{O}_3$ and KCl in the presence of moisture.^{17,18} Evidently, either the H^+ or OH^- ions have a high mobility along structural defects as compared to the bulk. For a rationalization of the present results it might be envisioned that the OH^- ions diffuse very quickly into the grain boundary and change either its structure or its potential or both such that the diffusion of the Na^+ ions is greatly enhanced. The observed effect can thus be termed extrinsic grain-boundary diffusion.

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¹ See P. Shewmon, *Diffusion in Solids* [McGraw-Hill Book Co., New York, (1963)] as a general reference.

² M. Wuttig and H. K. Birnbaum, *Phys. Rev.* **147**, 495 (1966).

³ J. F. Laurent and J. Bernard, *J. Phys. Chem. Solids* **7**, 218 (1958).

⁴ I. M. Hoodless and S. J. Thomson, *Phil. Mag.* **46**, 1131 (1959).

⁵ L. W. Barr, I. M. Hoodless, J. A. Morrison, and R. Rudham, *Trans. Faraday Soc.* **56**, 967 (1960).

⁶ J. Cabane, *J. Chim. Phys.* **59**, 1123 (1962).

⁷ J. Cabane, *J. Chim. Phys.*, Ref. 6, p. 1135.

⁸ R. Tucker, A. Laskar, and R. Thomson, *J. Appl. Phys.* **34**, 445 (1963).

⁹ Ya. E. Geguzin and E. R. Dobrovinskaja, *Sov. Phys.—Solid State* **7**, 1660 (1966).

¹⁰ Ya. E. Geguzin and E. R. Dobrovinskaja, Ref. 9, p. 2826.

¹¹ Ya. E. Geguzin, E. R. Dobrovinskaja, I. E. Lev, and M. V. Mozharov, *Sov. Phys.—Solid State* **8**, 2599 (1967).

¹² S. M. Klotzman, I. P. Polikarpova, A. N. Timofur, and I. Sh. Trachtenberg, *Sov. Phys.—Solid State* **9**, 1956 (1968).

¹³ N. Fuschillo, C. E. Nelson, and M. L. Gimpl, *Rev. Sci. Instrum.* **36**, 1341 (1965).

¹⁴ As communicated by Harshaw.

¹⁵ D. Mapother, H. N. Crooks, and R. Maurer, *J. Chem. Phys.* **18**, 1231 (1950).

¹⁶ J. F. Laurent and J. Bernard, *J. Phys. Chem. Solids* **3**, 7 (1957).

¹⁷ R. N. Tucker and P. Gibbs, *J. Appl. Phys.* **29**, 1375 (1958).

¹⁸ G. Geschwind and E. Machlin, *J. Appl. Phys.* **38**, 900 (1967).

Piezoelectricity in Polycrystalline 6-mm Films

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There has recently been controversy^{1,2} with respect to the crystallite orientation required for independent generation of the three mechanical modes by the cavity drive technique with polycrystalline films of materials in class 6 mm (ZnO and CdS). The author of Ref. 2 states that with "two adjacent crystallites both of which have their X_3 axes normal to the film surface and pointing in the same direction," but with the X_1 axis of one crystallite rotated about X_3 "so that its direction is 180° away from X_1 of the other crystallite," there will be cancellation of the shearing

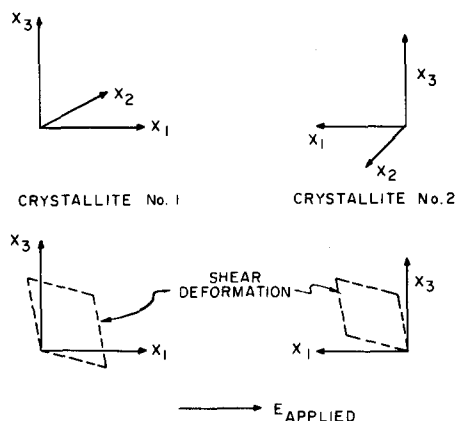


FIG. 1. Shear deformations for two crystallites of class 6 mm with X_3 axes parallel, X_1 axes antiparallel.

stress "for any electric field in the plane of the film." Reference to Fig. 1 shows that this statement is not correct. Right-hand axial systems are shown for both crystallites and X_3 directions are parallel, X_1 directions and X_2 directions antiparallel. The electric field is applied parallel to X_1 of crystallite #1 and antiparallel to X_1 of crystallite #2. Since CdS and ZnO have $d_{15}=d_{25}$ negative, an electric field parallel to X_1 causes a negative shearing strain. A shearing strain is positive "when a rectangle becomes deformed so that an acute angle lies in the quadrant between the positive directions of the axes that form the sides of rectangle." Thus for negative d_{15} and E parallel to X_1 the deformation of crystallite #1 is obtuse in the X_2X_1 plane between $+X_2$ and $+X_1$ as shown. For crystallite #2 E is negative with respect to X_1 so the deformation is acute between $+X_2$ and $+X_1$ in the X_2X_1 plane. The deformations are cumulative thus refuting de Klerk's statement.

¹ N. F. Foster and A. H. Meitzler, *J. Appl. Phys.* **39**, 4460 (1968).

² J. de Klerk, *J. Appl. Phys.* **39**, 4461 (1968).

³ Standards on Piezoelectric Crystals, 1949, *Proc. IRE* **37**, 1378 (1949).