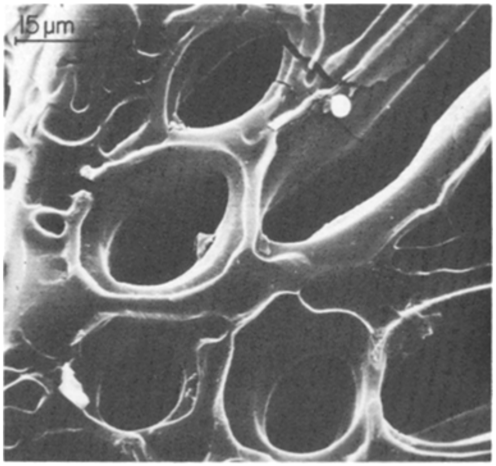

*Figure 5* Detail of surface of crystal shown in Fig. 2.

This behaviour is the opposite of normally observed cellular growth. In the present case, the instability is in the form of an array of ridges formed from steps on the surface. These enclose holes in a close-packed arrangement. The crystal grows from the ridges, developing the cellular hole structure.

We have made extensive observations of this behaviour under different conditions and shall report on this in full in a further contribution. We shall also discuss the factors determining step or surface instability. The former leads to hole formation while the latter leads to pyramids [1]. We shall also relate this to the type of solute and impurities in solution.

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## *Sintering kinetics of pure and $CdCl_2$–doped NaCl in air*

During densification of particle compacts there are so many complex changes that it appears almost impossible to develop a unifying theory of sintering [1]. Since sintering a porous compact is essentially a process of redistributing the mass, there has been considerable interest in the transport processes involved and much of the available evidence comes from the sintering behaviour of model systems.

Early studies on the sintering of NaCl using model systems showed that the particles bonded without an increase in the denisty of the mass [2, 3]. On the basis of limited results it was concluded that the rate-controlling mechanism of mass transport during sintering of NaCl is by evaporation–condensation [2], and these conclusions were confirmed [3], although a different model was used to explain the results. Mass transport by evaporation–condensation cannot cause a density increase during sintering [4] and it appeared that densification of NaCl was not possible. However, Morgan *et al.* [5] showed that substantial densification of NaCl compacts did occur, provided the particle size was small enough. They also showed that 0.1 mol% $CsNO_3$ co-precipitated with NaCl, decreased the amount of shrinkage compared to pure NaCl. Ammar and Budworth [6] established that densification of NaCl particles occurred if, (1) the particle size is small enough ($< 150\,\mu$m diameter), (2) the sintering temperature is high enough, and (3) the green density is low enough. Although evaporation–condensation does occur during sintering of NaCl it is clear that some other mass transport process is operating to cause densification. The present work investigates the densification kinetics of NaCl, and the effect of small quantities of $CdCl_2$ on the sintering behaviour.

All samples of NaCl were from one batch of

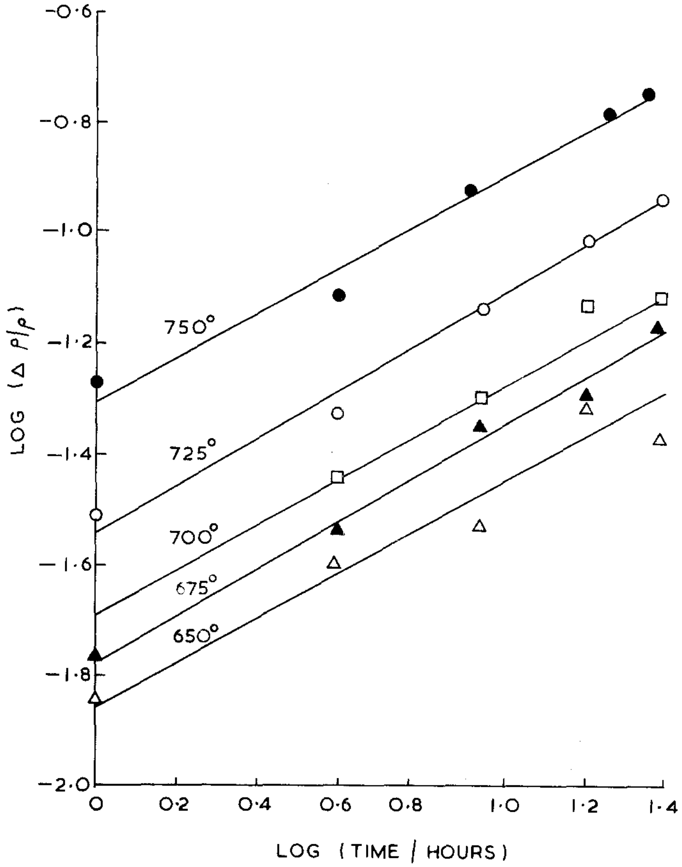

*Figure 1.* Densification of NaCl in air. Particle size 44 to 50 μm. Green density 1.447 g cm$^{-3}$.

powder which had the following maximum impurities: free acid 0.5 ml N/l, free alkali 0.5 ml N/l, and (in wt%), $SO_4$, 0.003; $NO_3$, 0.002; $PO_4$, 0.0005 Fe, 0.0005; Pb, 0.001; Ba, 0.003; Ca, 0.005; Mg, 0.005; K, 0.01; $NH_4$, 0.001; As, 0.0001. The $CdCl_2$ used had similar levels of impurities. The powder was dried at 150° C for 10 min, ground in a ballmill, then sieved into fractions. Before compacting, the powder was again dried and sieved. To obtain reproducible green densities, a weighed quantity of NaCl was pressed to a pre-determined volume in a die by using a massive steel spacer in parallel with the die.

Compacts were placed in an alumina boat and sintered in air. No heating or cooling corrections were made, and the time at temperature was taken as the sintering time. Temperature control was within ± 2° C. Density measurements were made at room temperature on the sintered compacts using the mercury balance technique [7]. The absolute accuracy of the density measurements were within 1% (as tested on various materials) but the sensitivity and reproducibility were better. NaCl doped with $CdCl_2$ was prepared by mixing two solutions, one of NaCl in distilled water and the other containing $CdCl_2$, evaporating to dryness, ball-milling, etc, as with the pure NaCl.

Preliminary results showed that densification did not occur with particle sizes of 130 to 144 μm, but did occur for all smaller particle sizes. It may be noted that the values 130 to 144 μm is a little lower that the previously observed lower critical size of about 150 μm [6]. All further work used particle sizes in the range 44 to 50 μm.

Considerable densification occurred during sintering (Fig. 1). An indication of the accuracy of the present method can be seen from the results in Table I, although individual sample to sample variation was usually not so good. Log densification/log time plots (Fig. 2) lead to the equation

$$(\Delta\rho/\rho_0) = Kt^n \qquad (1)$$

where $\Delta\rho = \rho - \rho_0$, $t$ is the time, and $K$ and $n$ are constants. The usual densification parameters are

TABLE I The effect of $CdCl_2$ additions on the density ($g\,cm^{-3}$) of NaCl sintered in air at 700° C for 16 h. Green density 1.447 $g\,cm^{-3}$

| | Pure NaCl | NaCl + 0.1 mol % $CdCl_2$ | NaCl + 0.5 mol % $CdCl_2$ |
|---|---|---|---|
| Lot 1 | 1.577 | 1.540 | 1.500 |
| Lot 2 | 1.577 | 1.544 | 1.502 |

TABLE II Values of $n$ in Equation 1 calculated from the data of Fig. 1, for the sintering of NaCl in air

| Sintering temperature (° C) | $n$ |
|---|---|
| 750 | 0.40 ± 0.03 |
| 725 | 0.41 ± 0.02 |
| 700 | 0.55 ± 0.07 |
| 675 | 0.42 ± 0.03 |
| 650 | 0.37 ± 0.04 |

$\Delta L/L_0$ or $\Delta V/V_0$ where $\Delta L = L - L_0$. The relation to the present parameter is

$$\Delta\rho/\rho \;=\; \Delta V/V_0 \;=\; 3\Delta L/L_0.$$

Calculated values of the paremeter $n$ using a $y = mx + c$ fit by least mean squares, are shown in Table II. The average value is $n = 0.43 \pm 0.05$. Assuming K contains a thermally activated term, the temperature dependence of $K$ is shown in Fig. 2 with a calculated activation energy of 231 ± 5.0 kJ $mol^{-1}$.

Various sintering models have been derived which embody Equation 1 [1, 2, 8], but considerable care is needed in interpreting densification kinetics [8] and there are limitations in the various models [9]. Sintering rates are usually followed by measuring continuously the shrinkage

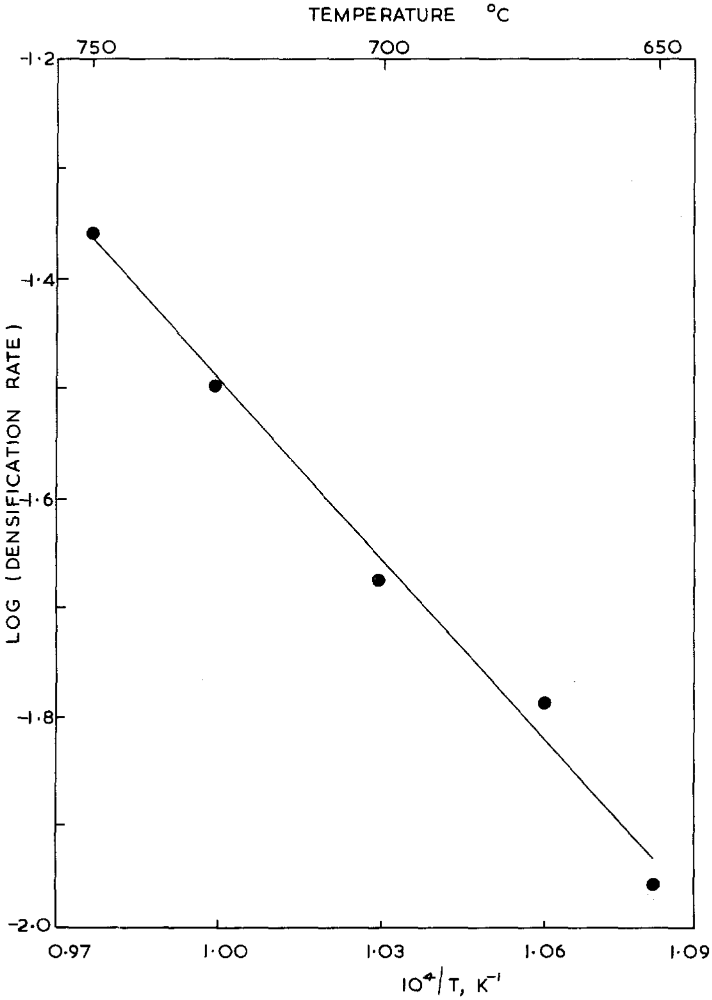

*Figure 2* Arrhenius function of the densification kinetics.

of a constant mass [1]. In the present case the change of mass due to evaporation of the sample necessitated a discontinuous method of obtaining data which is less accurate, and so a mechanistic interpretation of the $n$ value is not possible. However, the activation energy of 231 ± 5.0 kJ mol$^{-1}$ obtained in the present work is close to 260 kJ mol$^{-1}$ for diffusion of $Cl^-$ in NaCl [10] and suggests that volume diffusion is the mechanism of mass transport during sintering NaCl. When $CdCl_2$ is dissolved in NaCl the $Cd^{2+}$ on an $Na^+$ site is effectively an extra charge on the site, i.e. $Cd^+$. For charge neutrality in the crystal we then have

$$[Cd^+] + [V_{Cl}^+] = [V_{Na}^-]$$

where $[V_{Cl}^+]$ and $[V_{Na}^-]$ are the concentrations of charged anion and cation vacancies respectively, and an increase in $Cd^+$ will disturb the mass-action equilibria of anion and cation vacancies. The effect of adding $CdCl_2$ to NaCl is to decrease the concentration of vacancies for diffusion of the rate-controlling $Cl^-$. On this basis, the decrease in sintering rate on addition of $CdCl_2$ to NaCl (Table I) is due to a decrease in the rate of volume diffusion. Morgan *et al.* [5] interpreted a kink on the shrinkage–temperature curve of pure NaCl and NaCl containing 0.1 mol % $CsNO_3$ as possibly due to the interaction of the impurity atoms with dislocations, and further assumed that possible plastic flow was the cause of densification. The temperature dependence of volume diffusion and high temperature plastic flow would be similar since the plastic flow would involve either diffusional creep and/or some diffusion process whereby dislocation climb would permit movement of jogged or otherwise immobile dislocations. If the rate-controlling process is plastic flow, the role of the dissolved $Cd^{2+}$ would be hinder the motion of dislocations. In duscussion the precipitation hardening and dislocation locking in NaCl containing $CdCl_2$, Newey *et al.* [11] suggested that the most likely mechanisms of strengthening at high temperatures is the one that produces locking of stationary dislocations and imposes a drag on moving dislocations, and that impurity ion-generated vacancy dipoles are the effective locking agents. On the present results, both dislocation hardening and mass transport by volume diffusion appear equally possible as the transport process during sintering pure and $CdCl_2$–doped NaCl.

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## *Second harmonic generation in organic crystals*

Current interest in optical communication systems has stimulated the investigation of new, effective materials for electro-optic modulation. In most instances, the work has been restricted to inorganic materials of comparitively complex composition, e.g. lithium niobate, potassium tantalate niobate, barium sodium niobate. Severe problems have been encountered with the preparation of optically homogeneous specimens of these materials, usually because the concentrations of the individual elements are a function of growth rate, temperature, undercooling etc. Striation-free crystals are seldom available, even on a research