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ON THE EFFUSION OF DIVALENT IMPURITIES IN ALKALI HALIDES

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ABSTRACT

It is shown the possibility to calculate the amount of effused manganese on a NaCl crystal heated in air, assuming oxidation of the manganese on the surface and its diffusion into the matrix bulk. Conversely, the diffusion coefficient can be measured from the amount effused.

RESUMEN

Se muestra la posibilidad de calcular la cantidad de manganeso difundido en cristales de NaCl calentados en aire, si se asume la oxidación del manganeso en la superficie y la difusión del mismo en la matriz. Por otro lado, el coeficiente de difusión puede ser medido a partir de la cantidad de manganeso en la superficie.

1. INTRODUCTION

The vaporization rate of alkali halides has been shown to be dependent on the amount and type of divalent impurities present in the crystal(1,2,3). In some systems there is a higher impurity concentration on the surface compared with that within the bulk(4,5). The electric potential between the surface and the bulk of an alkali halide crystal(6) causes a variation in vacancy concentration that ought, in principle, segregate the divalent cation impurity to the surface(7).

It is not clear(3) whether surface agregation during vaporization occurs in order to establish equilibrium between the surface and bulk(4,5), as a result of the oxidation of the impurities on the surface(8,12) or as a result of a kinetic build up(2) because of surface recession. The surface recession could be produced by a faster vaporization of the matrix crystal compared with that of the impurities.

It has been reported previously that the manganese impurities contained in NaCl crystals effused to the surface during heat treatment(8-10). This fact has been used to study the nucleation of the thin film formed(11-13). Here, we study this system to elucidate the main contribution to the surface agregation, the thermodynamic equilibrium, the oxidation rate and surface recession.

2. THEORY

Each of the proposed models predicts different results as a function of heat treatment.

The proposed model for thermodynamic equilibrium assumes a very thin "charged layer" surrounding the crystal; these charges are in a zone a few atomic layers thick and the equilibrium state for a temperature near 500°C is obtained in a few hours(5). In equilibrium the amount of surface impurities should decrease rapidly towards the crystal bulk.

In the case of surface oxidation the model predicts a continuosly increasing amount of manganese on the surface effused from the bulk giving rise to a manganese concentration increasing toward the bulk.

The surface recession model predicts a continuosly increasing amount of manganese on the surface, here because of the higher evaporation rate of the NaCl. In this case the surface manganese should diffuse toward the bulk, producing a concentration decreasing toward the bulk.

To elucidate which of the above is the main mechanism we need only follow the time dependence of the amount of the manganese on the surface and the concentration gradient inside the crystal. We will also solve a simplified model for the oxidation rate.

We consider that any ion of Mn^{2+} which arrives at the surface becomes immediately oxidazed and that the diffusion of the MnO molecules into the crystal is negligible; then we can assume the surface to be a sink for the Mn^{2+} ions in the volume. Accordingly, knowing the diffusion coefficient, the temperature and the duration of the heat treatment we can then calculate the amount of MnO (or Mn_2O_3) on the surface for a one dimentional case. Using Fick's second law it can be obtained:

$$C(x,t) = \frac{4C_0}{\pi} \sum_{n=o}^{\infty} \frac{1}{2n+1} \exp\left(-\frac{\pi^2 Dt}{\ell^2}(2n+1)^2\right).\ \sin\frac{\pi x}{\ell}(2n+1), \qquad (1)$$

where the following initial and boundary conditions were used:

$$C = C_0 \quad (0 < x < \ell;\ t = 0) \qquad (2)$$

$$C = 0 \quad (x = 0, \ell;\ t \geqslant 0), \qquad (3)$$

where

$C(x,t)$ is the concentration in a point x at a time t,

C_0 is the uniform initial concentration,

D is the diffusion coefficient,

t is the duration of the heat treatment,

ℓ is the thickness of the plate, and

x is the distance to the left face.

Figure 1 shows the solution of Eq. (1) for different values of Dt/ℓ^2.

By integration of Eq. (1) from 0 to 1 we obtain the total amount of Mn in a volume defined by $1 cm^2$ area and the thickness of the crystal. Subtracting this amount from the quantity contained initialy in this volume, we obtain the quantity of Mn on the surface as

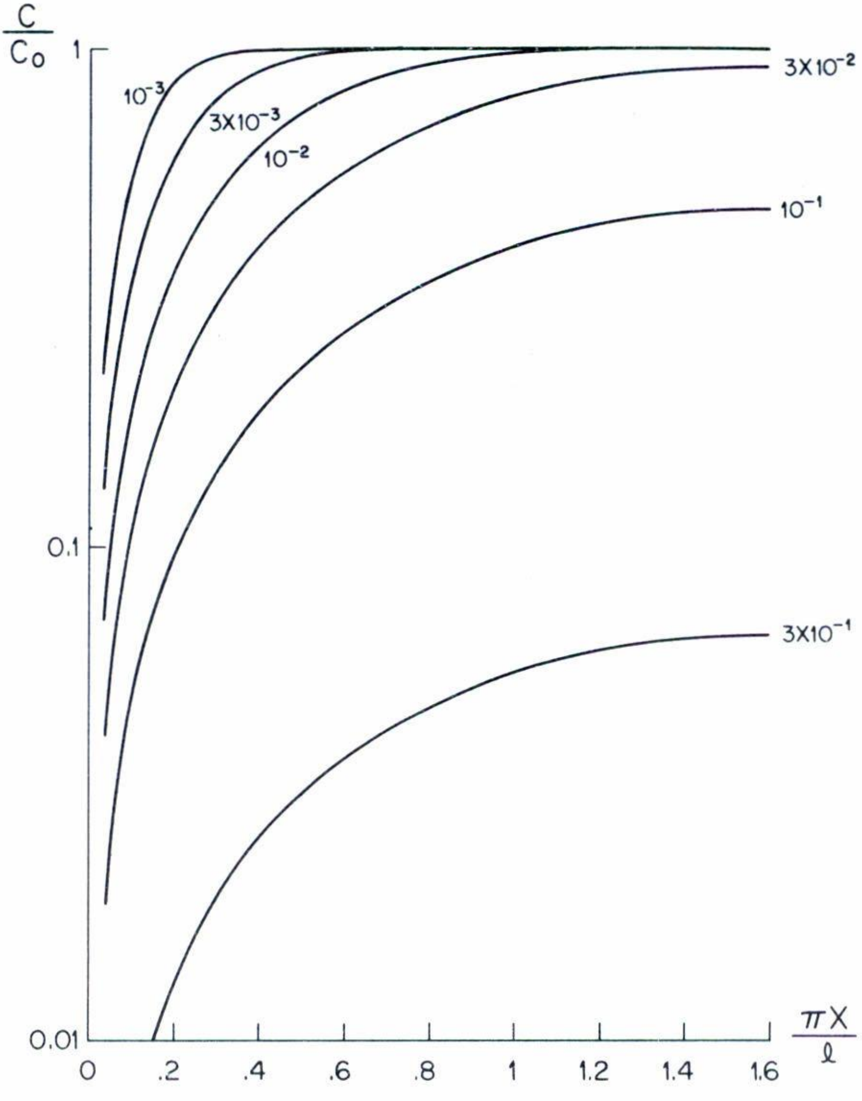

Fig. 1 Concentration as a function of depth x. It is shown only half of the symmetrical figure.

$$\frac{2N}{C_0 \ell A} = 1 - \frac{8}{\pi^2}\sum_{n=o}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{\pi^2 Dt}{\ell^2}(2n+1)^2\right), \tag{4}$$

where N is the amount of Mn on each of the boundary surfaces of area A.

Figure 2 shows the relation between the amount of Mn on the surface (normalized to 1) and the ratio t/ℓ^2 for different values of D. From this figure we can see that for different values of N, the values of D are sufficiently separated, only if the ratio t/ℓ^2 is sufficiently large; making possible to measure the diffusion coefficient, knowing N.

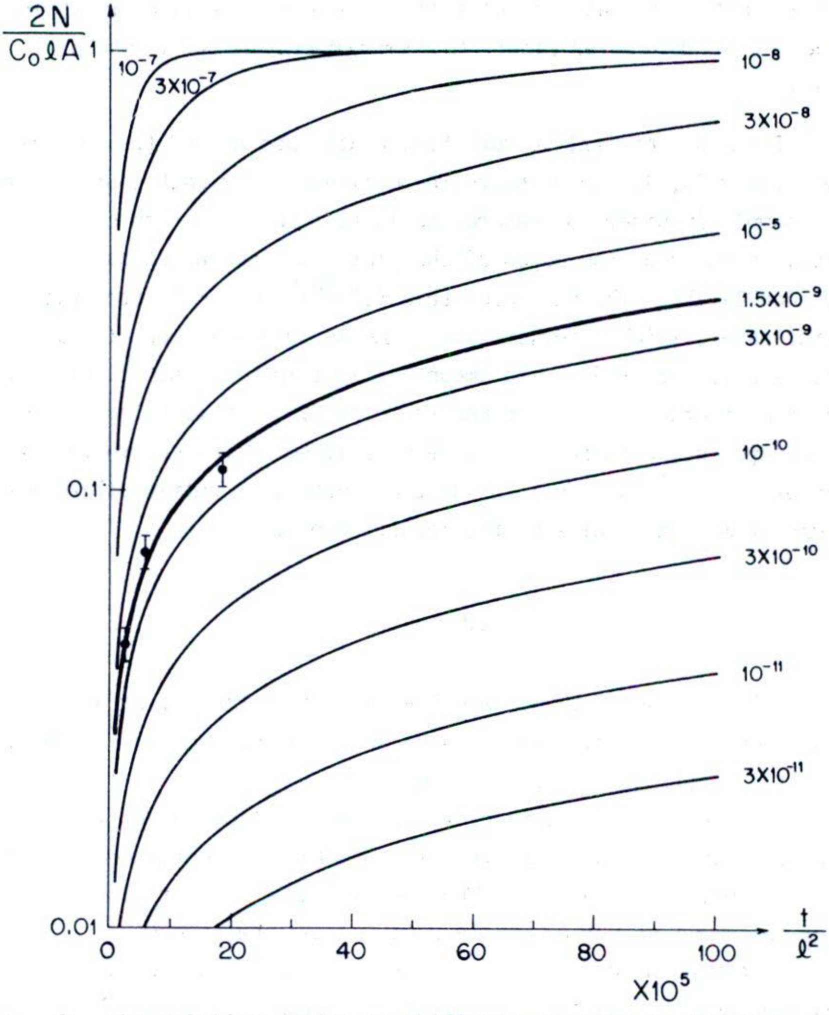

Fig. 2 The relative amount of oxidized manganese on the surface as a function of t/ℓ^2, for diferent values of D.

3. EXPERIMENTAL PROCEDURE

The samples were grown in our laboratory by means of the Czochralski method in controlled atmosphere (300 torr of Argon) in a glassy carbon crucible heated by induction. The $MnCl_2$ was added to the NaCl salt in a 1% in weight concentration. To obtain a more uniform Mn concentration the crystal was annealed at 650°C for 24 hours in an inert atmosphere (Ar) and cooled slowly to room temperature at a rate of 1.5°C/min.

From this crystal we cut three plates and heated them at 480°C in open air for 24, 48 and 96 hours respectively. For each plate we took a mirror sample in order to measure the initial concentration Co. After oxidation, we cut away the edges of the plates making the effusion unidimensional-like. The MnO-Mn_2O_3 thin film$^{(8,9)}$ was collected with a wet filter paper, which afterwards was immerse in a solution of HCl in order to disolve the oxide. The amount of NaCl left in the filter paper was measured in order to correct the value of N. To verify the agreement of the measurements with the model, we also measured the concentration gradient of the Mn^{2+} ions left inside the crystal, by cutting thin layers with a microtome, and analysing the resulting powder.

4. RESULTS

Figure 2 shows three experimental values for the effused manganese together with the calculated curve using the mean diffusion coefficient (15) of $D=(1.5 \pm .5)\times 10^{-9}$ cm^2/sec.

Figure 3 shows the theoretical concentration curves for a value of $D=1.5 \times 10^{-9}$ cm^2/sec. and the experimental data obtained be measuring the concentration profiles. These points have a great dispersion because of the small amount of sample used in this measurements.

Because the concentration of the manganese on the surface increased continuosly, and the concentration increased towards the bulk, we concluded that, in such system, the oxidation rate is the main mechanism. The agreement with the concentration profile could be better if the condition C=0 on the surface for the Mn^{2+} is eliminated. Also, at longer times there appears a contribution from the vaporization of the matrix and the impurities.

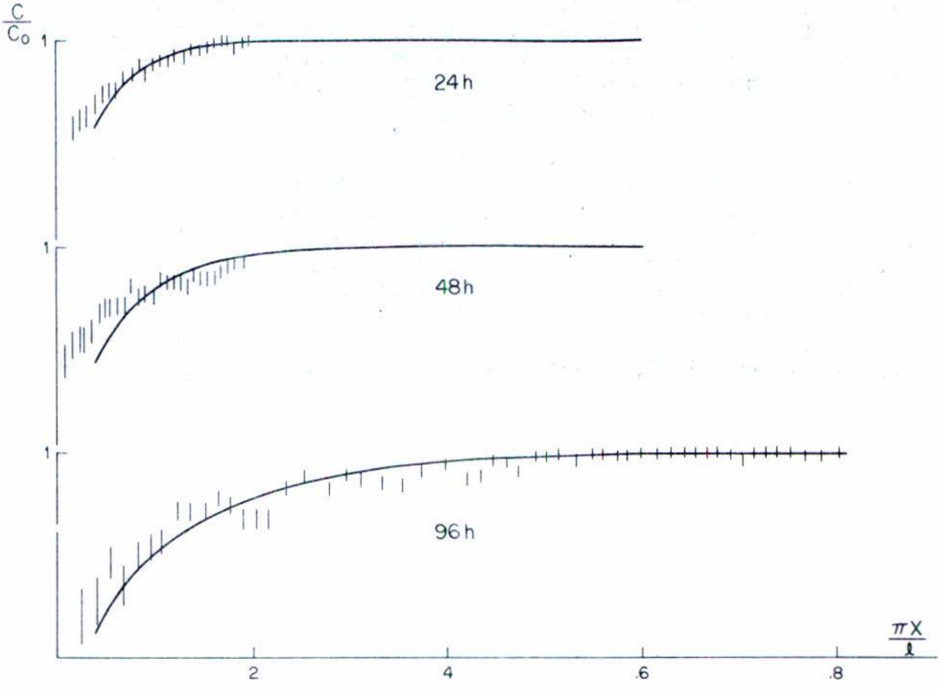

Fig. 3 Theoretical curves and experimental data points for the concentration profiles.

It has been shown(12) that the oxides appear after a heat treatment, even in high vacuum about 10^{-6} torr, in NaCl cruystals doped with any of the following divalent impurities: Ca, Mn, Fe, Co, Pb, Zn and Eu. To measure the calcium on the surface of NaCl in thermodynamic equilibrium, an oxigen-free atmosphere is used(4).

We have shown that it is possible to calculate the amount of effused manganese and the size of the depleted layer, information that is sometimes needed in thin film formation or when a crystal is going to be used after a heat treatment. Also it is possible to measure the diffusion coefficient by the amount of effused material, therefore avoiding the determination of a concentration profile.

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