Kinetics of etching and dissolution of gel-grown $CdC_2O_4 \cdot 3H_2O$ crystals

S. K. ARORA, TOMY ABRAHAM
Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

The kinetics of etching and dissolution of cadmium oxalate trihydrate single crystals in selective etchants such as 1 M HCl, 1 M HNO_3, 10% chromic acid, 4 M NH_4Cl, 4 M $CdCl_2$ and 4 M NH_4Cl–1 M HCl solutions are studied. Contrary to a previous report on semiconductor etching, in the present investigation the activation energy of etching in solvents having a reaction-rate controlled mechanism of dissolution was lower than in those having a diffusion-rate controlled dissolution mechanism. Three 3-component etch systems, i.e., $HCl–NH_4Cl–H_2O$, $HCl–CdCl_2–H_2O$, and $NH_4Cl–CdCl_2–H_2O$, are employed and constant etch rate contours are plotted which enable the part played by each component in association with the other components in the system to be understood.

1. Introduction

Dislocation etching, in spite of the vast advances of technology in Materials Science, remains a very powerful tool for the detection and characterization of crystal defects. The study of the identification, origin and characteristics of crystalline defects, such as grain boundaries, slip lines, dislocations, stacking faults, volume indentations, vacancies and so on, relies heavily on etching phenomena. The generally complex etching mechanism [1–3], which varies with the material and the etchant, is not quantitatively understood to-date. Although a number of generalizations and guidelines have been formulated over the years, etching techniques are still based on a qualitative and empirical basis. Though etch pits can be produced by an etchant, the generation of useful pits depends upon a delicate balance between the rates of dissolution parallel and transverse to a dislocation line [4].

An attempt to understand the mechanism of etching can be made by choosing a number of simple etchants for a given crystal. In this paper studies on the kinetics of etching of cadmium oxalate trihydrate crystals are described, using six different etchants whose reliability has been convincingly demonstrated elsewhere [5]. Also, three 3-component etchant systems, i.e., $NH_4Cl–HCl–H_2O$, $HCl–CdCl_2–H_2O$ and $NH_4Cl–CdCl_2–H_2O$, using all possible permutations, and combinations of the components in the system, have been employed for a more comprehensive study of etching kinetics. These investigations enable the action of each component in a system in promoting or contributing to dissolution to be estimated, in association with the other components of the system.

2. Experimental procedure

Damage- and inclusion-free crystals weighing about 20 to 30 mg were selected. They were subjected to etching by immersion in various etchants, i.e., 1 M HCl, 1 M HNO_3, 10% chromic acid, 4 M NH_4Cl, 4 M $CdCl_2$ and a mixture of 4 M NH_4Cl and 1 M HCl in the ratio 7:3 by volume (NH_4Cl–HCl etch), in a toluene regulated constant temperature water bath that stabilized the temperature to within $\pm 0.5°$ C. A specimen was initially weighed and put into the etch system whose composition was already known. After the required time had lapsed, the etching was arrested by putting the crystal into a beaker containing a large quantity of distilled water. It was dried and re-weighed to determine the amount of material dissolved. Weighing the crystal before and after etching, on the lines of Tuck [6, 7] for semi-

0022–2461/82/061723–06\$03.22/0 © 1982 Chapman and Hall Ltd.

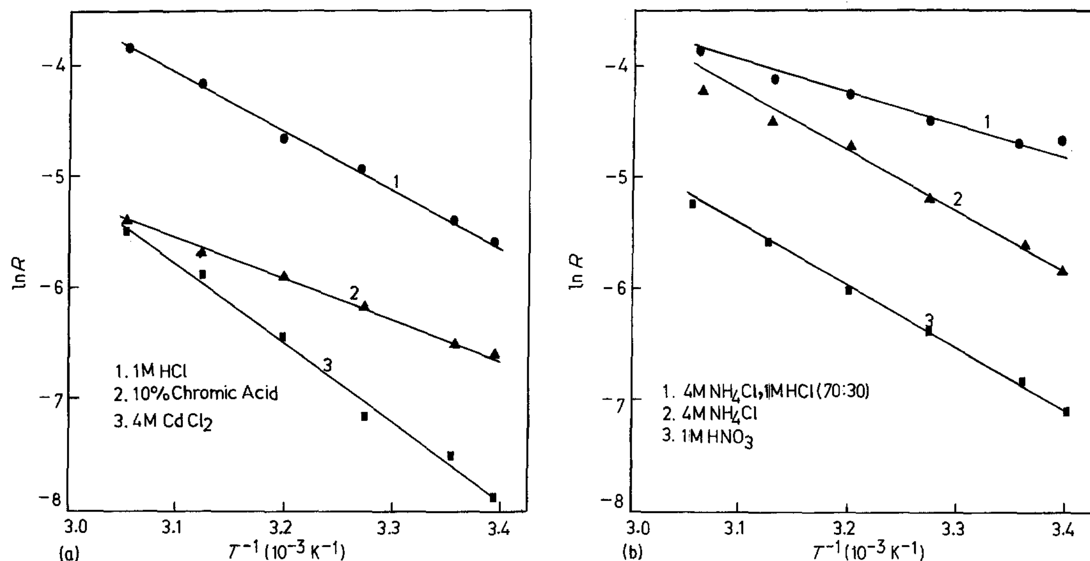


Figure 1 Plot of $\ln R$ against reciprocal temperature for (a) 1 M NHCl (Curve 1), 10% chromic acid (Curve 2), and 4 M $CdCl_2$ (Curve 3), and (b) NH_4Cl–HCl etch (Curve 1), 4 M NH_4Cl (Curve 2), and 1 M HNO_3 (Curve 3).

conductor crystals, was used as the basis for these investigations.

It may be mentioned that the crystal was agitated thoroughly and uniformly to bring all the faces in contact with the etching solution. The procedure of agitation and the estimation of dissolution by weighing was adopted in view of the difficulty in accurately measuring the volume of the etch pits. Though anisotropy can be anticipated in the present case of dissolution, the present study gives only an overall dissolution from all the crystal faces. The composition for a particular etch system was selected in such a way that the dissolution rate was above 1×10^{-4} g sec^{-1} per unit crystal mass in the case of HCl–$CdCl_2$–H_2O and NH_4Cl–$CdCl_2$–H_2O systems, and 2×10^{-2} g sec^{-1} per unit mass in the case of HCl–NH_4Cl–H_2O system. Thus, a large number of determinations on dissolution rate were made with different compositions, covering all possible ranges, where it was measurable.

3. Observations, results and discussion

3.1. Temperature dependence of etch rate

On account of the time dependent non-linear dissolution rate of cadmium oxalate trihydrate crystals, particularly in the initial part of etching [8], the etching period was kept constant throughout, and the etch rates at different temperatures were determined. The logarithm of dissolution rate, $\ln R$, was plotted against the reciprocal of absolute temperature, T^{-1}, and the results obtained are depicted in Fig. 1a and b for the six different solutions. The activation energy, E, for dissolution in different etchants was calculated from the slope of the curves. It is revealed from the results in Table I that the values of activation energies of etching in 1 M HCl, 4 M NH_4Cl, 1 M HNO_3 and 10% chromic acid are close to each other, though the rates of dissolution in these etchants are largely different. Etch solutions of 4 M $CdCl_2$ and NH_4Cl–HCl are characterized by relatively larger and lower values of activation energy, respectively. It should be mentioned that the composition (7 parts to 3 by volume) for the NH_4Cl–HCl system was selected from the etch contours (see Section 3.2), because it corresponded

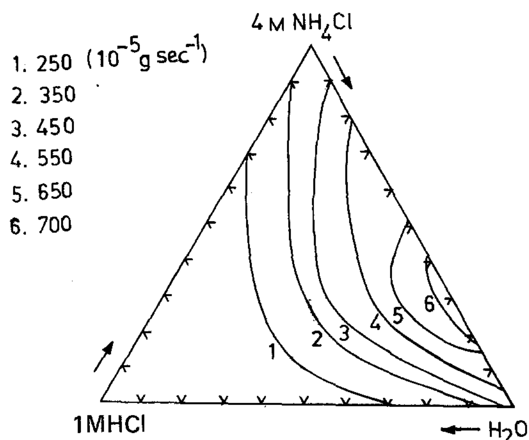


Figure 2 Constant etch rate contours obtained by etching in HCl–NH_4Cl–H_2O system.

TABLE I Experimental data of activation energy and pre-exponential factor of different etchants

Serial number	Etch solution	Activation energy, E (eV)	Arrhenius' pre-exponential factor, A (g sec^{-1})
1	70% NH_4Cl (4M)–30% HCl (1M)	0.24	1.36×10^2
2	10% $H_2Cr_2O_4$	0.44	5.10×10^2
3	1M HCl	0.45	2.19×10^5
4	4M NH_4Cl	0.47	3.41×10^5
5	1M HNO_3	0.48	3.98×10^5
6	4M $CdCl_2$	0.61	1.01×10^7

to the maximum etching rate. The faster etch rate in NH_4Cl–HCl may be because the fast etching is not sensitive to the energies of the atoms at the surface or to their geometric configuration [9]. It may be the fact that the chemical reaction and diffusion are both operating simultaneously, that makes the etching or dissolution process less sensitive to temperature change, and hence gives a very low value of the activation energy, as observed.

Etchants such as HCl, HNO_3 and chromic acid react with the crystal surface as the etching proceeds, to form oxalic acid, which, in turn, dissolves in water. These dissolutions are therefore reaction-rate controlled. On the other hand, the etch rate in $CdCl_2$ is observed to be low, giving the highest activation energy among the etchants presently investigated. Also, the dissolution in $CdCl_2$ is diffusion controlled, because of the common ion of the solution and the solvent. The observation that high activation energy characterizes diffusion-controlled dissolution (as of cadmium oxalate in cadmium chloride) is contrary to the observation by Abramson and King [10] and Tuck [6] on certain semiconductor materials in which the activation energy for a diffusion process was found to be less than that for a chemical reaction-controlled dissolution. It follows, therefore, that the other conclusion of Tuck's observation [5], that the diffusion-controlled mechanism of dissolution is not sensitive to changes in temperature, is contradicted in the present situation.

3.2. Compositional dependence of etch rate

The action of the three 3-component etch systems, represented by triangular co-ordinates in Figs 2, 3 and 4 needs proper elucidation. Each vertex corresponds to 100% of one of the components by volume. Though one of the vertices represents the amount of water, it does not give the total amount of water in the system, because the other two components are already diluted with water to give a particular normality of the stock solution.

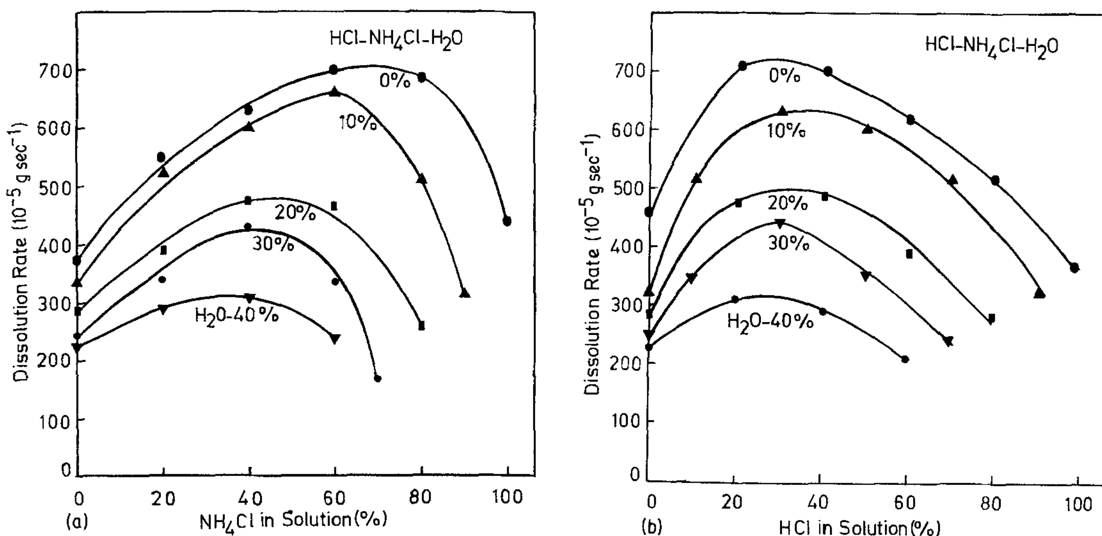


Figure 3 Plot of etch rate against the percentage of (a) 4M NH_4Cl, and (b) 1M HCl, in the HCl–NH_4Cl–H_2O etch system using different constant water percentages as the variable parameter.

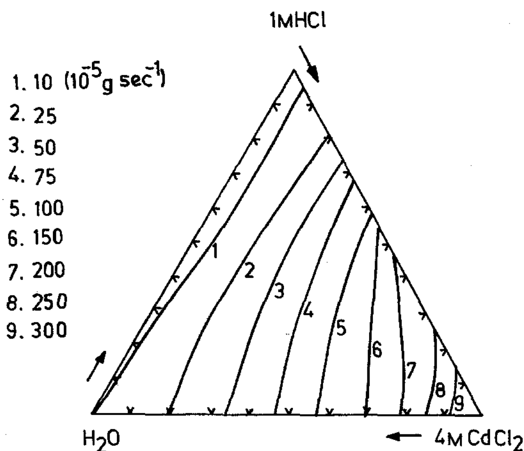


Figure 4 Plot of constant etch rate contours, obtained by etching in $HCl-CdCl_2-H_2O$ system.

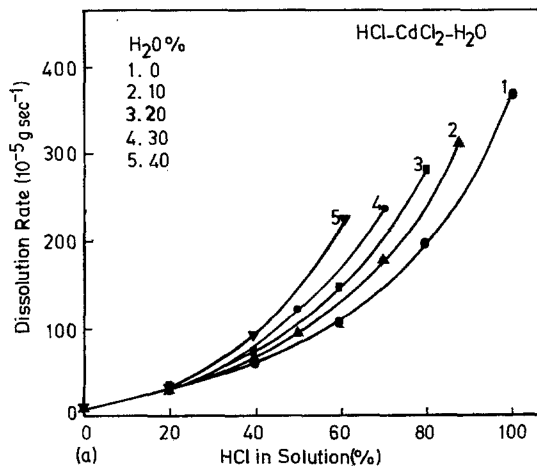
3.2.1. $HCl-NH_4Cl-H_2O$ system

The important features of the constant etch contours of this system, as shown in Fig. 2, can be summarized as follows. At higher concentrations of the NH_4Cl solution, the etching rate is more sensitive to the percentage of HCl and H_2O. The highest dissolution takes place between 60% and 80% NH_4Cl solution, with, of course, no water added. The part played by each component in the occurrence of dissolution can be seen from the plots of etching rate against percentage of NH_4Cl (Fig. 5a) and HCl (Fig. 5b) at various constant water percentages. It is interesting to note that the maxima of the curves for all the percentages of water (0 to 40%) lie exactly at 30% HCl (Fig. 3a) in the system. Since 30% of HCl and 70% of NH_4Cl together give the maximum solubility, this particular composition has been selected for the determination of the activation energy of the mixed system.

The two components of the system, HCl and NH_4Cl, have reaction controlled and diffusion controlled mechanisms of dissolution respectively. As activation energy is considered to be the factor by which the mechanism of the reaction is decided, then from our observations, where the reaction rate controlled mechanism has a lower activation energy (as for HCl, HNO_3, chromic acid), the resultant mechanism of etching of the $NH_4Cl-HCl$ etch can be thought of as reaction-rate controlled. However, such a hasty conclusion could be misleading since the values of the activation energies of etching of the crystals in NH_4Cl (0.47 eV) and HCl (0.45 eV) are indistinguishably close to each other. A co-operative phenomenon, therefore, better explains the faster dissolution rate, or the reduction of activation energy of dissolution in the $NH_4Cl-HCl$ etch. To elaborate, both reaction and diffusion are occurring side by side, thus making the process less sensitive to changes in the temperature of the system. From Fig. 3b, it is seen that the dissolution rate increases rapidly with an increase in the percentage of HCl and attains a maximum value at about 30%, for all the five different water percentages; it then gradually decreases to reach a minimum. However, in the case of the NH_4Cl percentage curve (Fig. 3a) the maxima move closer to the y-axis with increasing percentages of water added.

3.2.2. $HCl-CdCl_2-H_2O$ system

It can be seen from Fig. 4 that the dissolution rate is diminished with the addition of $CdCl_2$, as is



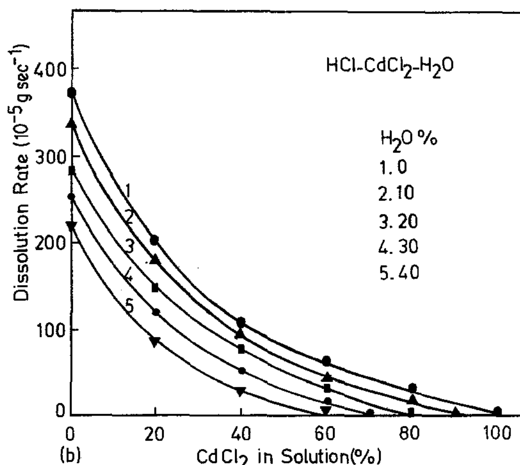


Figure 5 Plot of etch rate against the percentage of (a) 1 M HCl and (b) 4 M $CdCl_2$ in the $HCl-CdCl_2-H_2O$ etch system, using different constant water percentages as variable parameter.

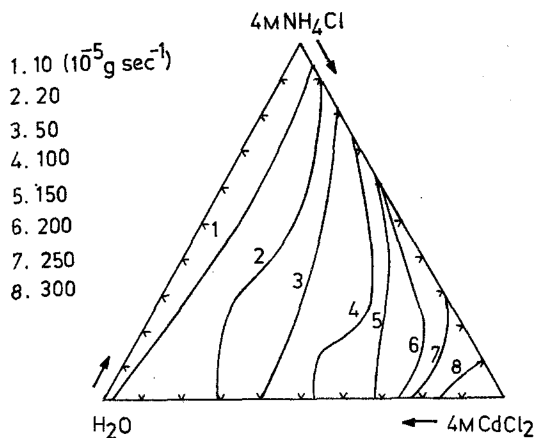


Figure 6 Constant etch rate contours obtained by etching the crystals in NH_4Cl–$CdCl_2$–H_2O system.

clear from the $CdCl_2$–H_2O base with minimum dissolution obtained at 100% $CdCl_2$. Also 22 ml of $CdCl_2$ added to 78 ml of HCl is observed to be sufficient to reduce the dissolution rate by 50%. Evidence for the dissolution suppression caused by $CdCl_2$ in association with HCl can also be seen in Fig. 5a. Considering a point on the graph corresponding to, say 60% HCl, it is found that a 40% addition of $CdCl_2$ reduces the dissolution rate to approximately 50% of that in the mixture which was made up by the addition of 40% water. No attempt was made to determine activation energies of dissolution because no composition in this system was of particular interest, quite unlike the case of the NH_4Cl–HCl–H_2O system which always showed a maximum rate of dissolution at a particular composition, as mentioned in Section 3.2.

The rate of dissolution against percentage of $CdCl_2$ plots (Fig. 5b) at different water percentages are approximately equidistant curves from one end to the other. One is inclined to infer that the dissolution rate is dependent on the hydrochloric acid percentage in the system, but is retarded by $CdCl_2$. Since the dissolution of $CdCl_2$ is diffusion controlled, and that in HCl chemical-reaction rate controlled, the inhibition action of $CdCl_2$ in HCl–$CdCl_2$–H_2O system can be explained without taking into consideration the change in viscosity [11] of the mixture. The large amount of $CdCl_2$ present in the mixture would hinder the faster dissolution of oxalic acid which is formed by the reaction of HCl on CdC_2O_4. The possible formation of the buffer by HCl, $CdCl_2$ and $C_2H_2O_4$ (produced by reaction) in the solution may, however, not be ruled out. That is why $CdCl_2$, in association with HCl, acts to reduce the dissolution rate of crystals by reducing the amount of HCl in solution.

3.2.3. NH_4Cl–$CdCl_2$–H_2O system

This sytem, in most of its characteristics, is similar to the HCl–$CdCl_2$–H_2O system. The constant etch rate contours are shown in Fig. 6, and the variations of etch rate with the percentage of NH_4Cl and $CdCl_2$ are given in Fig. 7a and b respectively. These figures are self explanatory on the lines of the previous system (Section 3.2.2). In this particular system, two salts, NH_4Cl and $CdCl_2$, are participating in the process of dissolution. Should one assume that the mechanism of dissolution in both the salts individually is diffusion rate controlled, the resultant system

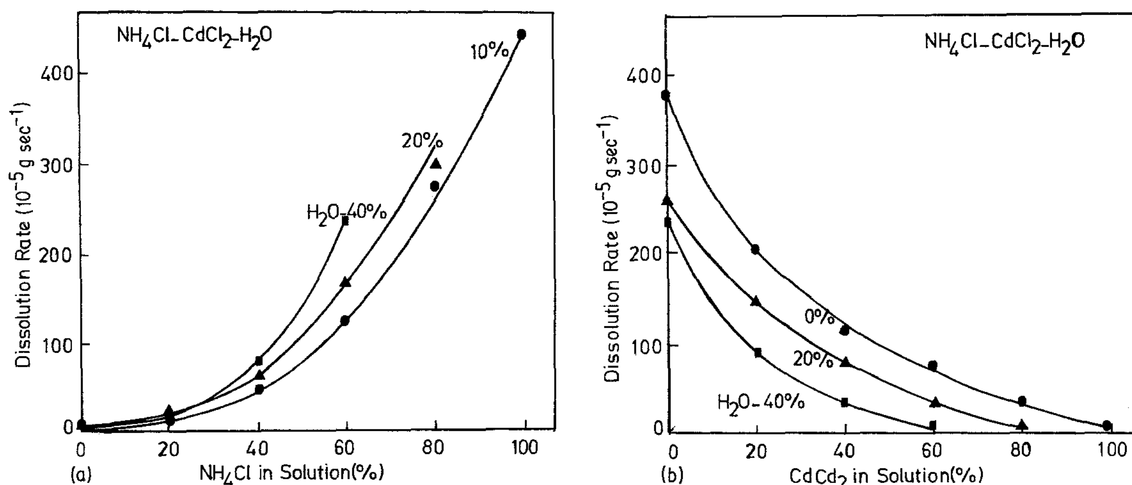


Figure 7 Plot of etch rate against the percentage of (a) 4 M NH_4Cl, and (b) 4 M $CdCl_2$ in the NH_4Cl–$CdCl_2$–H_2O etch system, using different constant water percentages as variable parameter.

could also be the same. But the marked reduction in the etch rate is not merely because the two salts exhibit markedly different dissolution rates of cadmium oxalate in their aqueous solutions. The clear inhibition action of cadmium chloride, when mixed with ammonium chloride, can be observed by similar considerations of the $HCl-CdCl_2-H_2O$ system, where the "Water curve" at a particular percentage of NH_4Cl is much higher than the "$CdCl_2$ curve" with the same percentage of NH_4Cl.

4. Conclusions

Conclusions can be drawn as follows:

(a) The mechanism of etching of cadmium oxalate crystals in etchants such as 1 M HCl, 1 M HNO_3 and 10% chromic acid is reaction rate controlled, whereas in 4 M NH_4Cl and 4 M $CdCl_2$, it is diffusion rate limited.

(b) The observation of Abramson and King [10] that the activation energy for reaction-rate limited etching is greater than that for diffusion-rate limited etching, is not true for cadmium oxalate dissolution.

(c) The mechanism, whether reaction-rate controlled or diffusion limited, could be hardly categorized by the knowledge of the values of the only experimental parameter as activation energy.

(d) The rate of dissolution of crystals in the 3-component system, $HCl-NH_4Cl-H_2O$ increases sharply, peaking at 30% HCl in the system, using different compositions, which is perhaps due to the co-operative phenomenon of reaction-controlled and diffusion-controlled processes.

(e) Cadmium chloride, when mixed with HCl or NH_4Cl, serves to suppress the reaction-rate considerably.

References

1. B. W. BATTERMAN, *J. Appl. Phys.* **28** (1957) 1236.
2. H. C. GATOS and M. C. LAVINE, *ibid.* **31** (1960) 743.
3. E. P. WARIKOIS, M. C. LAVINE, A. N. MARIANO and H. C. GATOS, *ibid.* **33** (1962) 690.
4. J. J. GILMAN and W. G. JOHNSTON, *ibid.* **27** (1956) 1018.
5. T. ABRAHAM, PhD thesis, Sardar Patel University, India (1981).
6. B. TUCK, *J. Mater. Sci.* **10** (1975) 321.
7. *Idem, ibid.* **11** (1976) 847.
8. S. K. ARORA and T. ABRAHAM, *J. Cryst. Growth* **52** (1981) 851.
9. H. C. GATOS, in "Crystal Growth and Characterization" edited by R. Ueda and J. B. Mullin (North Holland Publishing Co., Amsterdam, 1975).
10. M. B. ABRAMSON and C. V. KING, *J. Amer. Ceram. Soc.* **61** (1939) 2290.
11. A. F. BOGENSCHUTZ, K. LOCHERER and W. MUSSINGER, *J. Electrochem. Soc.* **114** (1967) 970.

Received 30 September and accepted 9 November 1981