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Etching and Micro-Topographical Studies of Barium Oxalate Crystals Grown in Agar Gel

Paresh V. Dalal[*], Kishor B. Saraf

P. G. Department of Physics, Pratap College, Amalner, India
E-mail:paresh10dalal@gmail.com

ABSTRACT

In the present study, the selection of an etchant for a particular crystal was purely made on empirical basis. The gel grown barium oxalate crystals were etched by HCl, HNO₃, BaCl₂, NH₄Cl, and NH₄Cl-HCl solutions. Micro-topographical studies have been made and it was found that elongated triangular etch pits and pits within pits were formed. Rectangular growth layers in the form of staircase and leaf like dendrite pattern were seen. Kinetics of etching was studied. Quantitative estimation of dissolved crystals in etchants was used for the determination of activation energy of reaction and pre-exponential factor with the help of Arrhenius equation.

Keywords: *Etching, Barium Oxalate, Micro-Topographical Studies, Activation Energies*

1. Introduction

In recent years, crystal growth in gel has attracted many investigators [1,2]. The agar gel technique is an inexpensive and simple for growing single crystals of certain class of materials like alkaline earth metal oxalates [3]. Oxalate crystals are insoluble in water and decompose before melting [4]. Therefore, single crystals of these materials cannot be grown by either slow solvent evaporation or melt techniques but they can be suitably grown by gel method. Barium oxalates is a pyro-nature material that shows great promise in pyrotechnic and high temperature electronic applications. The high dielectric constant and melting point of barium oxalate is an advantage to improve hardness of barium titanate in capacitor industries [5]. Nano-particles of barium oxalate [6] and barium titanyl oxalate have shown its effect on semiconducting properties [7]. A research program on etching and micro-topographical studies of barium oxalate crystals is being carried out in this laboratory. Etching has been the most convenient method for revealing dislocations in many crystals [8,9]. Successful, deliberate attempts to etch the surface at the sites of dislocations were made by Horn [10], and Patel and Desai [11]. Notable contributions on the theory and applications of etch methods were made by Honess [12], Miers [13], HariBabu and Subba Rao [14], and Patel and Desai [15]. Etch figures represent very early stage of crystal dissolution. The attack of solvent or chemical reagent on a seemingly

uniform solid surface is frequently localized during dissolution, and the depressions thus formed, are called 'etch pits'. There exists a report in the literature about etching [16,17] and kinetics of etching on barium oxalate dihydrates crystals [18]. However etch rate for different etchants was calculated by taking an average of measurements of a number of etch pits at a constant magnification [18]. This type of method, which is based on average measurements of pit as well as based on same magnification, cannot give the accurate measurements, because each etchants producing pits not necessarily exposed at the same magnification. Therefore weighing method used in the present work rather than the methods, based on the average measurement of number of etch pits for estimating etch rate is more reliable, simple and accurate.

2. Experimental Procedure

The barium oxalate crystals grown by the gel method reported earlier [19] were used for the etching studies. Crystals to be employed for etching studies were carefully picked up from the gel so that they were not damage during mechanical handling. An attempt to understand the mechanism of etching can be made by choosing number of simple etchants. AR grade HCl, HNO₃, BaCl₂ and NH₄Cl were used as etchants. Barium oxalate crystals were agitated thoroughly and uniformly to bring all the faces in contact with the etchant solution in 1 M HCl, 1 M HNO₃,

4 M $BaCl_2$, 4 M NH_4Cl and 4 M NH_4Cl + 1 M HCl{in 70:30 ratio} for 30 second, similarly other crystals were dipped for 1 minute in HCl, HNO_3, and NH_4Cl + HCl solutions. These crystals were arrested from the etchants, immediately washed with distilled water, dried in air and observed under microscope for micro-topographical studies.

For kinetic studies of etching, damage and inclusion free 10-20 mg crystals were selected. Each initially weighed crystal immersed in 0.5 M, 1 M, 1.5 M and 2 M HNO_3, 1 M HCl, 4 M $BaCl_2$, 4 M NH_4Cl and 4 M NH_4Cl + 1 M HCl at a constant temperature 28, 32, 49 and 520°C for 30 seconds. These crystals were taken out from the solution, washed immediately with distilled water, air-dried and weighed again. The amount of dissolved crystals was calculated from their loss in weight.

3. Observations, Results and Discussion

Micro-topographical studies are helpful in understanding growth mechanism of crystals under study. Detailed micro-topographical examinations of the grown crystals reveal that striations are common features. There is exhibit inclined striations. Sometimes, these striations were found to cover the whole surface under examination. In fact these striations are divided into strips. The width of the strips is not uniform. There are some irregularly spaced inclined striations strictly oriented 300 to C axis of the crystal as shown in **Figure 1**. In addition to horizontal striations, some faces are observed elongated elliptical or rectangular growth hillocks. One such case of dissolution of rectangular growth hillocks in the form of staircase is illustrated in **Figure 2**. **Figure 3** shows randomly oriented, crowded, triangular etch hillocks directed in one particular way. Because of truncation and rounding of a corner of etch pits, they look like elongated triangular etch pits. **Figure 4** shows a rectangular platelet with leaf like dendrite pattern on its face. Some portions of platelet are irregularly eaten away and edges are formed. These edges act as initiation centers of dendrite patterns. In the present observation, platelets may be developed first and then dendrite pattern may be formed as reported [20]. It is also interesting to see pits within pits, as in **Figure 5**, similar to an observation reported [21] in case of natural CaF_2 crystals. The smaller pits, which are seen near the bottom of the larger enveloping pit suggesting the division of a pit, continuing with time may be believed to be due to a number of other dissolution lines meeting and forming nodes, thereby giving rise to a dislocation network in the body of the crystal.

In order to study the kinetics of etching in barium oxalate crystals, the etch rates were determined by calculating the amount of dissolved crystals from their loss in weight at different temperature, keeping etching time
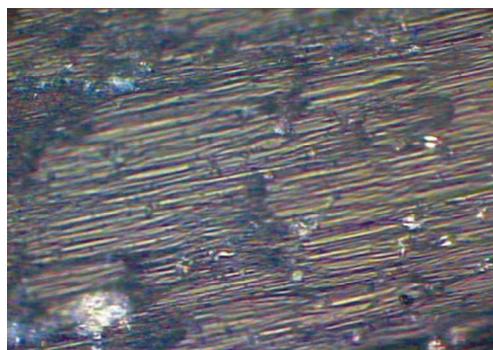
Figure 1. Striations making an angle of 30 with C-axis.
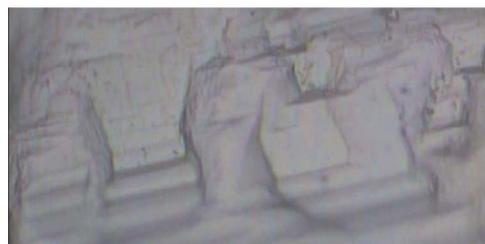
Figure 2. Rectangular growth layers in the form of staircase.

Figure 3. Randomly oriented, crowded, triangular etch hillocks.
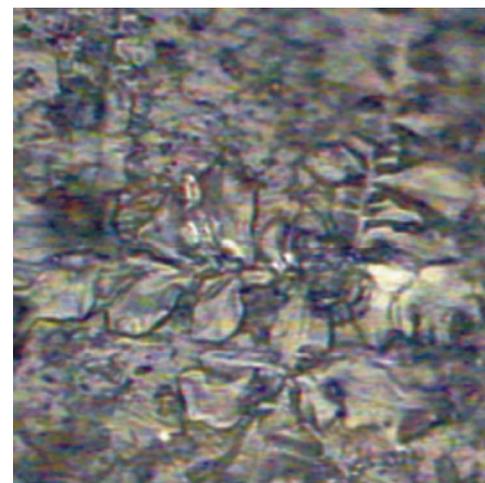
Figure 4. Rectangular platelet with leaf like dendrite pattern.
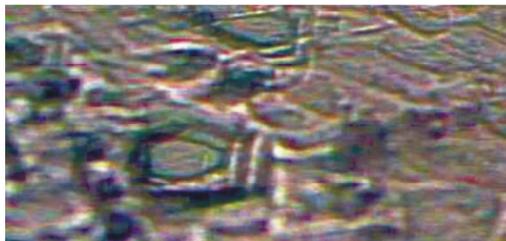
Figure 5. Elongated triangular pits within pits.

constant through out the experiment. The natural logarithm of the etch rate, lnR; was plotted against the reciprocals of the absolute temperature, and the results obtained are depicted in **Figure 6** and **7** for the five different solutions. Evidently the curves follow the Arrhenius equation [22]:

$$R = A\exp(-E/KT),$$

where A is the pre-exponential factor, E the activation energy of the etching process, K is the Boltzmann constant and T is the temperature of etchant. From these Arrhenius graphs, the values of activation energy E and pre-exponential factor A thus calculated are shown in **Table 1**.

It was observed that the values of activation energy E, for etching in HCl, NH_4Cl and HNO_3 solutions are close to each other, though the rates of dissolution in these etchants are largely different. $BaCl_2$ and NH_4Cl + HCl etch solutions are characterized by relatively larger and lower values of activation energies respectively. The faster etch rate in NH_4Cl-HCl may not be due to the energies of the atoms at the surface or due to their geometric configuration [23], but may be due to both; the

chemical reaction and diffusion are operating simultaneously, that makes the etching or dissolution process less sensitive to temperature change, and hence a very low value of activation energy was observed. The etchants such as HCl, HNO_3 reacts with the crystal surface to form oxalic acid, which in turn dissolves in water. These dissolutions are therefore reaction rate controlled. On the other hand, the etch rating in $BaCl_2$ solution is observed to be low, giving the highest value of activation energy among the etchants used. And, the dissolution in $BaCl_2$ is, doubtlessly, a diffusion controlled phenomenon, because of the common Ba^{2+} ion between the solute and the solvent. This observation of the highest activation energy characterizing diffusion controlled dissolution is contrary to the observation reported chemical reaction controlled on certain semiconductor materials [24,25]. Similarly, the observation made by Tuck [25] that the diffusion controlled mechanism of dissolution is not sensitive to change in temperature, gets itself contradicted in the present situation.

It was revealed from the data (**Table 1**) that the values of activation energy remain constant for the different concentration of acid, whereas the pre exponential factors A were increased, with increasing acid concentration.

4. Conclusions

From the studies we observe that:

1) The mechanism of etching barium oxalate in etchant such as 1 M HNO_3 is reaction rate controlled whereas in the case of 4 M NH_4Cl, 4 M $BaCl_2$ it is diffusion rate controlled.
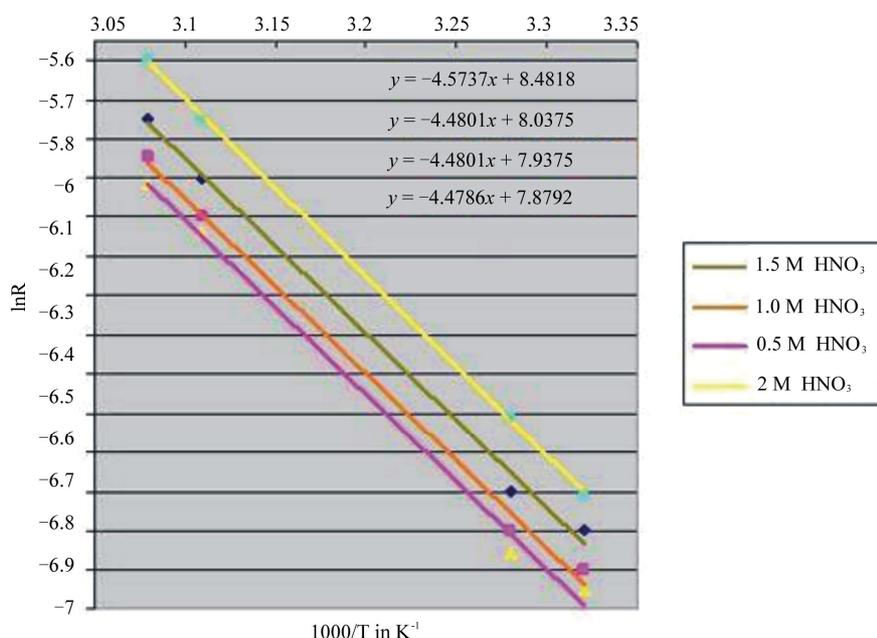
Figure 6. Plot of lnR against reciprocal temperature for HNO_3.
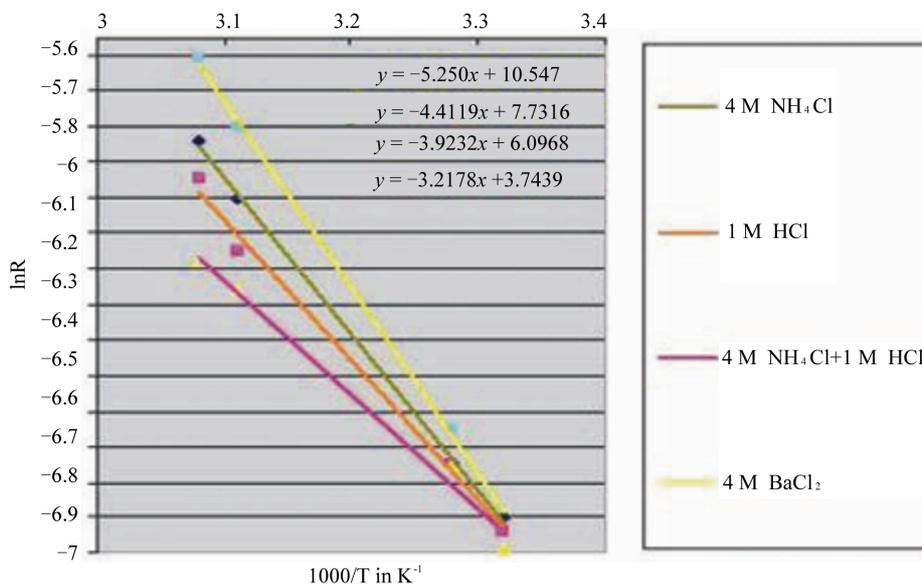
Figure 7. Plot of lnR against reciprocal temperature of 1 M HCl, 4 M NH₄Cl, 4 M BaCl₂ and 4 M NH₄Cl + 1 M HCl.

Table 1. Activation energies and pre-exponential factors of different etchants calculated from arrhenius plots.

S. No.	Etchant	Activation energy E (in eV)		Arrhenius pre-exponential factor A (in g·sec^{-1})
		0.5 M	0.39	2.6×10^3
01	HNO₃	1.0 M	0.39	2.8×10^3
		1.5 M	0.39	3.1×10^3
		2.0 M	0.39	4.8×10^3
02	4 M NH₄Cl	0.38		2.3×10^3
03	1 M HCl	0.34		4.4×10^2
04	4 M BaCl₂	0.45		22.3×10^3
05	4 M NH₄Cl + 1M HCl	0.28		0.4×10^2

2) The observation of Tuck [25] that the activation energy for reaction rate controlled etching is more than that of the diffusion rate controlled one, is not found true for barium oxalate dissolution.

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

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