International Journal of Materials Science
ISSN 0973-4589 Volume 12, Number 2 (2017), pp. 259-268

http://www.ripublication.com

Etching and Kinetic Studies of Gel Grown Strontium Oxalate Crystals

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Abstract

Strontium oxalate crystals have been grown by agar gel method. Chemical etching studies were carried out using HCl, HNO_3, $SrCl_2$, NH_4Cl and NH_4Cl-HCl etchants to analyze the dislocation centers. Micro topographical studies have found dislocations like striations; rectangular pits and V-shaped layer growth in grown crystals. Kinetics of etching was also studied. Quantitative estimation of dissolved crystals in etchants was used for the determination of activation energy of reaction and pre-exponential factor using Arrhenius equations. Overall observations on kinetic dissolution process suggest that highest activation energy is characterizing by diffusion controlled dissolution while that of lower activation energy by chemical reaction dissolution. Determined pre-exponential factor is more in strontium chloride solution than the other etchant may be due to the fact that the successive collision rate of strontium chloride molecules with strontium oxalate molecules was more during dissolution process.

Keywords: strontium oxalate, gel method, etching, kinetic studies

1 INTRODUCTION

Growth of crystals in gel media has attracted many investigators [1-4], because it is useful for the substances, decomposed before melting [5] and having low solubility [6]. It has been observed that gel, in particular agar-agar gel is inexpensive, simple and found unique place due to its characteristics of suppression of nucleation centers [2].

Most of the oxalates and molybdates crystals have wide applications in electro- and acousto-optical devices [7-9]. Oxalates and particularly barium and strontium oxalates play a vital role in increasing the hardness of barium and strontium titanate for their applications in multilayer ceramic capacitors [10-11]. Oxalates have many applications like good ionic conductivity [12], as precipitation agent [13], in nano particle synthesis, in magnetic and luminescent devices [14-16]. Pyro nature of strontium oxalate has gained recognition of material scientist for its application in pyro techniques and high temperature electronic devices [17].

Synthesis of rare earth oxalates [18-20] and transition metal oxalates using gel method have been reported [21]. Barium copper oxalate crystal [22], barium oxalate [23-24] and cadmium oxalate [25] were grown in silica hydro gel, whereas barium oxalate [26-27] and cadmium oxalate [28] were grown in agar gel. Strontium was used in doping [29], and in mixed oxalate crystals [30]. However, large size prismatic and transparent strontium oxalate crystals grown with controlled nucleation using additives in agar gel media are reported in previous work [31]. The purpose of the present work is to study the kinetics of etching of strontium oxalate crystals. Etch rate is determined by weighing method, which is based on calculating the amount of dissolved crystal from their loss in weight at different temperatures keeping etching time constant throughout the experiment.

2 EXPERIMENTAL

The strontium oxalate crystals grown by the gel method [31] were used for the etching studies. Etching studies of strontium oxalate crystals were carried out similar to that reported for barium oxalate crystals [32].The selection of an etchant (solvent) for a strontium oxalate crystal was purely made on empirical basis. 1M HCl, 1M HNO_3, 4M $SrCl_2$, 4M NH_4Cl and 4M NH_4Cl+ 1M HCl (70:30 ratio) were used as etchant.

The crystals were immersed one by one in different etchant for 30seconds and then transferred to distilled water for cleaning. The etched crystals were dried in air and observed under microscope for micro-topographical studies.

For kinetic studies of etching, damage and inclusion free strontium oxalate crystals were separately immersed at temperature 28, 32, 49, and 52 ^{0}C in the 1M HCl, and 1M HNO_3, 4M NH_4Cl, 4M NH_4Cl + 1M HCl (70:30) and 4M $SrCl_2$ etchant to determine the etch rate. Similar experimental procedure was adopted as reported in case of barium oxalate crystals [32].

3 RESULTS AND DISCUSSION

Micro topographical examinations were carried out under an optical microscope (Carl Zeiss optical microscope with CCD camera attachment). These examinations reveal that hillocks in the form of molehills are common features. Figure 1 shows that striations of uneven sizes and growth hillocks in the form of molehills were observed. From Figure 2, rectangular pits edges converted to sharp edges and layer growth could be observed. V-shaped layer growth can be observed in Figure 3. Figure 4 is showing elongated triangular growth, where edges were rounded off from one end to another. The height of the triangular pit is observed 460.2μm while that of rectangular growth pit is having the width 438.05μm. Tiny molehills, striation and layer growth can also be observed from these Figures. The bright line in Figure 5 is the tip edge of the crystal. On both sides of this edge, symmetry pattern of striations making about 30^0 angles with one another can be observed. Figure 6 shows striations in the form of rectangular strips while the curved striations are seen on opposite side of rectangular strips. In Figure 7, step growth of rectangular pits can be observed. Many tiny triangular pits of an average 4.32 μm sizes are shown in Figure 8. Figure 9, Figure 10 and Figure 11 are also showing tiny triangular pits, rectangular pits and striation.

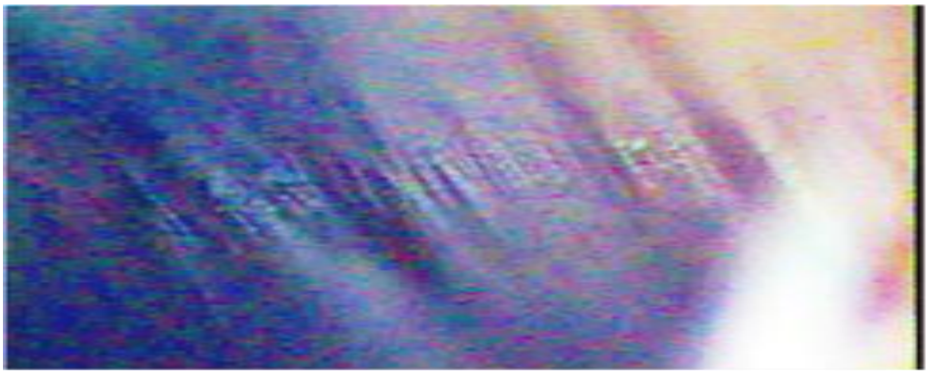

Figure 1: Striation

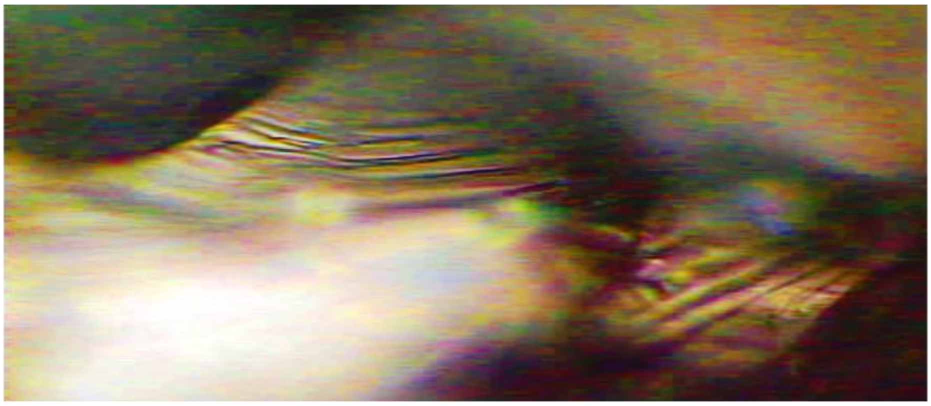

Figure 2: layer growth

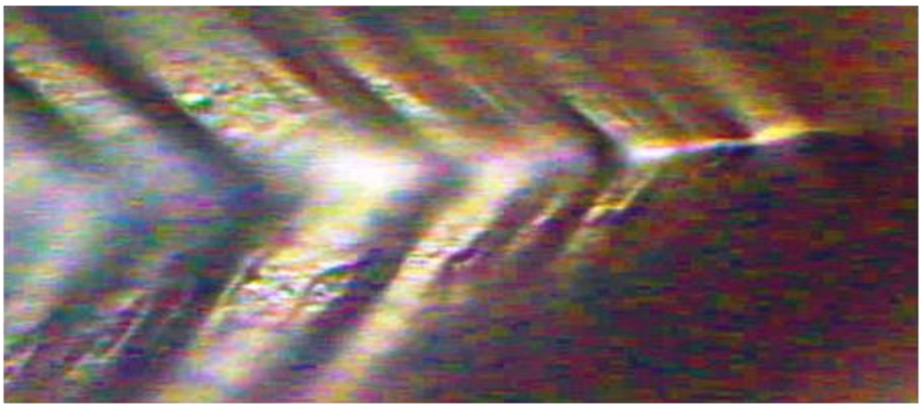

Figure 3 : V-shaped layer growth

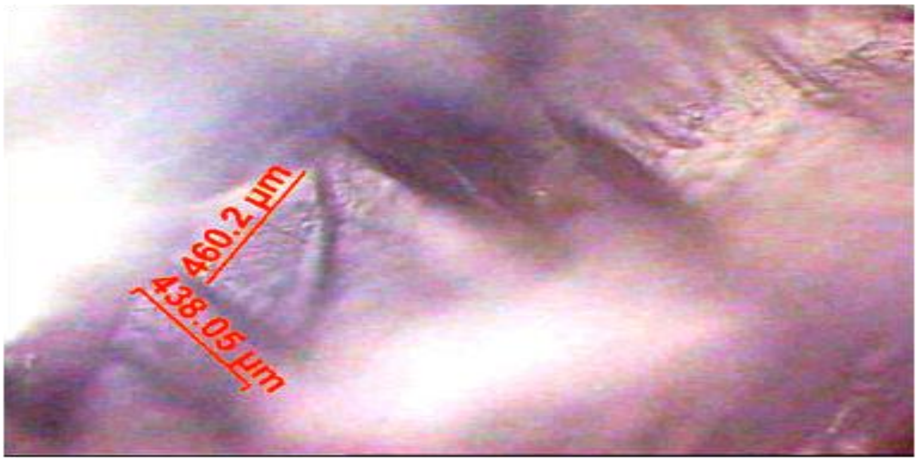

Figure 4: Triangular etch pit

Figure 5: Striation

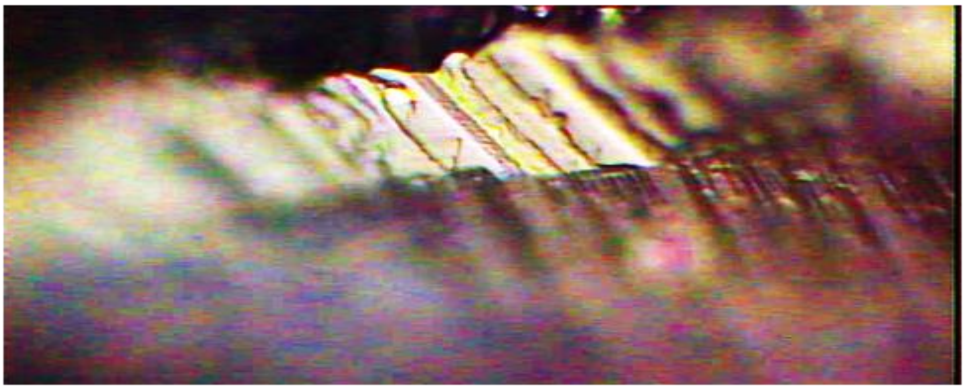

Figure 6: Striation in the form of strip

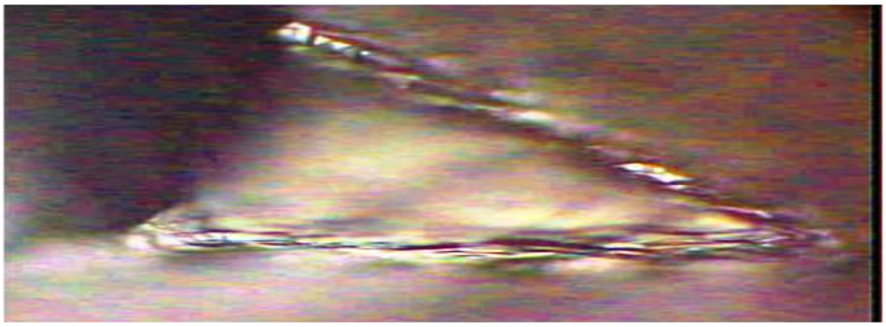

Figure 7: Rectangular pits

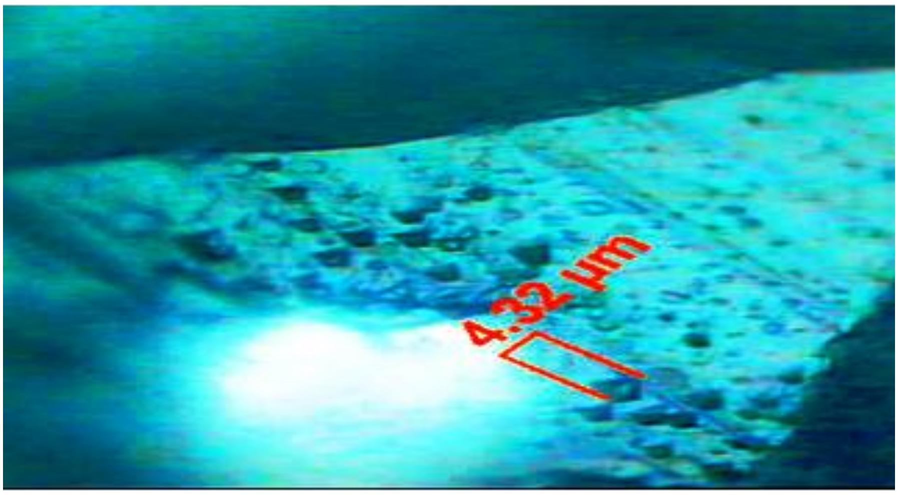

Figure 8: Tiny triangular pits

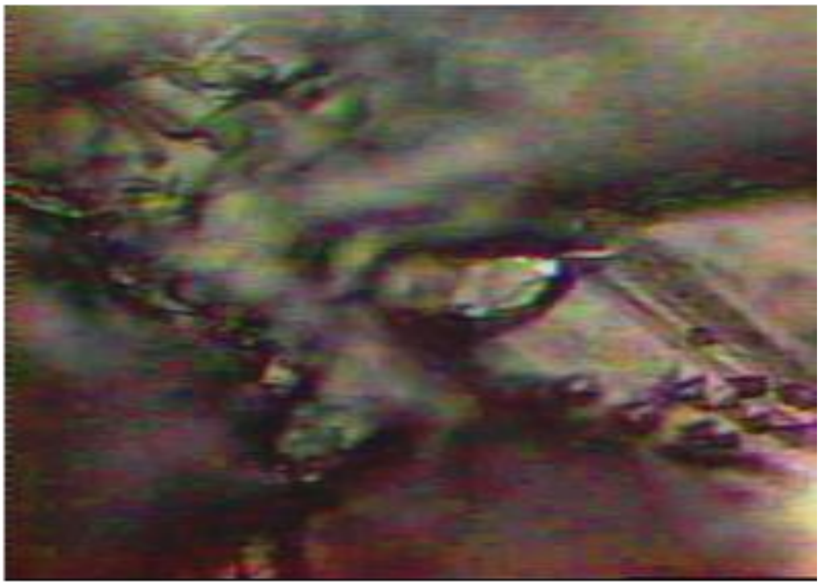

Figure 9 : Tiny triangular pits

Figure 10 : Tiny rectangular pits

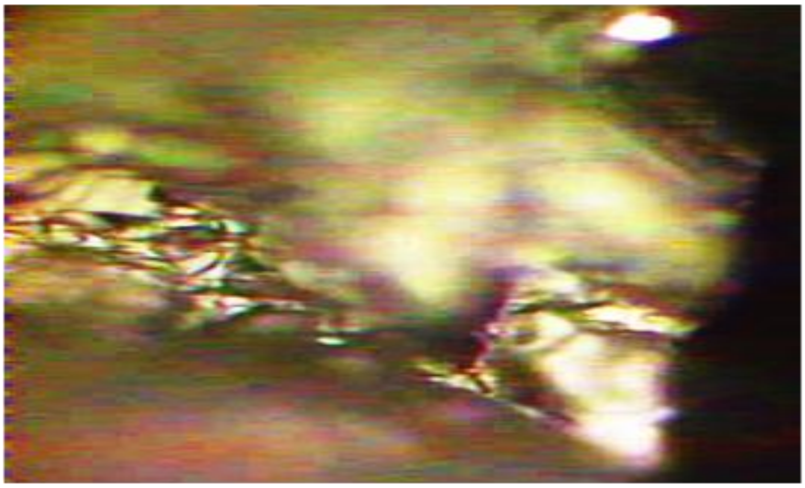

Figure 11 : Tiny swallow pits

Overall studies show that microstructures exhibit triangular etch hillocks in the form of molehills. These molehills somewhere densely populated and somewhere in few numbers. The crowded molehills are indicating of high density of nucleation. It may also be concluded that growth of the crystal took-place by two dimensional growth mechanisms.

In order to study the kinetics of etching in strontium oxalate crystals, a graph was plotted between the natural logarithm of etch rate (R); lnR and the reciprocal of the absolute temperature as shown in Figure 12.

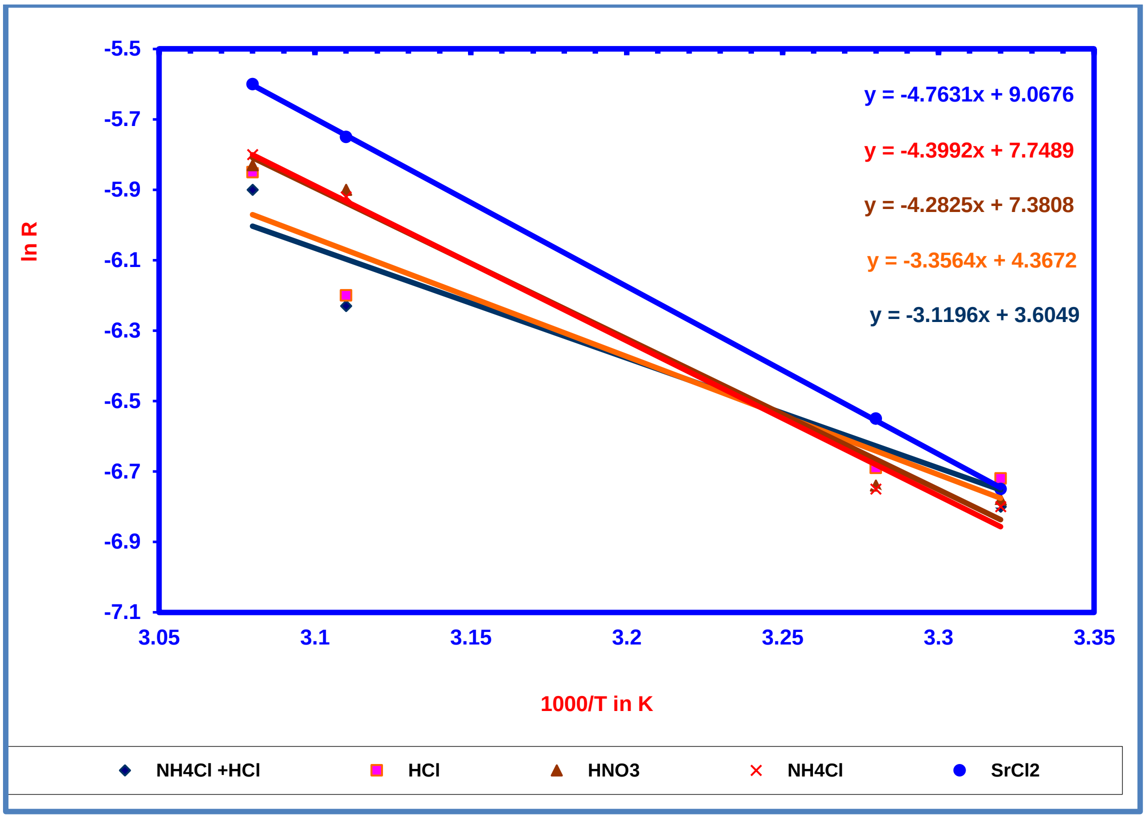

Figure 12: A plot of etch rate versus reciprocal of absolute temperature

The slopes of the graphs were used to determine the activation energies in each etchant, whereas intercepts of the graphs were used to calculate pre-exponential factors for each corresponding etchant. The calculated values of activation energies and pre- exponential factors are depicted in Table 1.

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 (in g sec^{-1})
01	4M $SrCl_2$	0.41	2 X 10^4
02	4M NH_4Cl	0.38	5.3 X10^3
03	HNO_3	0.37	3.7 X10^3
04	1M HCl	0.29	1.8 X 10^2
05	4M NH_4Cl + 1M HCl	0.27	0.84 X10^2

It was observed from the results, depicted in Table 1 that the lowest value of activation energy is obtained for 4M NH4Cl+1M HCl etchant solution while in 1M HCl solution, it was slightly increased, and again increased in HNO3 solution. These all reactions were chemical reaction controlled. On the other hand, the activation energy was observed maximum for 4M SrCl2 and slightly lower in 4M NH4Cl. These both the reactions were diffusion controlled. Hence one can be concluded that the observation of highest activation energy is characterizing by diffusion controlled dissolution while that of lower activation energy by chemical reaction dissolution.

Also it was observed that the pre-exponential factor is more in strontium chloride solution. It may be due to the fact that the successive collision rate of strontium chloride molecules with strontium oxalate molecules will be more during dissolution process.

4. CONCLUSION

From systematic investigations on etching and kinetic studies of gel grown strontium oxalate, following are the point wise conclusions:

1) Micro structures exhibit triangular etch hillocks in the form of molehills.
2) It is concluded that growth of the crystal took-place by two dimensional growth mechanisms.
3) From the studies of kinetics of etching, it is concluded that the observation of highest activation energy is characterizing by diffusion controlled dissolution while that of lower activation energy by chemical reaction dissolution.
4) Highest pre-exponential factor in strontium chloride solution may suggest that the successive collision rate of strontium chloride molecules with strontium oxalate molecules will be more during dissolution process.

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