

## Microstructures of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ Single Crystal Grown in Silica Gel

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(Received 30 September 2016; published online 23 December 2016)

As part of our work on the growth of cadmium oxalate single crystals in silica gel, an attempt has been made to investigate the growth mechanism of the crystals. This paper deals with the study of surface structures of cadmium oxalate single crystals grown in silica gel. Observation of microstructure is also useful for geologist as crystallization processes in the laboratory have similarities with those in nature. Various growth features such as growth layers as developed etch pits and liquid inclusion have been observed using optical and scanning electron microscopy techniques. Thermal analysis showed that the grown crystals were dehydrated thermally even from lower temperatures. The infrared spectrum (FTIR) revealed the presence of oxalate ligands and water of hydration in both the pure crystals.

**Keywords:** Surface structure, Overgrowth, Etches pits, Silica gel.

DOI: [10.21272/jnep.8\(4\(2\)\).04075](https://doi.org/10.21272/jnep.8(4(2)).04075)

PACS numbers: 61.05.a, 61.05.C, 68.37.Hk, 78.20.e

### 1. INTRODUCTION

Crystal growth is one of the fascinating fields for mankind due to symmetry, structural simplicity and purity. Crystal have ample of applications in the field like chemistry, metallurgy, ceramics, physics, mineralogy, medicine, engineering etc. Crystal growth gel method techniques [1-2] have been known to be endowed with high perfection and uniformity, as they grow at nearly ambient temperatures. The oxalates of transition metals are employed as precursors to produce mixed metal oxides of the required stoichiometry at relatively very low temperature. Recently these are also extensive used for preparation of high temperature modern superconductive materials, nano-materials, and metallurgical powders. The study of surface structure of crystal faces allows an understanding of growth and development of habit faces in particular and crystal in general. The microstructure of various crystals [3-6] put forward independently, two – dimensional nucleation theory for the growth of crystals.

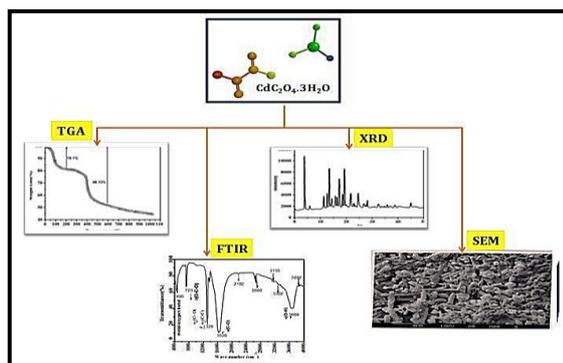


Fig. 1 – Schematic aim of the present paper

The aim of the present work is to study a detailed investigation cadmium oxalate (shown in Fig. 1). The present deals with carried out on surface structure of gel – grown crystal of cadmium oxalate to understand the mechanism of growth of these crystals.

### 2. EXPERIMENTAL PROCEDURE

Single crystal of cadmium oxalate were grown at ambient temperature at PH value of 4.5. The crystal were grown using various concentration of feed solution of cadmium chloride from (0.1 to 1 N) Transparent crystals were bounded by (001) (100) and (010) faces were obtained from the diffusion two reactants of cadmium chloride and oxalic acid as described earlier [7]. The crystals were thoroughly cleaned with acetone and coated with silver films in vacuum coating unit. They were then examined under metallurgical and scanning electron microscope (SEM).

### 3. RESULT AND DISCUSSION AND DISCUSSION

#### 3.1 TGA and XRD Analysis

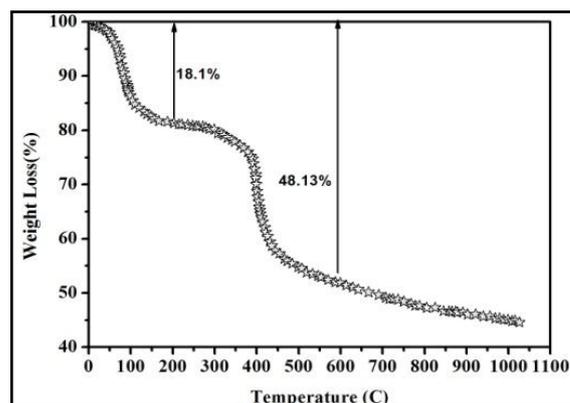
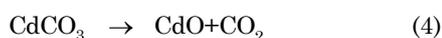
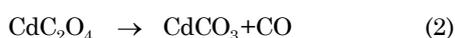


Fig. 2 – TGA analysis of cadmium oxalate

The hydrate cadmium oxalate crystals have been found losing their three molecules of water of crystallization by storing them over calcium chloride. From the thermo gravimetric analysis carried out with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  Fig. 2. As can be seen in TG curves,

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the weight lost occurred in two steps. It is seen that the crystal starts losing its water molecules (due to loss of moisture) at 80 °C, becoming completely dehydrate at 193 °C. The shape of thermal decomposition curve of  $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  in the temperature range (30-193) °C shows a single step dehydration reaction. The measured weight loss for this decomposition stage is about 18.1 % of the total weight resulting in the elimination of three water molecules. Further dehydrate salt start decomposing at 310 °C. The 48.1 % losses in weight, in the temperature range, 200-600 °C, suggest loss of CO. The compound remains stable up to 1030 °C. It may be due to loss of  $\text{CO}_2$  above 600 °C and the material is reduced to cadmium oxide. This thermal behaviour in terms of scheme may be explained as below [8-10].



### 3.2 Spiral Growth

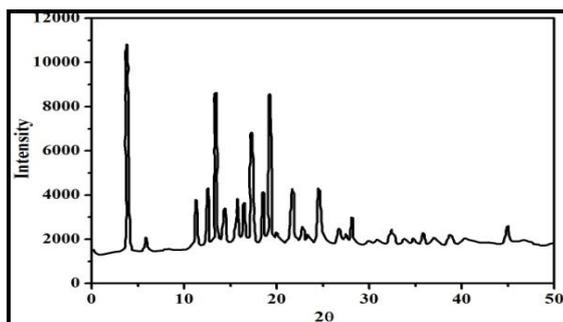


Fig. 3 – XRD analysis of cadmium oxalate

The powder XRD diffractogram Pure single crystals of cadmium oxalate hydrate  $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  is shown in Fig. 3.



Fig. 4 – Low concentration (below 0.2M) of  $\text{CdCl}_2$  solution shows presence of grown spiral structure on (001)

### 3.3 Growth Layers From the Edges of the Crystals

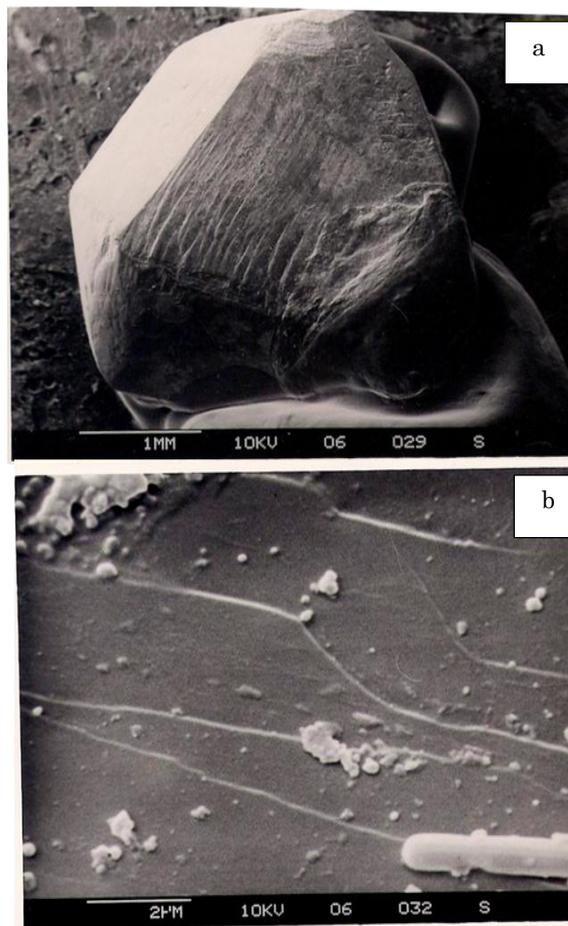
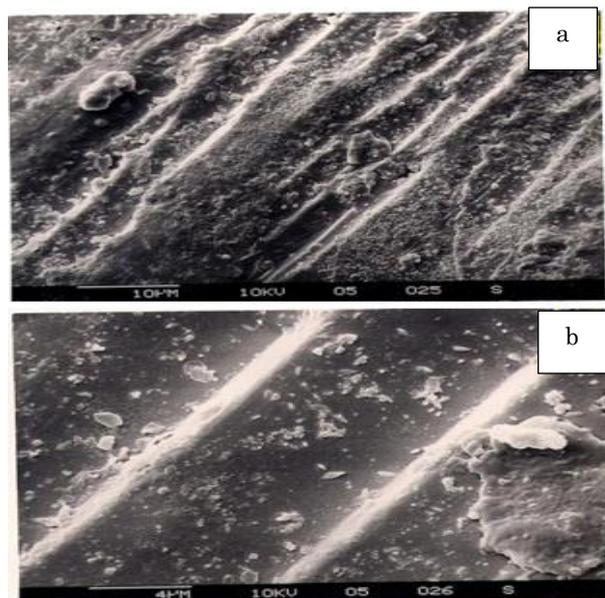


Fig. 5 – The strating of growth layers from the edges of crystal (a). The growth layer on the crystal surface clearly see (b)

It is general observation that the edges of the crystal of large steps on the crystal surface sometimes works as elegant centers for initiation of growth layer. Several examples illustrated the effect are observed in the (001) faces of crystals grown in silica gels using  $\text{CdCl}_2$  and oxalic acid as reactants. Figure 5 (a) shows the starting of growth layers from the edges of cadmium oxalate crystal. Figure 5 (b) shows the growth layers on the crystal surface clearly using scanning electron microscope (SEM) at higher magnification. The SEM photographs of growth layers on the opaque cadmium oxalate crystal surface are shown in figure 6 (a) and (b). These crystal are opaque because of very high PH value of the gel. Therefore, the growth layers are not sharp but they are dense layer. This may be due to the buildup of material in crystal surface towards the centre indicating that edge nucleation is the predominant growth mechanism at high concentrated feed solution.

### 3.4 Spiral Growth

Crystal obtained using feed solution of low concentrated (below 0.2M) cadmium chloride showed the presence of spiral structure on (001) faces as shown in Fig. 4. At lower concentration of the feed solution, (001) faces are the slowest growing faces and hence are larger in size than (210) and (101) faces. Observation of growth



**Fig. 6** – (a) and (b) The SEM photographs of growth layers on the opaque crystal surface

spirals on (001) faces of cadmium oxalate at lower concentration of feed solution suggest that these faces might have grown by spiral growth mechanism. It is suggested that as the growth proceeds, internal stresses develop giving rise to slip step producing screw ledges on these faces and growth around the such ledges and results into spiral turns.

### 3.5 Growth Layer from as Developed Etch Pits on the Growth Faces



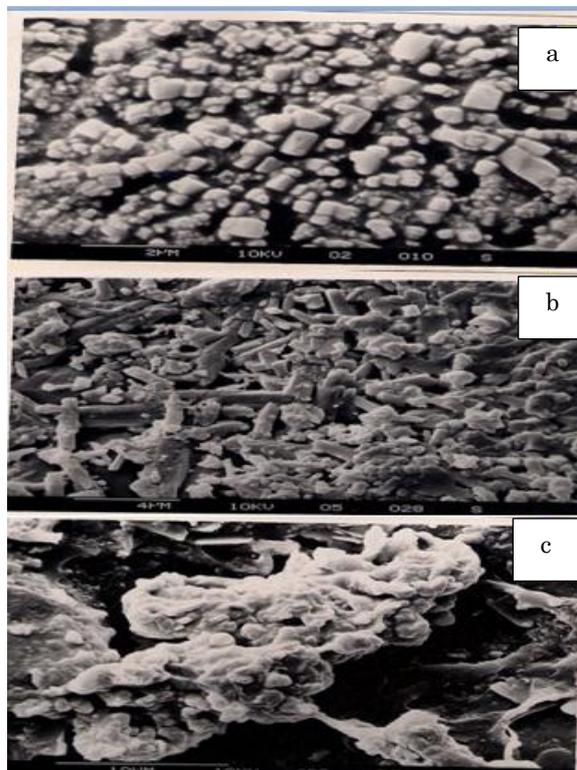
**Fig. 7** – (a) As grown Etch pit are seen on the growth faces (b). The growth layers from the etch pits (black patches on the photograph)

Some times as developed etch pits were observed on growth faces as shown in Figure 7 (b). Shows the SEM picture of the growth layers associated with etch pits. The formation of etch pits. may be due to the selective dissolution of crystal faces in the solution in the gel. It can also be interpreted that when growth ceases after the crystal reaching the maximum size, then also dissolution possible with selective etching. Figure 7 (b) clearly

shows the starting of the growth layers from the etch pits (black patches on the photograph). It is interesting to note that these growth layers are oriented along the (110) direction and in straight lines.

### 3.6 Overgrowth on the Crystal Surfaces

Sometimes overgrowth of quite large size (from a few angstroms to several microns) were observed on the (001) faces of the host (primary) crystals. Figure 8 (a) to (c) show overgrowth on the (001) faces in the form square, needle like and lumps respectively. According to Buckley [11] overgrowth on crystal surface occurs owing to interruption in continuity of deposition due to change in growth condition, such as temperature changes or the temporary exhaustion of solution after an active burst of crystallization.



**Fig. 8** – Overgrowth on the crystal surface (001) (a) Square (b) needles (c) lumps

### 3.7 Liquid Inclusions

An example of liquid of inclusion in the (001) face of cadmium oxalate crystal is shown Figure 9 (a) & (b) These inclusion are advancing along the (001) direction. That the inclusion shows a tendency to have (010) indicates that the surface energy of the (010) is less than that of any other plane. Liquid inclusions are produced when an area of a crystal face ceases to grow while the neighboring area continue to grow normally and after some time the available liquid id enclosed. The reason for cessation of growth may be adsorption of some impurity or some minor fluctuations in temperature during growth [13]. The liquid trapped in the crystal is probable cadmium chloride resulting from the by- product of reaction waste product during crystallization of  $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ .

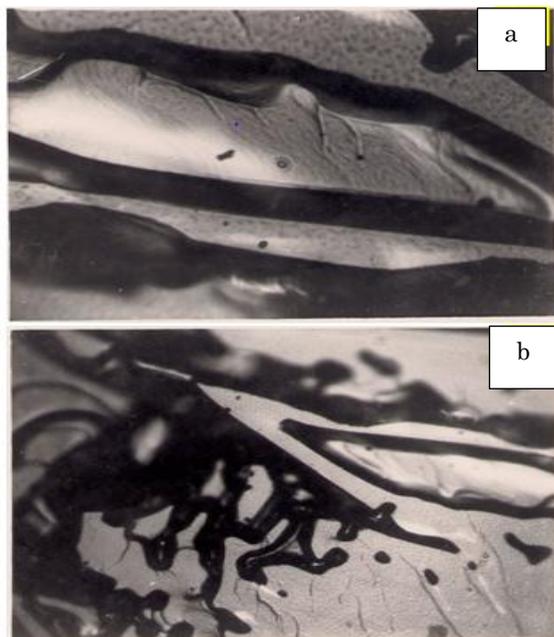


Fig. 9 – (a) and (b) liquid inclusions on the face of the crystal

### 3.8 Ftir Studies

FTIR studies have been carried out in the region 400-4000  $\text{cm}^{-1}$  using KBr pellet technique shown in Fig. 10. We have just brief the main bands [14-16] observed in the samples are  $\nu(\text{O-H})$  to 3669  $\text{cm}^{-1}$  (b, vs),  $\nu(\text{C-O})$  to 1628  $\text{cm}^{-1}$  (vs),  $\nu_s(\text{C-O})$  and  $\nu_s(\text{C-C})$  overlapped to 1380  $\text{cm}^{-1}$  (s),  $\nu_s(\text{C-O})$  and  $\delta(\text{O-C-O})$  overlapped to 1320  $\text{cm}^{-1}$ ,  $\nu_s(\text{C-C})$  and  $\delta(\text{O-C-O})$  overlapped to 723  $\text{cm}^{-1}$  (s) and 490  $\text{cm}^{-1}$  due to metal oxygen bond (CdO). 3669 and 3882  $\text{cm}^{-1}$  attributed to the water OH stretching and the water bending. Normally a band at 1628  $\text{cm}^{-1}$  ought to be overcast by the oxalate band ( $(\text{C}_2\text{O}_4)_2$  ion) observed. The sample that has oxalate ( $\text{C}_2\text{O}_4$ )<sub>2</sub> ion is endorsed by the broad peak merged in the strong intense wide band in the region 1628  $\text{cm}^{-1}$ , which is attributed to the asymmetric stretch of  $\text{CO}_2$ . Well-pronounced sharp peak at 1320  $\text{cm}^{-1}$  and a weak but sharp peak at 1380  $\text{cm}^{-1}$  correspond to the  $\text{CO}_2$  symmetric stretching. The sharp band which was observed at 723  $\text{cm}^{-1}$  is may be due to the combined effect of in-plane deformation of  $\text{CO}_2$  and the presence of a metal-oxygen bond. The ab

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sorbed IR bands at 490  $\text{cm}^{-1}$  are assigned to the metal oxide MeO bond (CdO) [10, 16, 17]. The infrared spectral studies confirm the presence of water of crystallization and oxalate group in the grown crystals.

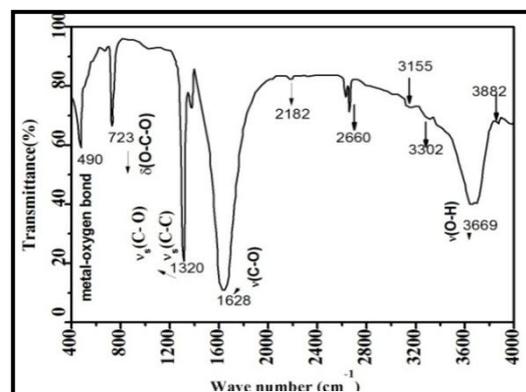


Fig. 10 – FT-IR spectra of cadmium oxalate

### 4. CONCLUSIONS

It has been observed that at very low concentrated feed solution, the crystals were grown by screw dislocation mechanism.

At higher concentrated feed solutions, layer growth mechanism is predominant.

X-ray power diffraction has revealed the crystallinity of the material.

The study of characteristic peaks obtained (IR) reveals the presence of metal oxygen bond. Presence of water of crystallization and the oxalate phase formation was identified from the FT-IR band assignments.

The growth layer initiates from the edges steps and inclusions on the crystal surface, Overgrowth mechanism of square, needle like and lump type structures have been observed on that liquid entrapment is the main source of defect in the gel growth cadmium Oxalate crystals.

### ACKNOWLEDGEMENTS

The author wish thank to Prof. Venkateswara Rao , Head , Department of Physics, Shivaji university, Kolhapur for providing the laboratory facilities and also thanks Dr. J.K. Nandgave and Dr. P.K. Patil for their kind support.

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