X-RAY DIFFRACTION STUDIES OF DIVALENT OXALATE CRYSTALS GROWN BY GEL TECHNIQUE

Babita Saiyed

Principal, Shree P.M. Patel College of Electronics & Communication, Anand
Email: babita_saiyed@yahoomail.com

ABSTRACT

Single Crystals of Cadmium Oxalate trihydrated have been grown using the famous gel technique. The growth of the crystal was carried out at room temperature and in the optimum condition for the growth. The XRD Studies were carried out. Using the data the lattice parameters were obtained. From the studies the crystal system of the grown crystal was triclinic was confirmed.

***Keywords*:** Gel growth, Cadmium oxalate, XRD, etc

INTRODUCTION

The gel technique has the advantage of producing macroscopic crystals with perfection of the highest order, because the medium itself permits the reactions to occur at a reasonably slow and controlled rate (Bahadur,1990). Nevertheless, nucleation control in gel medium remains one of the serious, yet interesting, problems facing a crystal grower because of several factors involved in the process which affect the growth rate of the crystals, as they indeed are the driving potential of crystallization and diffusivity in the gel. Other oxalates were grown and characterized and reported (Dalal,2006, Parekh2008, Dalal2009). Characterization describes the features of composition, crystallographic structure and some relevant characteristics of the material.

Experimental Method

Aqueous solution of oxalic acid of a particular strength/molarity (0.5 M) was taken in a beaker and SMS of a particular specific gravity was added dropwise, using a pipette, constantly stirring the solution in the beaker with a view to avoiding excessive local ion concentration which may cause premature local gelling and make the final medium inhomogeneous and turbid. This process of gelling is found to be exothermic. During gelation, pH of the mixture was constantly measured using a pH meter (CONTROL DYNAMICS, Digital pH meter, model – APX 175). Then, after getting the gel with the desired value of pH, it was transferred to several test-tubes, in fixed amount, without giving any chance to the formation of air bubbles, by pouring the mixture to fall steadily along the sides of the test tubes. After that, mouths of all test tubes were closed with cotton, essentially to prevent the entry of dust particles, fast evaporation, and contamination of the exposed gel

surface. Double distilled water, wherever required, was used throughout the crystal growth experiment.

To confirm the crystallinity of the grown crystals and for analysis of the crystal structure, X-ray diffraction technique has been used, because the wavelength of X-rays is $\lambda \approx 2d$, d being the interplaner spacing. The 'Philips, Holland, Xpert MPD' powder diffractometer was used.

RESULTS AND DISCUSSION

The single crystals of cadmium oxalate trihydrate have been obtained with the following optimized values: Temperature 30^0C, Gel pH 3.0, Gel density 1.04g.cm^{-3} Concentration of reactants1 M $CdCl_2$ and 0.5 M oxalic acid, Amount of supernant liquid 20 ml, Ageing time 6-7 days. The diffraction data, viz. the prominent d and hkl values as obtained, are displayed in Table 1. The computer fitted (calculated) d-values are closely matching with the standard d-values to the greatest accuracy. The computer program has been found to conform the d-values to the triclinic structure. The axial angles and the unit cell dimensions as computed are displayed in Table 2. The standard formulae (Cullity,1978), have been used for the determination of lattice parameters.

$$\sin^2\theta = \frac{\lambda^2}{4d^2} \qquad (1)$$

$$\frac{1}{d^2} = \frac{1}{V^2}\left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + S_{13}hl\right)$$

$$V^2 = 4a^2b^2c^2\left(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma\right)$$

$$S_{11} = b^2c^2\sin^2\alpha$$

$$S_{22} = a^2c^2\sin^2\beta$$

$$S_{33} = a^2b^2\sin^2\gamma$$

$$S_{12} = abc^2\left(\cos\alpha\cos\beta - \cos\gamma\right)$$

$$S_{23} = a^2bc\left(\cos\gamma\cos\beta - \cos\alpha\right)$$

$$S_{13} = ab^2c\left(\cos\alpha\cos\gamma - \cos\beta\right)$$

Density and Number of Molecules

Accurate measurement of the pycnometric density of grown single crystal has been carried out and the value is found to be D = 2.637 gm·cm^{-3}. With the knowledge of pycnometric density as determined, along with certain other constants, the number of molecules per unit cell, Z for $CdC_2O_4{\cdot}3H_2O$ has been found out, using the relationship,

$$Z = \frac{DVNa}{M} \qquad (2)$$

$$V = \sqrt{4a^2b^2c^2\left(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma\right)}$$

$=313.2185\times10^{-24}$ cm^3 'a', 'b', 'c' , 'α', 'β' and 'γ' being the lattice parameters, Na (Avogadro number) = 6.023×10^{23},M (molecular weight) = 254.45 gm. Thus, Z = 1.955 ≈ 2 has been obtained.

$$\therefore \text{X-Raydensity } D = \frac{ZM}{VNa} = \frac{2*254.45}{\left(313.2185\times10^{-24}\right)*\left(6.023\times10^{23}\right)}$$

$$= 2.697 \text{ gm}\cdot\text{cm}^{-3}$$

Table 1. Computed d values and (hkl)

Sr.No.	2 θ	θ	2sin θ	d_{std}	d_{obs}	I/I_0	(hkl)
1	13.925	6.9625	1.25652	6.5	6.3544	100	(010)
2	15.46	7.73	1.98465	5.7	5.7268	38.8	$(\bar{1}01)$
3	19.85	9.925	-0.9592	4.51	4.4691	11.8	(110)
4	24.025	12.0125	-1.052	3.75	3.701	12.6	$(\bar{1}11)$
5	26.05	13.025	0.88544	3.42	3.4178	4.4	(020)
6	27.575	13.7875	1.87897	3.2	3.1901	57.3	(002)
7	28.985	14.4925	1.87506	3.07	3.078	3.9	$(\bar{1}02)$
8	31.65	15.825	-0.2335	2.85	2.8246	10	$(\bar{2}11)$
9	33	16.5	-1.4236	2.72	2.7121	19	(200)
10	33.83	16.915	-1.8691	2.66	2.6474	31.3	(120)
11	35.855	17.9275	-1.5937	2.54	2.5024	3.2	$(2\bar{2}0)$
12	36.29	18.145	-1.2954	2.45	2.4734	6.4	(210)
13	38.565	19.2825	0.83909	2.37	2.3326	3.5	$(\bar{1}21)$
14	39.005	19.5025	1.21506	2.31	2.3073	3.1	$(\bar{2}20)$
15	40.44	20.22	1.95999	2.22	2.2616	4.7	$(\bar{2}12)$
16	42.375	21.1875	1.43979	2.13	2.1313	9.8	(030)
17	44.25	22.125	-0.2669	2.02	2.0452	6.4	$(\bar{3}03)$
18	46.635	23.3175	-1.9405	1.93	1.946	7.1	$(\bar{3}12)$
19	48.305	24.1525	-1.6613	1.87	1.8826	2.8	$(\bar{2}30)$
20	50.965	25.4825	0.68534	1.79	1.7904	2.2	$(\bar{3}10)$

Table 2. Some computed crystal parameters

X-ray data	Values
a	7.55 Å
b	10.06 Å
c	6.47 Å
α	90^0
β	102^0
γ	98^0
Z	2
ρ (g/cm^3)	2.6975
Crystal system	Triclinic
Space group	$P_{\bar{1}}$

CONCLUSION

The grown crystal using del method were of good quality and the lattice parameter computed from the X-ray diffraction data were in good agreement with the reported values. The crystal system was triclinic.

REFERNCES

1. S. Asath Bahadur, R. Saravanan, R. K. Rajaram and V. Ramakrishnan, *Cryst. Res. Technol.,* **25** (1990) K273.
2. P.V. Dalal and K.B.Saraf, Bull. Mater. Sci., **29** (2006) 421.
3. B. B. Parekh, P.M.Vyas and M. J. Joshi, Bull. Mater. Sci., **31** (2008) 143.
4. P.V. Dalal , K.B.Saraf and S. S. Shah, *Cryst. Res. Technol.*, **44** (2009) K273.
5. B. D. Cullity, *Elements of X-ray diffraction,* 2nd edition, (John Wiley, New York, 1978).