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GROWTH AND STUDY OF CADMIUM TARTRATE OXALATE SINGLE CRYSTALS BY SOL GEL TECHNIQUE

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In this research work mixture of two acids were used for changing the P^H of the solution. Single crystals of cadmium tartrate oxalate were grown by gel technique using single diffusion method at optimum temperature. The effect of varying various process parameters such as P^H of the gel, gel setting time, gel concentration of the reactance on the growth of crystals were studied. In the gel preparation process sodium meta silicate (Na_2SiO_3 is mixed with the mixed solution of oxalic acid($C_2H_2O_4$) and tartaric acid($C_4H_6O_6$) in the desired mole fraction.The harvested crystals were characterized by X-ray powder Diffractogram, Fourier Transform Infrared Spectroscopy, quantitative elemental analysis of EDAX and Scanning Electron Microscope. Powder XRD results indicates the polycrystalline nature of this materials. FTIR for these crystals show all the bands expected from the metal tartrate oxalate with water of crystallization. Further the presence of cadmium, carbon and oxygen is confirmed by EDAX.SEM images shows the structure in the form of flat and the plates with the sharp edges.

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1. Introduction

In recent years crystals growth in gel medium has attracted the attention of many investigators [1-5]. Scientifically and technologically crystal growth and characterization have became an interesting research area in the past decades. All basic solid materials are made up of single crystals and they are backbone of the modern technology. The influence of single crystal is noticed in the semiconductors, optics and acoustics, in various medical applications and in jewellary industries [6-9]. Cadmium Tartrate crystals, CdC4H4O6, 3H2O, is isostructural with other elctroseramic divalent metal ions. Some divalent metal ion tartrates are exhibiting non-linear optical and spectral characteristics and hence are used in transducers and many linear and non-linear mechanical devices (10-13).

A lot of publications have been reported in recent years for the preparation of oxalate of metallic ions. The oxalate ion is engaged in constructing a large variety of molecular and frameworks by incorporating suitable metal ion in the crystal lattice. The gel method is in fact useful for the growth of single crystals which decompose at temperature below their melting points and also for those not having suitable solvents for recrystallization[14-17].

The composition reduces their size and perfection, and therefore it is obviously desirable to suppress the nucleation until ideally, only one crystal grows in a predetermined location available techniques [18-19].

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2. Materials and Methods

Cadmium tartrate oxalate crystals were grown from free solution of oxalic acid, tartaric acid and cadmium chloride. Silica gel were prepared by adding oxalic acid (1M) and tartaric acid (1M) mixture to sodium meta silicate (water glass) solution of specific gravity 1.04 drop by drop till the P^H of the gel adjusted to 3.5, 4.0 and 4.5. Continuous stirring is needed to avoid excessive local ion concentration, which may cause premature local gelling and make final solution inhomogeneous[20]. The solution with the desired value of P^H is transferred to several glass tubes. The gel found to set in 30min to 24 hours, depending upon its P^H and the environmental temperature. Once gelled, feed solution of aqueous cadmium chloride of concentration 1.5M was carefully placed with the help of a pipette over the set gel in order to avoid the surface damage and breakage of the gel. The cd^{2+} ions diffuses slowly through narrow pores of the gel to react with the oxalate and tartrate ions, giving rise to the formation of single crystals.

All chemical used such as oxalic acid, tartaric acid, and sodium metasilicate and cadmium chloride were of AR grade to avoid impurity accumulations.

After harvesting the fully grown Cadmium tartrate oxalate crystals, structural characterization was performed using X-ray powder diffraction technique. XRD patterns were obtained using a Philips analytical X-ray diffractometer with cu Kα(λ=1.5406Å) radiation. The FTIR spectra were recorded for the crystals in the wave number range of 400-40000cm^{-1} using bruker vector 22 spectrometer using KBr pellet technique.

3. Results and discussion

The crystal size as a function of time was noted day by day. The crystal size increases with time. The crystal size gradually increases with time and finally the growth rate ceased after a period of 240 hrs.

The nucleation rate of Cadmium tartrate oxalate crystals grown for three different pH values in 3.5,4.0 and 4.5.the number of crystals increases as of growth period increases. The gelation time depends on many parameters such as concentration of ionic species inside the gel, gel pH and temperature of the gel.

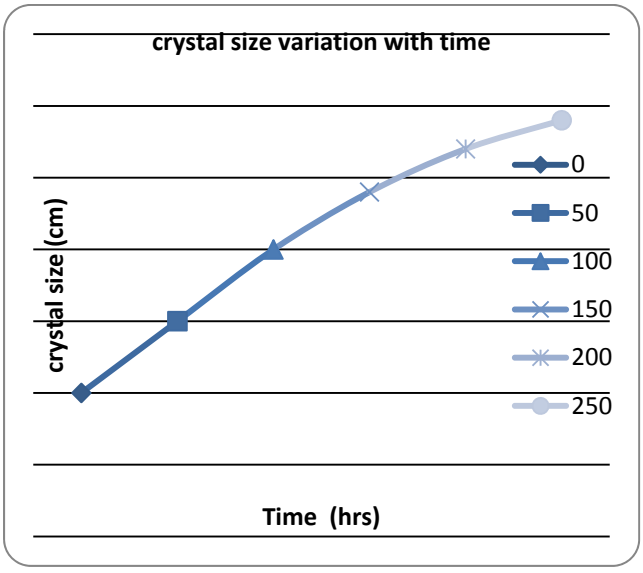


Fig. 1.Crystal size vs time.

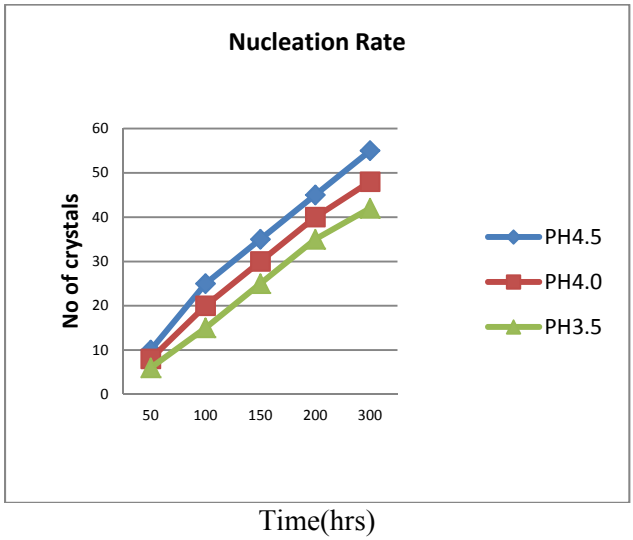
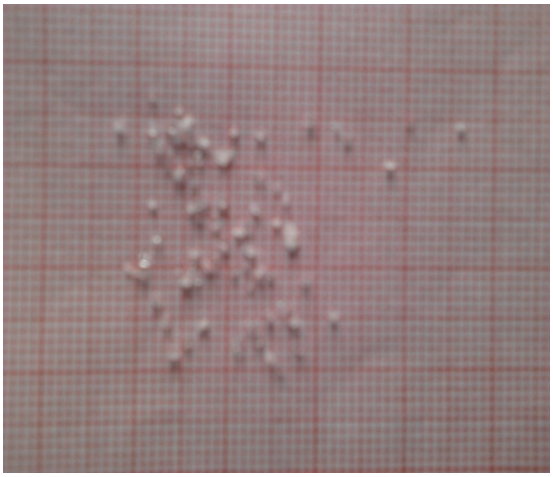


Fig. 2.Time vs. No of crystals.

The size and parameters of single cadmium tartrate oxalate crystsal grown in silica gel.

The crystal size as a function of time was noted every day. It was observed that the crystal size gradually increases with time.



Optimized growth parameters of crystals

S.No	Various process parameters	Values
1.	Density of Na_2SiO_3	1.04 g/cm^3
2.	Concentration of oxalic acid	1M
3.	Concentration of tartaric acid	1M
4.	Concentration of cadmium chloride	1.5M
5.	Gel setting period	10h
6.	Gel aging	3 weeks
7.	Period of growth	30 days
8.	Temperature	Room temperature

X ray diffraction analysis:

The crystal structure of the sample compound was studied by powder x ray diffraction method.

The X-ray diffraction was recorded by miniflex-rigaku model japan with CuKα radiation of wavelength λ=1.54056.

Determination of grain size from XRD spectrum

The grain size is determined by measuring the width of the line with highest intensity peak. The grain size can be calculated by using formula.

Grain size $D = 0.9/\beta\cos\theta$

Where β is full width of half maximum in radian and D is grain size of the crystal.

$D = 0.9 \text{ X } 1.54056 / 0.06 \text{ X } \cos(15.886)$

$= 1.38654/0.057708$

$= 24.0268Å$

The calculated average grain size is 24.0268Å. The analysis of different diffraction peaks indicates the formation of system. The diffraction peaks at 2θ value were measured very carefully and converted into d value using the Bragg's equation putting n=1.By measuring the peak heights above the background in nm and scaling the value up so that the tallest peak has a value of 100.

Powder X –ray Diffraction pattern

A

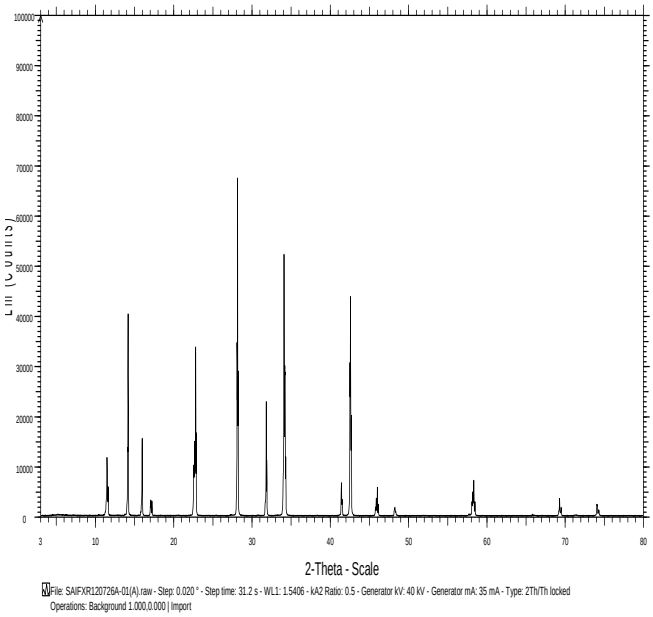


Fig. 3. shows the recorded XRD spectrum

Intensity tabulation for 'd' value

2θ	'd' value	Intensity count
4.604	19.17552	150
11.393	7.76039	11677
14.086	6.28247	40443
15.877	5.5773	15480
17.144	5.16807	2905
22.606	3.93018	14896
27.307	3.26326	183
28.188	3.16331	28998
30.718	2.90827	188
31.763	2.81495	22887
34.052	2.63073	52354
41.496	2.17438	3269
42.554	2.12278	43890
46.977	1.93269	17.7
48.237	1.8851	1665
58.323	1.58084	7099
65.994	1.41445	189
69.323	1.35443	3457
71.313	1.32145	151
74.131	1.27802	2164

FT-IR Spectrum

The infrared spectrum in the range of 400-4000 cm^{-1}shows strong band centered at about 3493.22 cm^{-1} attributed to the water OH stretching and the water bending[21].The bands observed below 1700 cm^{-1} in the pure Cadmium tartrate oxalate trihydrate crystals grown in silica gel are assigned to oxalate vibrational modes[22].Usually a band at approximately 1620cm^{-1} should be overcast by the oxalate band observed at approximately 1614.22cm^{-1z}[23].On the other hand, the band around 1300 cm^{-1} corresponds to the asymmetric stretching mode of C-O. The absorbed IR bands at 515 cm^{-1} are assigned to the meta oxide of cadmium (Cd-O) [24].The infrared spectral studies confirm the presence of water of crystallization and oxalate and tartrate group in the grown crystals. The detailed band assignments of some selected absorption bands/peaks observed in the FT-IR spectrum are shown in the following table.

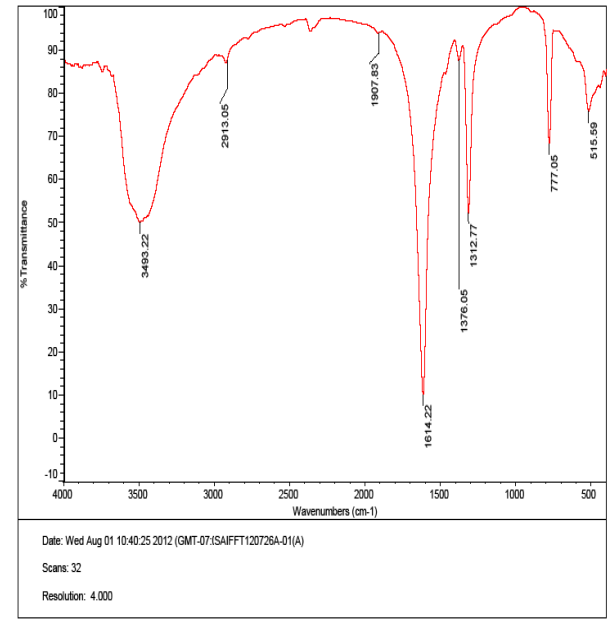


Fig. 4. Shows the recorded FTIR spectrum

Assignment of some selected FTIR bands (cm^{-1})

S.No	IR bands(cm^{-1})	Assignment
1.	3493.22	Water (OH)
2.	2913.05	OCO
3.	1614.22	H_20
4.	1376.05	CO+O-C=O
5.	1312.77	CO+CC
6.	777.05	OC=O +M-O
7.	515.59	MO

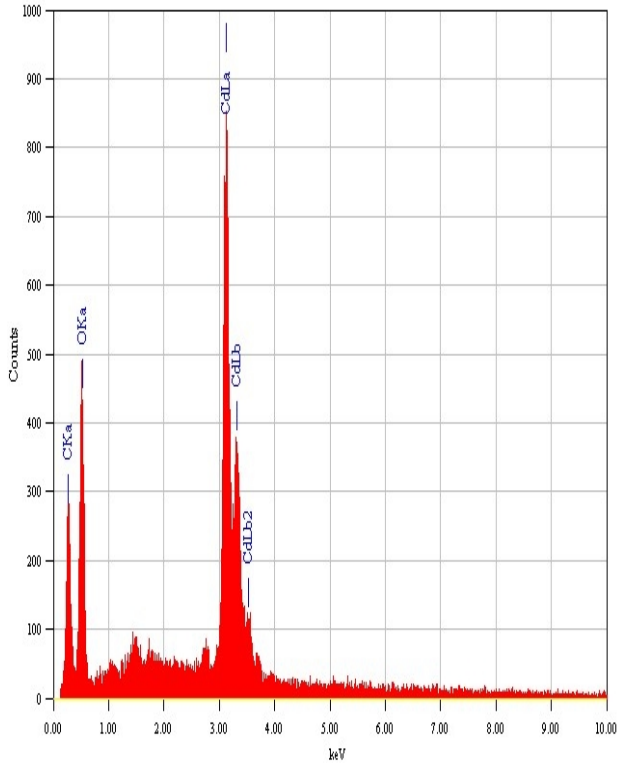


Fig. 5. reveals the EDAX analysis

EDAX

In order to confirm the presence of cadmium, quantitative elemental analysis were performed on the application of EDAX. The EDAX spectra shown in figure reveals prominent peaks due to cd Lα, CKα and OKα. This confirms the formation of cadmium tartrate oxalate crystals. The weight [%] and atomic weight [%] calculated from the peaks height further confirms the expected proportion of carbon, oxygen and cadmium crystals.

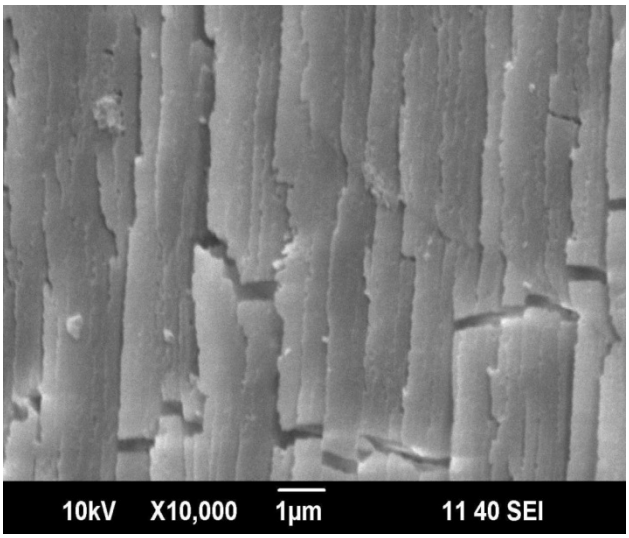
EDAX data

Element	**(keV)**	**Mass%**	**Atom%**	**K**
C K	0.277	14.42	48.51	0.7727
O K	0.525	9.56	24.15	0.294
Cd L	3.133	76.03	27.34	1
Total		**100**	**100**	

SEM:

The SEM studies of the crystal gives valuable information about its internal structure. It shows plate like crystal morphology. These crystals are grown by layer deposition. Thick and thin layers are seen in figure. The individual plates of sample are flat and the plates with the sharp edges were observed.

SEM image of cadmium tartrate oxalate crystal



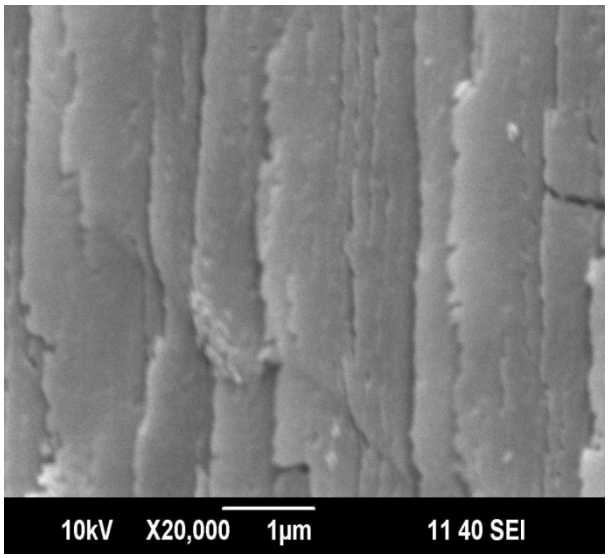


Fig. 6. SEM image

4. Conclusion

The grain size of Cadmium tartrate oxalate is small when compare to cadmium tartrate crystals and cadmium oxalate crystals. This changes may be due to the mixing of two acids. Some of FTIR band values of Cadmium tartrate oxalate crystals are equal to cadmium oxalate crystal bands. The infrared spectrum range of 400-4000 cm^{-1} is suitable for crystals of cadmium tartrate oxalate crystals. The different characters of cadmium tartrate oxalate crystals can be obtained by changing parameters like gel density, gel aging, P^H of gel and concentration of reactants. The SEM photographs shows plate like morphology of the crystals.

References

[1] H.K.Henisch,J.Dennisand J. I. Hanoka, J. Phys. Chem. Solids, **26**, 493 (1965).
[2] H.K.Henisch,Crystal Growth in Gells, Pennsylvania State University Press, UniversityPark, Pennsylvania, 1970.
[3] S.M.Dharma Prakash,P.Mohan Rao Bull. Mater. Sci. **4**, 511 (1986).
[4] M.R.Shedam,Venkateswara Rao Bull.. Mater Sci. **16**, 309 (1993).
[5] S.L.Garud,K.B. Saraf Bull. Mater. Sci. **31**, 639 (2008).
[6] PS.Raghavan; P.Ramaswamy; Crystal Growth Process and Methods, KRU Publications,2000.
[7] E.Knaepen,J. Mullens,J. Yperman, L.C.VanPoucke, preparation and thermal decomposition of various forms of strontium oxalate, thermo-chim. Acta **284**, 213 (1996).
[8] G Madhurambal; P Anbu Srinivasan, Cryst. Res. Technol., **41**, 231 (2006).
[9] BB Parekh; MJ Joshi; ADB Vaidya; Current Sci., **93**, 373 (2007).
[10] RethinamF.J.,Arivuoli D.,Ramasamy S.andRamasamy.P, Mater.Res.Bull. **29**, 309 (1994) .
[11] Nakatani N Jpn.J.Appl.Phys. 30, 1961.
[12] Selvarajan P., Das B.N., Gon H.B. and Rao K.V. J.Mater.Sci.Lett. **12**, 1210 (1993)
[13] Arora S.K., Kothari A. and Amin B. Solid State Physics (India), **46**, 683 (2003).
[14] Nickl,H.k.henisch,j.electrochem.soc.**116**,1258 (1969).
[15] A.R.Patel,A.Venkateswara Rao, J.cryst.growth **49**, 89, (1980).
[16] A.R.PatelA.Venkateswara Rao.Ind.J.Pure Appl.Phy.19,1981.
[17] M.RSehdam,A.Venkateswara Rao,Bull.Mater.Sci., **16**,309 (1993).
[18] J.Dennis,H.K.Henisch, J.Electrochem.soc.**114**, 263 (1967).
[19] H.KHenisch,crystalgrowthin gels, Pennsylvania state university press, USA,1970
[20] S.N.Patill,A.Venkteswararao, growth of single crystals of calcium sulfite in silicagels, Cryst.Res.Technol. **26**, 841 (1991).
[21] T.A.S hippy ,Vibrational Studies of calciumoxalate,monohydrate (Whewellite) and an anhydrous Phase of calcium oxalate, J.Mol.Struct. **63**, 157 (1980) .
[22] G.C.Jones,B.Jackson,Infrared Transmission Spectra of Carbonate Minerals, Chapmanand hall,London,1993.
[23] K.Nakamoto,Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, London, 1997.
[24] K Kamada; A Yoshikawa; T Satonaga; H Sato; A Beitlerova; M Nikl; N Solovieva; T.Fukuda; Opto-Electro. Review, **12**, 365 (2004).