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Study of Gel Grown Mixed Calcium-Cadmium tartrate crystals

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ABSTRACT

Calcium Cadmium tartrate single crystals were grown in silica gel at ambient temperature. The effects of various parameters like gel pH, gel aging, gel density and concentration of reactants on the growth of these crystals were studies. Crystals having different morphologies and habits were obtained. Transparent, pyramidal shaped like diamonds crystals of Calcium cadmium tartrate were obtained. Some of them were faint yellowish, milky white due to fast growth rate attached crystals are obtained; faces are well developed and polished. The crystals grown were characterized by X-ray powder diffractometry, infrared spectroscopy. The results of these observations are described and discussed.

Keywords: Gel technique, Calcium cadmium tartrate,FT-IR, XRD

INTRODUCTION

The advances in the science of the solid state and material science depend upon the availability of good quality single crystals. Consequently, tremendous amount of efforts has been made on the development of crystal growth techniques, each having its own importance and potentiality with certain limitation.

The new rapidly developing branches of science and technology, such as quantum electronics, quantum and non linear optics, semiconductor instrumentation, Laser and masers etc. all involves the use of single crystals and their singular properties. So several techniques have been developed and are still being to be developed in rapid succession to synthesize better and better quality of crystals, which are rare in nature, or not yet grown in laboratory.

Crystals are the unknown pillars of modern technology. The modern technological developments depend greatly on the availability of suitable single crystals, whether it is for lasers,

semiconductors, magnetic devices, optical devices, superconductors, telecommunication etc. In spite of great technological advancements in the recent years, we are still in the early stage with respect to the growth of several important crystals such as diamond, silicon carbide, gallium nitride and so on. Unless the science of growing these crystals understood precisely, it is impossible to grow them as large single crystals to be applied in modern industry. The large number of crystals is used in electronic, optical and in industries. Hence today's demand is to grow large single crystals with high purity and symmetry.

In recent years crystals growth in gel medium has attracted the attention of many investigators [1-5].The principle relies on the slow migration of crystal constituents (ions) through silica gel so that a very slow reaction occurs with the formation of a sparingly soluble compound. When the concentration of this compound exceeds the solubility limits, crystals will be formed, the main function of the gel being to control the flow of reacting ions.

Mixed crystals growth has scarcely been studied by employing the gel technique [6-7] and the field is in an early stage of development with many opportunities to create new species. Most of the tartrate compounds are in soluble in water and decompose before melting. Hence single crystals of such type of compounds cannot be grown by either slow evaporation or melt technique. In this situation gel method is the appropriate one for their growth. The growth of single crystals oh Calcium tartrate was reported [1] and single crystals of strontium tartrate was reported [8].thermal studies on tartrate crystals grown by gel method were reported by many investigators [9-11]. Tartrate crystals are of considerable interest, particularly for basic studies of some of their interesting physical properties. Some crystals of this family are ferroelectric [12-14], some others are piezoelectric [15] and quite a few of them have been used for controlling laser emission [16]. As tartrates are sparingly soluble in water and decompose before melting, the gel method is found to be more promising than the high temperature crystal growth methods.

MATERIALS AND METHODS

Good crystal can be grown in gels in a variety of ways; the single diffusion method was employed in the present work for the growth of calcium cadmium tartrate crystals. The growth process involves the diffusion of mixed calcium chloride-cadmium chloride solution in to agel in which tartaric acid is impregnated beforehand. The silica gel was used as a growth media. The chemicals used for growth mixed tartrate were $C_4H_6O_6$, $Cacl_2$, $Cdcl_2$ and Na_2SiO_3 all chemicals were of AR grade. The crystallization apparatus consist of borosilicate glass test tubes of length 20 cm and diameter 2.5 cm placed vertically on wooden stands. Tartaric acid, calcium chloride and cadmium chloride solution were prepared by dissolving these compounds in an appropriate amount of distilled water to give the required molarities. Gels of required specific gravity were prepared by adding to the solution of sodium metasilicate, a calculated amount of redistilled water and a stock solution was kept ready for doing further experiments. Tartaric acid solution of particular strength was taken in a 100ml beaker and sodium metasilicate solution of a suitable gravity was added drop wise using a tephlon cock burette, constantly stirring the solution in a beaker by magnetic stirrer. Stirring is done to avoid the excessive local ion concentration which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. Here tartaric acid acted as a lower reactant. The systronic digital pH meter model number 335 was used to measure the pH. The solution after noting pH values, being allowed to fall along

the side of a test tube without giving chance for the formation of the bubbles. Test tubes were then closed with rubber corks or cotton to prevent evaporation and contamination of the exposed surface of the gel by dust particles of the atmosphere. The solution was found to be strongly depends on pH. High pH value gel takes lower time to set than low pH value, depending on the environmental temperature. After ensuring firm gel setting, the saturated mixed solution of calcium chloride and cadmium chloride (supernatant) of particular strength was poured over the set gel with the help of a pipette. The solution being allowed to fall along the wall of the test tube to prevents the gel surface from cracking. The supernatant ions (Ca^{++} and Cd^{++}) slowly diffused in to the gel medium where it reacts with inner reactant.

The following reaction is expected to take place in the formation of calcium cadmium tartrate crystals.

$2C_4H_6O_6 + x\ Cacl_2 + (1-x)Cdcl_2 \rightarrow Ca_xCd_{(1-x)}(C_4H_4O_6)_2.xH_2O + 4Hcl.$

The systematic growth experiments were performed by adding $Cacl_2$,$Cdcl_2$, as feed solution of strength varing from 0.2m to 1.2m over the set gel of pH range 4 to 4.5 the gel density range 1.02gm/cm^3 to 1.05 gm/cm^3.

RESULTS AND DISCUSSION

The various optimum conditions for the growing crystals were found and are given in table 1.Table2 tabulated the Effect of concentration of reactants of habits, quality and size of $Ca_xCd_{(1-x)}(C_4H_4O_6)_2$

Table 1 Optimum condition for growth of Calcium cadmium tartrate

Conditions	Calcium cadmium tartrate.
Density of sodium meta silicate solution	1.04 gm/cm^3
Concentration of tartaric acid	1.25M
Volume of tartaric acid	7ml
Volume of sodium meta silicate solution	23ml
pH of the gel	4.2
Concentration of $Cacl_2$	1M
Concentration of $Cacd_2$	1M
Temperature	Room temperature

Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel aging time, etc have considerable effect on growth rate. Figure 1. Show the optical photograph of growth of Calcium Cadmium tartrate inside the test tube. Figure 2(a), (b), (c) illustrates different morphologies of pure Calcium Cadmium tartrate crystals grown under different conditions of growth. The crystals grown are Faint yellowish, Milky white, Transparent, Semitransparent; needle shape well defined crystals of Calcium cadmium tartrate were obtained. Some of them were transparent diamond shaped, due to fast growth rate twined crystals are obtained; faces are well developed and polished.

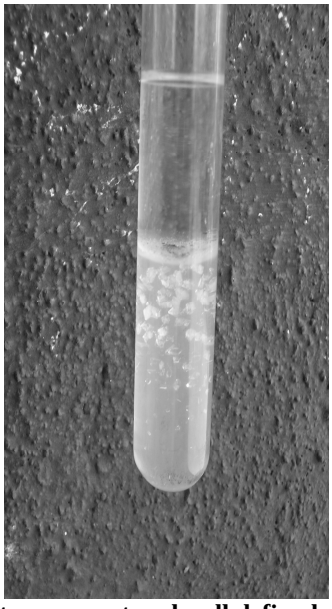

Figure 1 **Prismatic transparent, semitransparent and well defined crystals of Calcium cadmium tartrate In gel of density 1.04 gm/cm^3**

Figure 2 (a) **Faint yellowish, Milky white, Transparent, Semitransparent, needle shape Well defined crystals of Calcium cadmium tartrate**

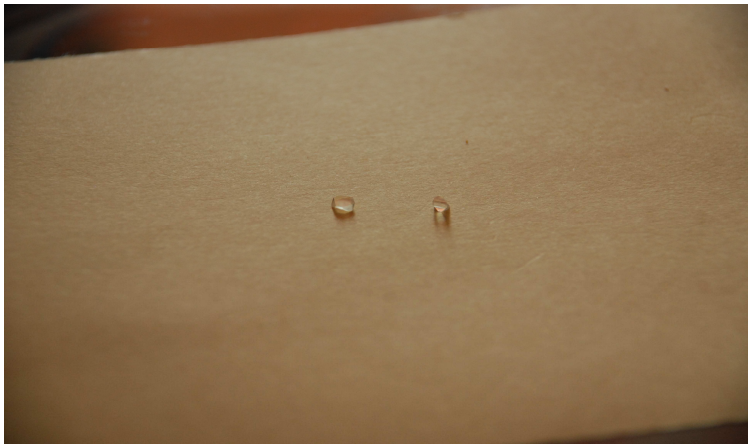

Figure 2(b) **Prismatic transparent crystals of Calcium cadmium tartrate**

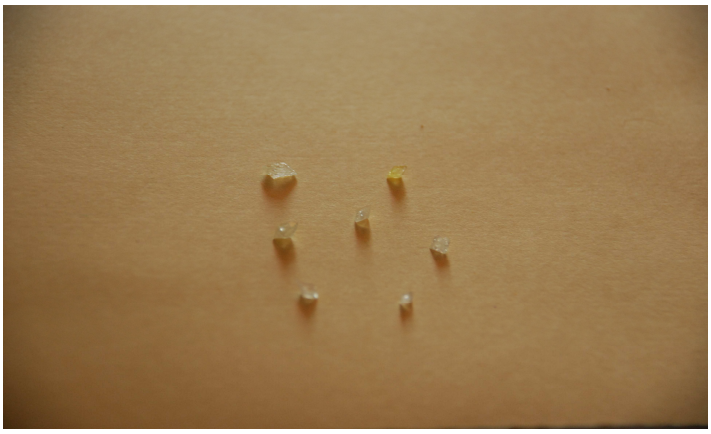

Figure 2 (c) **Translucent Pyramidal shaped like diamonds crystals of Calcium cadmium tartrate**

Table 2 Effect of concentration of reactants of habits, quality and size of $Ca_xCd_{(1-x)}(C_4H_4O_6)_2$

Conc. of reactant in gel	Conc. of reactant above gel	Habit	Quality	Size(mm)
$C_4H_6O_6$ 1m (7ml,pH 4.2)	$Cacl_2$,$Cdcl_2$ 1m (15ml)	Prismatic	Opaque	2×5×1
$C_4H_6O_6$ 1.25m (7ml,pH 4.2)	$Cacl_2$,$Cdcl_2$ 1m (20ml)	Prismatic	Good (Transparent)	3×6×2
$C_4H_6O_6$ 2.25m (7ml,pH 4.2)	$Cacl_2$,$Cdcl_2$ 1m (25ml)	Dendritic	Poor(Twined)	5×10×4

4. *Characterizations.*

Mixed tartrate crystals grown were characterized by FT-IR and XRD.

4.1 Fourier Transform infrared(FT-IR) Spectral analysis

FT-IR is used for structural analysis. In the present study IR spectrum of Calcium cadmium tartrate sample was recorded using Perkin Elmer spectrophotometer at Department of Physics, Pratap College, Amalner (M.S.) Figure 3.shows FT-IR Spectrum of Calcium cadmium tartrate. The IR spectra of these grown crystal was recorded in the wave number range 630cm^{-1}- 4400cm^{-1}.face.The band at 3411.50$cm^{=1}$are due to O-H stretching and water of crystallization and the bands at 2880.76cm^{-1}, 2360.53cm^{-1} are assigned to C-H stretching vibrations. Strong asymmetrical band at 1581.82 cm^{-1} is attributed due to C=O stretching in Carboxylate ion.The

bands at1482.14cm^{-1},1381.88cm^{-1}are due to C=O weaker symmetric stretching in Carboxylate ion and at 1327.15cm^{-1},1281.51cm^{-1} are due to O-H in plane bending. The bands at 1145.59cm^{-1} ,1059.93cm^{-1} ,1011.03cm^{-1} are due to C-O stretching mode. The absorption bands are found at 958.18cm^{-1} ,814.69cm^{-1}, 709.55cm^{-1} are due to the metal oxygen bonding.

It is confirmed that Water of crystallization and metal oxygen bonding is presented in the reported. The IR spectrum obtained in the present study for Calcium cadmium tartrate crystals is similar to the IR spectrum Calcium tartrate crystals reported [17, 18].

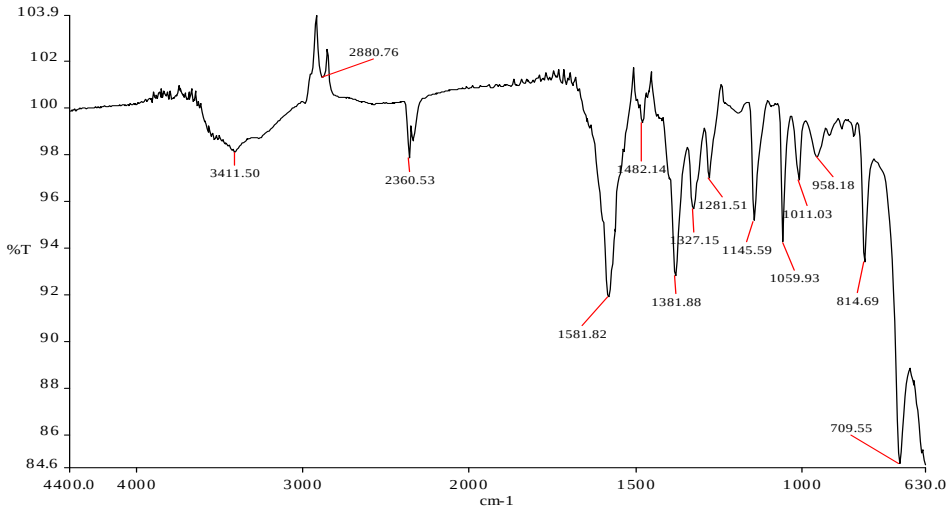

Figure 3 FT-IR spectrum of Calcium cadmium tartrate crystal.

Table 3 XRD data of Calcium Cadmium Tartrate crystals

Peak	d-spacing A^0		Intensity	Indices	2 Theta Deg.		Diff.
	obs.	Calc.		(hkl)	Obs	calc.	
1	3.3237	3.3200	84	1 2 0	26.80	26.83	-.030
2	3.0973	3.0972	167	2 1 1	28.80	28.80	-.000
3	3.0557	3.0556	270	0 1 2	29.20	29.20	-.002
4	2.8465	2.8517	122	1 1 2	31.40	31.34	.060
5	2.6496	2.6470	83	3 0 0	33.80	33.83	-.034
6	2.5615	2.5665	155	2 0 2	35.00	34.93	.070
7	2.1994	2.2011	129	1 3 1	41.00	40.97	.033
8	2.0741	2.0767	229	2 3 0	43.60	43.54	.057
9	1.9877	1.9853	85	4 0 0	45.60	45.66	-.058
10	1.8864	1.8864	207	2 1 3	48.20	48.20	.000
11	1.5691	1.5739	147	1 4 2	58.80	58.60	.197
12	1.5452	1.5457	109	5 0 1	59.80	59.78	.023
13	1.5176	1.5150	114	2 1 4	61.00	61.12	-.119

4.2 X-ray diffraction:

X-ray diffractogram of gel grown Calcium cadmium tartrate was recorded using powder rotation photograph method on 'Minislex Regaku' X-ray diffractometer at department of Physics, North Maharashtra University, Jalgaon. CuKα-radiation (wavelength λ=1.54051 A^0) was used. The recorded x-ray diffractogram is as shown in figure 4. From these diffractogram, intensity's'

values and (hkl) were computed. The observation table 3 Gives the indexed XRD data for the grown Calcium cadmium tartrate crystals'' values and (hkl) were calculated by computer program POWD (Integrative powder diffraction and indexing program). The unit cell parameters and system Calculate by the computer program are given in the table 4.These parameters satisfy the conditions for Orthorhombic system i.e. a≠ b≠ c and α =β= γ =90^0. From X-ray diffraction study it may be concluded that the grown crystals of Calcium cadmium tartrate have orthorhombic system.

Table 4 Unit cell parameters

Parameters	Calcium Cadmium tartrate
System	Orthorhombic
a	7.9411A^0
b	7.0396 A^0
c	6.7271 A^0
γ β α	90^o
V	390.48 $(A^0)^3$

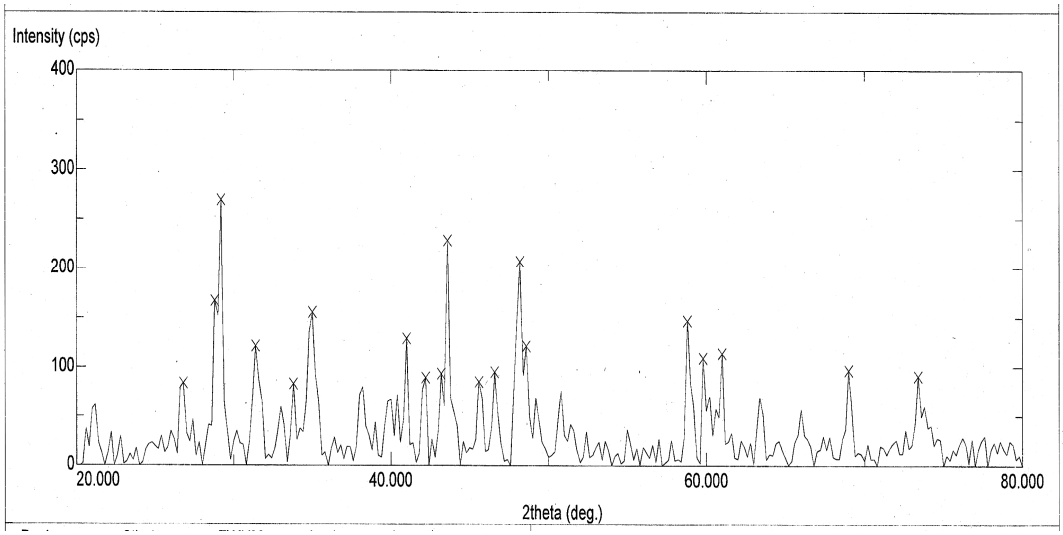

Figure 4 X-ray diffractogram of gel grown Calcium cadmium tartrate

CONCLUSION

From the experiments on the growth of Calcium cadmium tartrate crystals in the system $Cacl_2$-$Cdcl_2$-Na_2SiO_3-$C_4H_6O_6$, the following conclusions may be drawn.

1. The growth of Calcium cadmium tartrate crystals is accomplished by allowing diffusion of Calcium chloride .Cadmium chloride through silica gel impregnated with tartaric acid in a single-gel-single tube system.
2. The crystals exhibit Transparent, pyramidal shaped like diamonds morphology even under varied conditions of growth. Maximum size of the growth crystal under optimum conditions was 2mm-6mm in length.

3. Different habits of Calcium cadmium tartrate crystals can be obtained changing parameters like gel density, gel aging, pH of gel Concentration of reactants, Concentration of impurities etc.
4. It is found that well-developed single crystals of Calcium cadmium tartrate are obtained at 1M concentration of feed solution in the pH range 4 to 4.5 of the gel.
5. XRD analysis reveals that Calcium cadmium tartrate crystals belong to orthorhombic system.

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