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Growth and Characterizations of Pure and Calcium Doped Cadmium Tartrate Crystals by Silica Gel Method

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ABSTRACT
In the present course of investigation, pure and calcium doped cadmium tartrate crystals were grown in silica gel at room temperature. The optimum conditions were obtained by varying various parameters such as pH of gel, concentration of gel, gel setting time, concentration of reactants etc. Crystals having different morphologies were obtained such as whitish semitransparent, star shaped, needle shaped. Especially, effect of doping of calcium into cadmium tartrate has been studied with respect of size and transparency. It is found that doping enhances the size and transparency of the crystals. As-grown crystals were characterized using scanning electronic microscope (SEM), UV, Energy dispersive X-ray spectroscopy (EDAX).
Keywords **-** Crystal Growth, XRD, SEM, UV, EDAX

I. INTRODUCTION

The subject of crystal growth has held a high level of useful information, both of scientifically and technologically, for a very long period [1]. Hence an understanding of how crystals are grown is an important aspect of the science material [2]. The impact of single crystals is clearly visible in industries like semiconductors, optics etc. and the field of the nonlinear optics and the practical implementation was possible with the applications of nonlinear optical crystals. Now a day great attention has been devoted the growth and characterization of doped tartrate crystals with the aim of identifying new materials for practical purposes [3].The effects of doping on various purpose of crystals are of great interest from solid state science as well as technological point of view. The crystals of cadmium tartrate grown in silica gel medium doped with barium, strontium, lithium, calcium have already been reported [4]. In the present course of investigation we have attempted to grow pure and calcium doped cadmium tartrate crystals by gel technique [5].

II. EXPERIMENTAL WORK

In the present work the calcium doped cadmium tartrate crystals were grown by single diffusion gel method. Most of the tartrate compounds are insoluble in water and decompose before melting. Hence, such type of compounds cannot be grown by either slow evaporation or melt technique but can be grown by solution gel method [5]. A single diffusion method (Henish 1973) was employed to grow pure and calcium doped cadmium tartrate crystals in the gel method.

The AR grade (Loba) chemicals were used for the present work. The crystallization apparatus employed was borosilicate glass tubes (25mm diameter and 200mm length). Gels were prepared by mixing sodium meta silicate solution of appropriate specific gravity and 1M solution of L (-) tartaric acid so that the desired pH of the mixture could be obtained. The specific gravity and pH were varied between 1.02 gm/cc to 1.05 gm/cc and 4 to 5 respectively. After mixing, the solution was allowed to set for about 48 hours. Over the set gel, 1M cadmium chloride solution and 1m, o2% calcium chloride solution was gently poured with the help of a pipette, so as to allow the solution to fall steadily along the walls of the tube without disturbing the gel surface. The supernatant ions (Ca^{++} and Cd^{++}) slowly diffuse into the gel medium where it reacts with inner reactant. The open end of the test tube was closed with cotton to avoid dust from entering into the glass tube. The solution was faint milky and transparent, initially, but with lapse of time its color slightly change. The test tubes were kept undisturbed at room temperature. For doping of calcium, an aqueous solution of calcium chloride of varying concentration 0.2- 1.0 M was mixed with the top solution. After one month the crystal was taken out from the test tube and cleaned for the further characterization. The best quality crystals were grown for 4.2 pH is shown in fig 1a and 1b.

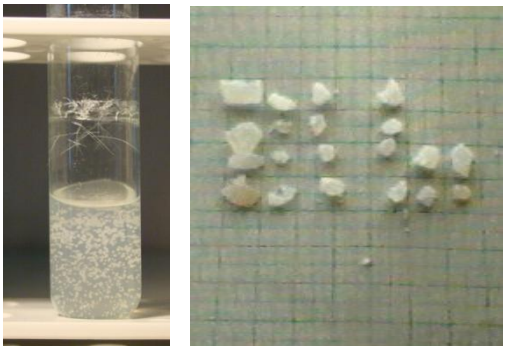

Figure 1(a). Shows Single Diffusion Method, (b) Shows CCT Crystal

Chemical reaction:

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

$$(C_4H_6O_6) + {}_XCaCl_2 + {}_{(1-x)}CdCl_2 \rightarrow Ca_xCd_{(1-x)}$$
$$(C_4H_4O_6)\,H_2O + 4HCl.$$

III. RESULT AND DISCUSSION

The various optimum conditions for the growing crystal were found and are given in table no.1 and the effect of doping of calcium in cadmium crystals in respect of size and transparency is given in table no. 2 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. Fig.2 shows optical photographs of calcium cadmium tartrate crystals inside the test tube and Fig. 3 illustrates the different morphologies of calcium cadmium tartrate crystals grown under different conditions of growth. The crystals grown are whitish, milky white and transparent, semitransparent and rectangular in shape well defined crystals of calcium cadmium tartrate crystals were obtained. Some of them were transparent small diamond shaped due to fast growth rate, twin crystals are also obtained faces are well developed and polished [7].

Table1. Optimum conditions for growth of CCT

Conditions	CCT crystal
Density of sodium meta silicate solution	1.05 g/cc
Concentration of tartaric acid	1M
Volume of tartaric acid	8ml
Volume of sodium meta silicate solution	28ml
pH of the Gel	4.5
Concentration of $CaCl_2$	0.2M
Concentration of $CdCl_2$	1.0M
Temperature	R.T.

Table2. Effect of concentration of reactants and habits quality and size of the crystals

Concentrations of reactants in gel	Concentration of reactants above gel	Habits	Quality	Size -mm
$C_4H_6O_6$ 1M(8ml,pH 4.2)	$Cacl_2$,$CdCl_2$ (20ml)	Prismatic	Opaque	3x2x2
$C_4H_6O_6$1M(8ml ,pH 4.2)	$CaCl_2$$CdCl_2$ 0.5 M(25ml)	Prismatic	Good transparent	2x3x2

IV. XRD ANALYSIS

To study the crystal structure of the CCT crystal by powder X-ray diffraction method, X-ray diffraction was recorded on the (Bruker) with CuKα radiation recorded 2θ within the range of 20-80^0. The figure 2 shows the XRD pattern of the CCT crystals.

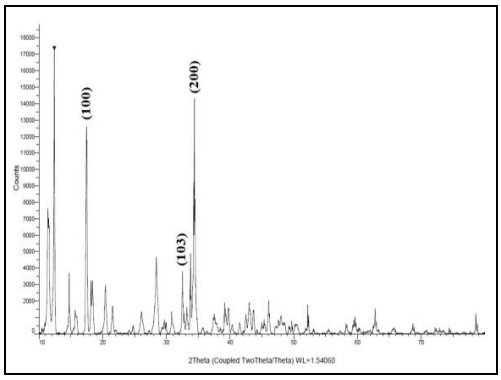

Figure2. XRD pattern of CCT crystal

XRD pattern shows very sharp peaks having high intensity, which leads to extremely good crystalline perfection of the CCT crystals. The lattice parameters a, b & c was found to be 5.98, 5.98 & 9.65Å respectively (a=b≠c). The XRD spectrum reveals that the sample is polycrystalline having hexagonal structure. Percentage of crystallinity is very good, it is 79.99%. The grain size was 6.148 nm calculated by using the following formula:

$$D = 0.94\,\lambda / \beta \cos\theta$$

Where β is full width at half maximum (FWHM=.235), λ=1.54060 Å is the wavelength of X-ray, 2θ is diffraction angle. X ray diffraction study of CCT crystals was carried out using bruker axsd8 advance model X ray diffraction with CuKα1 (λ=1.54056 Å) radiation in the 20 range 10^0 -80^0. The scanning speed of the specimen was 2^0 /min. In the present study of X-Ray powder pattern of calcium doped cadmium Tartrate crystals grown in gel medium was obtained and used to identify the grown material. The XRD patterns of CCT crystal are

shown in figure 2. The spectrum match with the data reported in JCPDS files No26-0282. From this diffractogram intensity and hkl values were computed. The observation table give the index XRD data for the grown crystals value and hkl plane were calculated the unit cell parameter satisfy the condition for hexagonal system that is a= b≠ c and α=90 β=90 γ=120^0. From X-ray diffraction study it may be concluded that the grown crystal of CCT crystal have hexagonal system. The observed and calculated d values are given in Table No1.The diffracting are index observed d values are in good agreement with calculated values. It is very interesting to note that CCT crystals are hexagonal structure.

V. FOURIER TRANSFORM INFRARED (FT-IR) SPECTRAL ANALYSIS

Infrared spectroscopy is one of the most power analytical techniques, which offers the possibility of chemical identification and structural analysis. In the present study IR spectrum of CCT sample was recorded within the range of 500-4500 nm wave number at research center lab, M.J. College, Jalgaon. The figure 3 shows the IR spectra of CCT crystals.

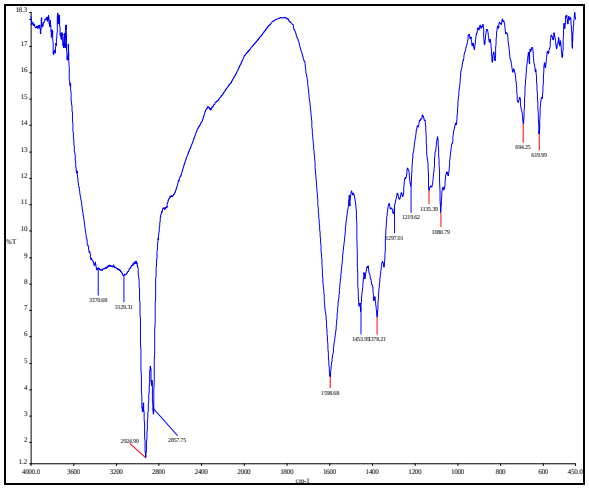

Figure 3(a). IR Pattern of CT Crystals

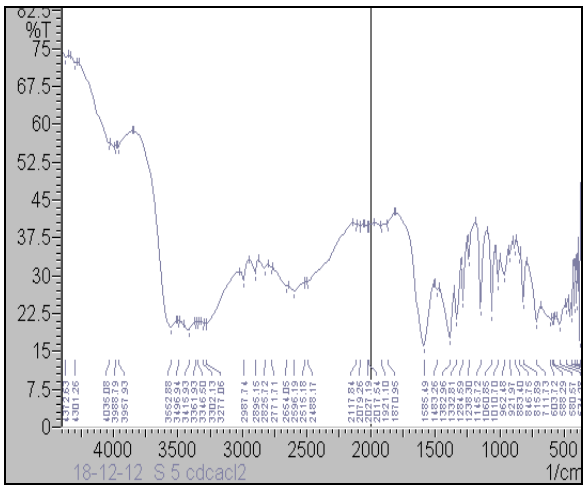

Figure 3(b). IR Pattern of CCT Crystals

The FT-IR analysis is a technique that provides information about the chemical bonding or molecular structure of material. The FT-IR spectrum of the grown crystals was recorded in the wave number range 400-4000 cm^1 using an IR Affinity-1 CE FT-IR SHIMADZU 2450. In the IR spectrum of CCT crystal, the absorption bands at 3562.33 cm^{-1} are due to O-H stretching bending and water of crystallization. Band at 2896 cm^{-1} 2488 cm^{-1} are assigned to C-H stretching vibrations. Strong asymmetrical band at 1555.49 cm-1 is attributed due to the C=O weaker symmetric starching in carboxylate ion. The peaks at 1485 cm^{-1}, 1384 cm^{-1} are due the O-H in plane bending. The bands at 1145 cm^{-1} and 1060.85 cm^{-1} are due to the C-O stretching mode. The absorption bands at 962.15 cm^{-1} – 711.73 cm^{-1} are due to metal oxygen bonding (Metal = Ca-Cd). It is confirmed that in the present work water of crystallization and metal oxygen bonding is present [8, 9].

VI. UV-VIS ABSORPTION SPECTROSCOPY

Absorption spectra of CCT crystals were recorded using SHIMADZU UV-1800 Eng. 240 V SOFT UV-Vis Spectrophotometer over the wavelength range 200nm to 800nm at Nano Research lab M.J College, Jalgaon. Figure 4 shows UV absorption spectra of pure and CCT crystals.

The absorbance spectrum reveals that the sample has sufficient transmission in the entire visible and IR region. The absorption coefficient is high at lower wavelength and the wide transparency from 240nm suggestive their suitability for second and third harmonic generations of the 1064 nm radiation [10, 11].

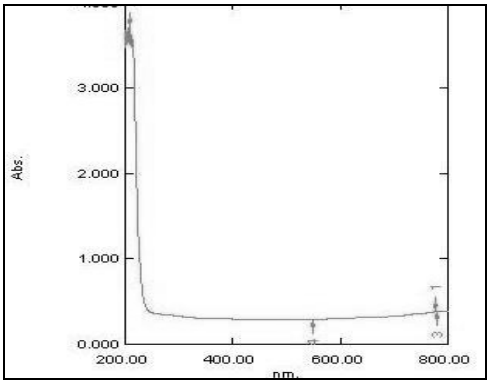

Figure4 (a). Absorbance Spectra of CT Crystals

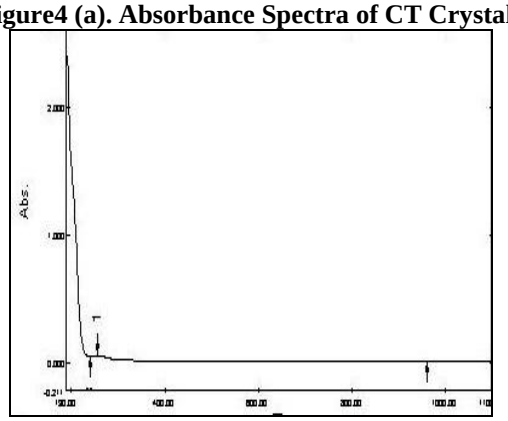

Figure4 (b). Absorbance Spectra of CCT Crystals

The band gap energy of the CCT and pure crystals found to be 4.52 and 5.63 eV respectively.

VII. SCANNING ELECTRON MICROSCOPY (SEM)

The surface morphology can be done by using SEM. In the present work powdered sample of CCT crystals was examined by using SEM technique at the UDCT, N.M.U., Jalgaon.

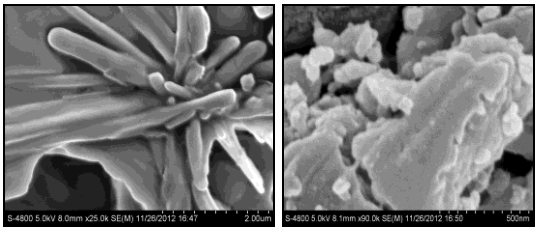

Figure5 (a: b). SEM images of CCT crystals

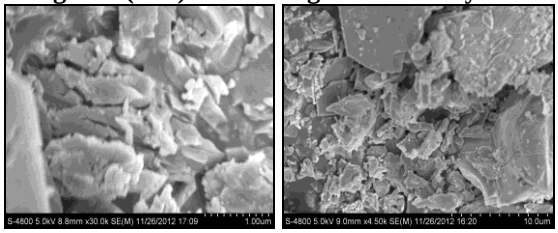

Figure6 (a: b). SEM images of pure CT crystals

The study of the surface morphology of the crystals gives valuable information about its internal structure. Figure 5 represents the SEM photographs with two different images of CCT crystals. The SEM images reveal that the flower type structure and petals are come out from edge. The petals of boundary were clear. Figure 6 shows the SEM photographs with two different photographs of pure CdTr crystals. The high depth of field of the SEM images makes its especially suitable for the study of the fractured surfaces and complex microstructure such as those found in composite material. These crystals are grown by layers deposition. Thick and thin layers are seen in figures. The plates with the sharp edges were observed and some plate further growth was observed.

VIII. EDAX ANALYSIS

Elemental dispersive analysis by X-rays (EDAX) is used for the quantitative analysis. When a beam of electron strikes a specimen, a fraction of the incident electrons excites the atom of the specimen, which then emits X-ray when they return to their ground state. In the present work elemental analysis of gel grown CCT crystals was carried out at the UDCT, NMU Jalgaon. Figure 6 shows EDAX spectrum of CCT crystals.

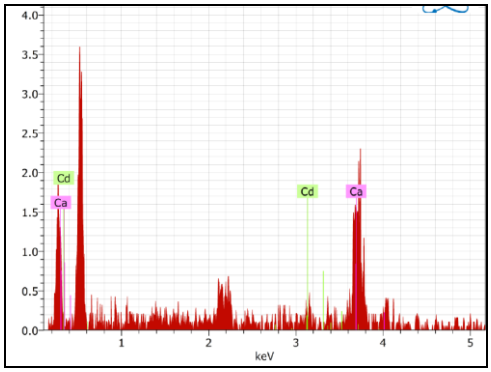

Figure6. EDAX Spectra of CCT Crystals

The average atomic percentage was found as Ca = 3.06 and Cd = 58.09. Table 3 shows the value of elemental content of the crystals as measured by EDAX technique (At. %) and the theoretical calculation from molecular formula (Wt %).

Table3. Value of elemental content of CCT crystals

No	Elements	Experimental Value Wt%	At%
1	C	21.76	44.10
2	O	11.61	25.48
3	Cl	3.25	2.43
4	CO	0.12	0.15
5	Si	2.11	2.08
6	Ca	3.06	1.40
7	Cd	58.09	24.36

IX. COLLUSION

The XRD spectrum revealed that the sample is polycrystalline in nature and hexagonal in shape. In the present course of investigation the lattice parameters almost matches with the JCPDS data of cadmium tartrate.

The IR spectrum confirms the presence of water molecules, O-H band, C-O and carbonyl C=O bands. The C-OH in plane bending and out of plane bending is identified.

The presence of metal cadmium and calcium identified was confirmed by chemical analysis.

Energy band gap is affected by the doping. The energy gap of pure CT and CCT found to be 4.2 & 5.63 eV respectively.

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