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Structural, Optical and Thermal Characterization of Calcium Tartrate Crystal Grown Under the Influence of Magnetic Field

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Abstract: **Nowadays great attention has been devoted to the growth and characterization of pure and doped tartrate crystals with the aim to identify new materials for practical purposes. The effects of dopants on various properties of single crystals are of great interest for solid state science. Several applications of calcium tartrate crystals are reported in the literature. In the present work, calcium tartrate crystals are grown by single diffusion gel method in the presence and in the absence of the magnetic field. The cell parameters are obtained from single crystal XRD analysis. The crystals are characterized by FTIR spectroscopy and UV spectroscopy. The influence of magnetic field on crystal stability is studied from Thermo gravimetry analysis (TGA) and differential scanning calorimetry (DSC) analysis. This study reveals the locking of water molecules in the lattice with different strengths. The decomposition is observed from the endothermic peaks of DSC.**

Keywords: **organometallic compounds; Crystal growth; DSC; TGA; X-ray diffraction; optical properties.**

1. INTRODUCTION

During the last decades the growth of single crystals has assumed enormous importance for both academic research and technology. The range of field involved is vast: from electro optics to metal corrosion, from semiconductors to magnetic bubble materials [1].The capability of the externally applied magnetic field to decrease the nucleation rate and to increase the crystals has been reported. The calcium tartrate crystals have been identified as ferroelectricmaterial [2].Tartaric stabilization of red, rose and white wines with calcium tartrate crystal seeding has been reported by Minguez and Hemandez[3]. Single crystals of most of the tartrate compounds are grown by gel method.The effect of gel density, concentration of reactants,pH of gel and ageing of gel on the growth rate of tartrate crystals are reported[4]. In this paper, we report thecomparative analysis of the optical and thermal characterization of calcium tartrate crystal (CaTr) grown without the influence of magnetic field, and with the influence of magnetic field (CaTrmf) with sodium metasilicate gel as the medium.

2. EXPERIMENTAL WORK

Single diffusion method was employed to grow these crystals. The chemical reaction taking place in the gel medium was as follows [5].

$C_4H_6O_6 + CaCl_2 \rightarrow CaC_4H_4O_6 + 2HCl$

The crystallization apparatus is borosilicate glass test tube of length 25 cmand diameter 2.5 cm placed vertically on thermocole stand. Sodium metasilicate (SMS)solution of 1.04gm/cc is prepared. 1M tartaric acid of 9.5 ml quantity is added to 10 ml of sodium metasilicate solution taken in the test tube. The pH of the gel is maintained at4.2. 1M calcium chloride solution of 10 ml is added over the set gel along the walls of the test tube with the help of pipette in order to avoid any gel breakage. SMS gel not only facilitates the nucleation and subsequently the growth of crystals, but also plays

important role in forming a compound,which is not possible by reacting two solutions directly[6].The calcium ions diffuse throughthe narrow pores of the gel to react with tartrate ions, which are present in the gel as inner reactant. More number of crystals of small size were formed near the interface. Though the number of crystals formed is less, when we go deeper from the interface, the size of the crystals were found to be large. For growing the crystals under the influence of magnetic field the set gel is subjected to the magnetic field 5 hours before adding the outer reactant. The crystals growing in the absence of magnetic field and in the presence of magnetic field are shown in Figure1

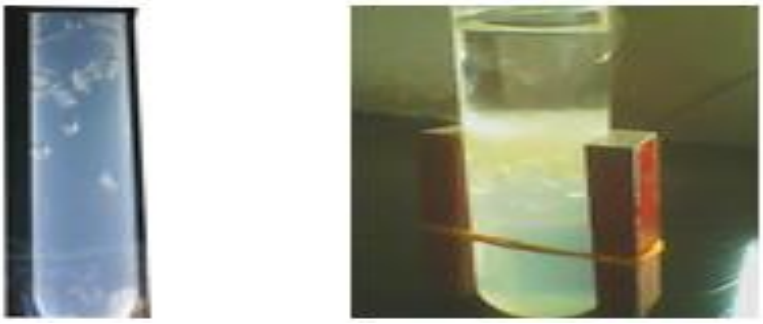

Figure 1

3. CHARACTERIZATION

3.1. SINGLE CRYSTAL X-RAY DIFFRACTOGRAM (XRD) ANALYSIS:

Single crystal XRD is taken at IIT, Chennai with Bruker Kappa (APEX II) .Mo- kα is used as the source in single crystal X-ray diffractometer. Lattice parameters are determined and the crystal system is identified. The crystallographic parameters of CaTr and CaTrmf are given in Table 1.

Table 1: crystallographic parameters

Parameters	Reported[7]	CaTr	CaTrmf
a Å	9.2256	9.23	9.25
bÅ	9.6586	9.62	9.67
cÅ	10.6048	10.57	10.61
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Volume($Å^3$)	944.9553	938	949

3.2. FOURIER TRANSFORMS INFRARED (FTIR) ANALYSIS:

The FTIR spectra of the CaTr and CaTrmf are shown in Figure 2. Spectrum RX1 Perkin Elmer make with the range of operation between 4000 cm^{-1}-400 cm^{-1} FTIR spectrophotometer is used.

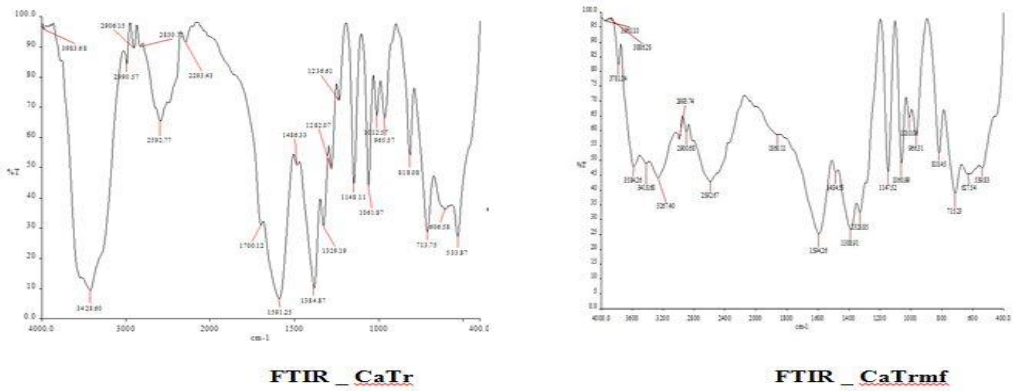

Figure 2

In the present investigation, KBr pellet method is used. The functional groups involved in vibrational frequencies are identified.The phenomenological behavior of the phase transitions can be understood only by correct frequency assignments. A free tartrate ion has two hydroxyl groups.So two bands can be expected for the stretching vibration of hydroxyl group.The assignment of OH stretching frequency of the alcoholic hydroxyl group of the tartrate ion and that of water of crystallization in these compounds is uncertain as they may overlap. The vibrational frequencies agrees with that of reported [5-10]values. The observed vibrational frequencies and their assignments are presented in Table 2. It is found that although the radiations are absorbed at same frequency in both the crystals, the percentage of transmittance of crystals grown under the influence of magnetic field is less than that of crystals grown in the absence of magnetic field.

Table 2: FTIR Spectroscopic analysis

Vibrational frequencies reported[9]	Vibrational frequencies CaTr	Vibrational frequencies CaTrmf	Assignment
3426.11	3428.6	3418.68	-OH stretching
2987.31	2990.57	2993.74	OH stretch (water)
1589	1591.25	1594.26	C=O stretch
1385	1384.57	1388.91	λ(C=O) + δ(O–C=O)
1282.8	1282.07	-	OH plane bending
1147.0	1148.11	1147.52	δ(C–H) + π(C–H)
1061	1061.87	1060.99	Out of planeOH deformation
1010.8	1012.57	966.31	C-O stretching
816.9	818.08	818.45	
711.8	713.75	715.23	Metal oxygen bonding

3.3. UV SPECTRALANALYSIS

The optical transmittance and lower cut off frequency are important in growncrystal. The UV spectrum was recorded in the spectral range of 190-1100 nm using Lambda 35 Perkin-Elmer Spectrophotometer. The UV-Vis NIR transmittance spectrum of CaTr and CaTrmf are shown in Figure3. There is a small variation in the energy gap of the crystals. The percentage of transmittance of the crystals grown in the absence of magnetic field is greater than the percentage of transmittance in the crystals grown with the influence of magnetic field.

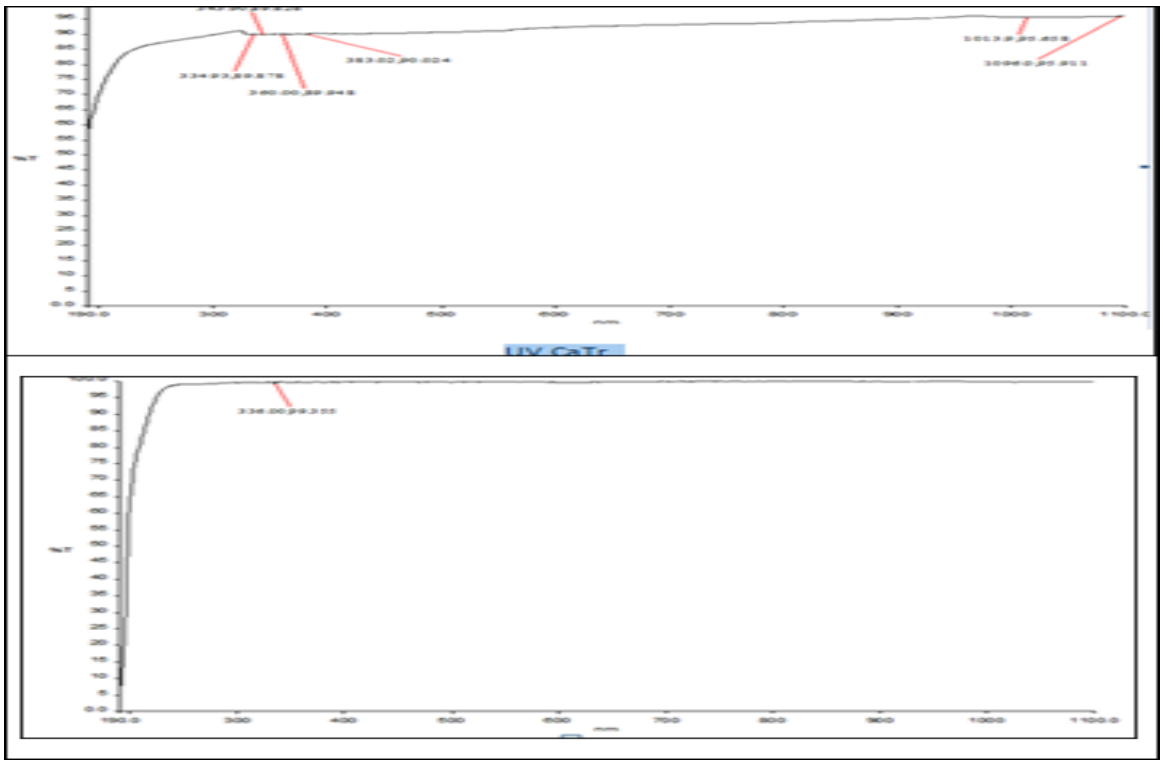

Figure 3

The crystalsshow optical transmittance in the entire visible region[9-13].The band gap energy is calculated from the formula E_g=1240/lower cutoff frequency. The lower cutoff frequency is 195.5 nm for CaTr and 194.5 for CaTrmf.The bandgap energy of CaTr is less than CaTrmf.The refractive index is calculated [14] as 1.856 for CaTr and for 1.853 CaTrmf.

3.4. THERMAL ANALYSIS:

3.4.1. Thermogravimetry Analysis (TGA):

The crystal is a water coordinated compound[5-9].The TGA curve of Ca Tr and Ca Trmf are Shown in the Figure 4.It losses some of its water molecules while heating .It was observed that the onset of first decomposition begins slightly at different temperatures for calcium tartrate crystals grown in the presence and absence of magnetic field. As the water molecules are ejected from the lattice in two different stages, it appears that the water molecules are locked up in the lattice in two different ways.

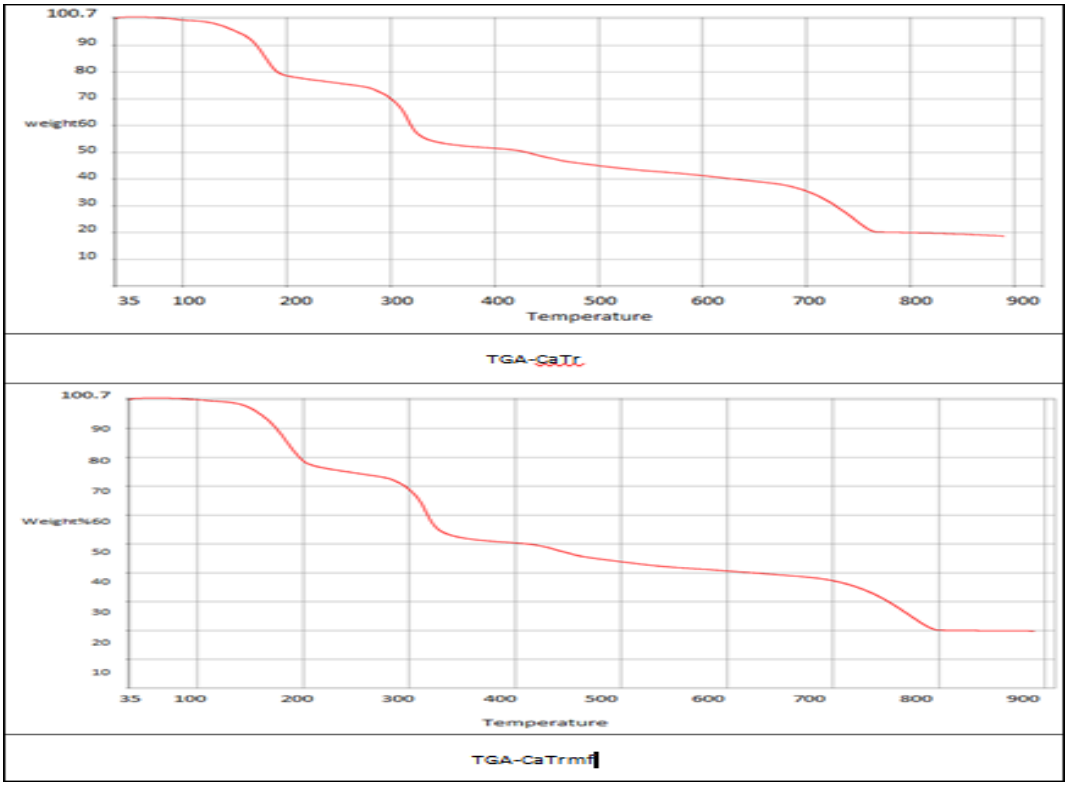

Figure 4

The thermal decomposition reactions are usually endothermic. The final solid products of thermal decompositions of these crystals are carbonates. The thermal study reveals that the water molecules are locked up in the lattice with different ways.The decomposition results of CaTr and CaTrmf are compared and the results are given in the Table 3.

Table 3:Comparative decomposition analysis

Stage	Crystals	Temperature range	Mass loss %		Reactions
			Observed	Calculated	
I	CaTr CaTrmf	67.5-183.4 100-200	20 23.5	20.088	$CaC_4H_4O_6.4H_2O \rightarrow CaC_4H_4O_6.H_2O$
II	CaTr CaTrmf	183.4-327.8 200-327.8	25 25	26.12	$CaC_4H_4O_6.H_2O \rightarrow$ C-Coo, C-Coo > Ca
III	CaTr CaTrmf	327.8-761.16 327.8-800	35 32	34.20	C-Coo, C-Coo > Ca → $CaCO_3$

3.4.2. Differential Thermal Analysis (DTA):

The DTA curve of CaTr and CaTrmf are shown in the Figure 5 .Three endothermic peaks at 173.37ºC ,306.67ºC and 740ºC are observed .In the first stage of decomposition ,Peak at 173.37ºC corresponds to the loss of water molecules followed by another endothermic peak at 306.67ºC due to loss of more water molecules .

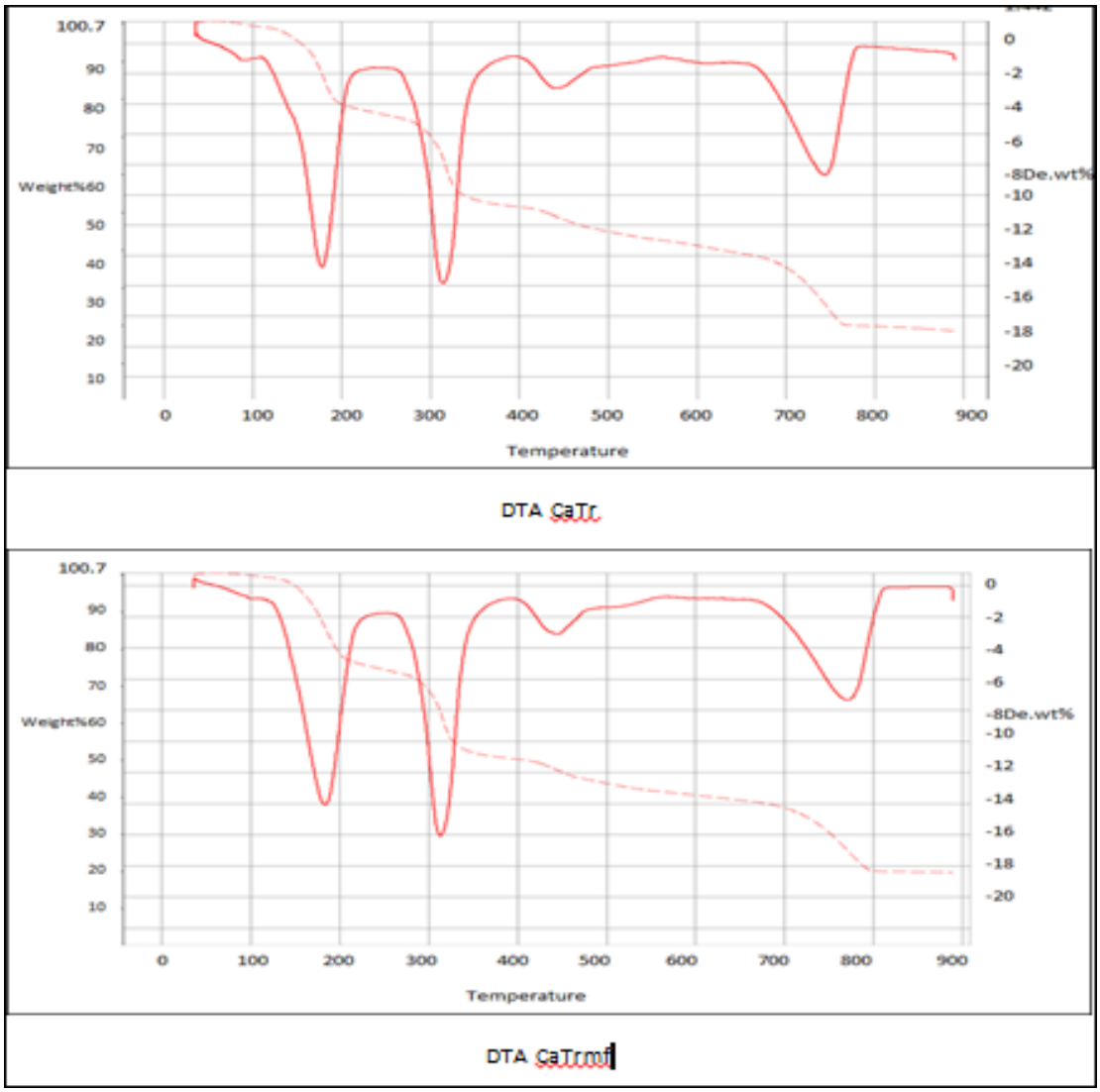

Figure 5

Thermal decomposition reactions are usually endothermic. Some of the DTA peaks are exothermic, the reason being concomitant oxidation reaction taking place along with decomposition.

3.4.3. Differential Scanning Calorimetry (DSC):

The differential scanning calorimeter is a fundamental tool in thermal analysis. The difference in the amount of heat required to increase the temperature of the sample and reference is measured as the function of temperature.The DSC curve of CaTr and CaTrmf are Shown in the Figure6.The DSC of CaTr shows three endothermic peaks and the DSC of CaTrmf has four endothermic peaks. DSC of CaTr show a well defined endothermic peak at 187.5°C corresponding to evaporation of water molecules .Another peak at 275°C corresponds to the total dehydration.DSC of CaTrmf has a small broad peak at 137.5°C and a well defined endothermic peak at 175°C corresponding to evaporation of water molecules .Another peak at 275°C corresponds to the total dehydration.The peak at 312.5°C corresponds to the initial stage of decomposition into calcium carbonate.The peak at 137.5°C is new in CaTrmf crystal.The heat flow for CaTr andCaTrmf at the same temperature 175°C are different.It is 47.5 mW for CaTr and 27.3mW for CaTrmf.For the endothermic peaks at higher temperatures the heat flow for CaTr is around 23mW and around 20.3mW for CaTrmf.

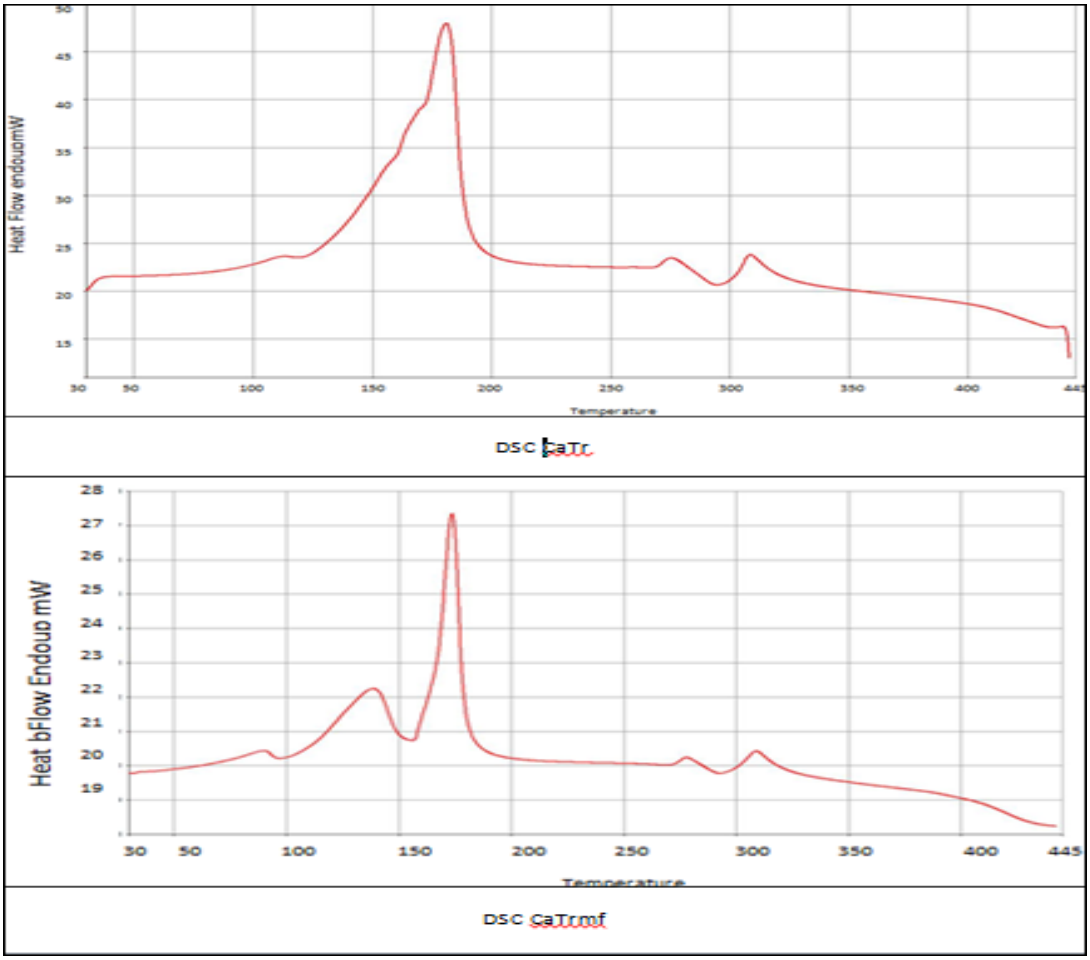

Figure 6

4. RESULT AND DISCUSSION

4.1. XRD analysis:

The cell parameters are determined. The space group is identified.There is a small variation in the lattice parameter .The volume ofCaTrmf is 10 units greater than that of CaTr.

4.2. FTIR analysis:

The functional groups are identified. There is no marked variations except the additional peaks in CaTrmf. The possible mechanism for the increase in the number of absorption peaks may be the lowering of molecular symmetry as a result of the orientation in favor of the easy magnetic direction.The assigned vibrational frequencies are in good agreement with the reported values.

4.3. UV analysis:

The grown crystals show transmittance in the entire visible region,which is the desired quality for the material to be used as NLO material.Band gap energy for calcium tartrate crystal grown in the absence of field is less than that of crystal grown in presence of magnetic field.The lower cutoff frequency is calculated from the graph between λ_{avg} and $dT/d\lambda$.The bandgap energy of CaTr is 6.3427eV and CaTrmf is 6.375eV.

4.4. Thermal Characterization:

The thermal study reveals that the water molecules are locked up in the lattice with different strengths in the grown crystals.Peak width in DSC is a valuable measure of purity.An increase in thermal stability is observed in CaTrcrystals.There is an additional peak observed in DSC of CaTrmf.There is some change in the heat flow of the crystals grown in the presence and absence of magnetic field.

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