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Growth and Thermal Studies of Mixed Crystals of Ca-Ba Tartrate in Silica Gel

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ABSTRACT

Mixed crystals of Calcium-Barium Tartrate were grown by a single diffusion method. The optimum conditions were established by varying various parameters such as pH of gel solution, gel concentrations, gel setting time, concentration of reactants etc. Crystals having different morphologies were obtained .Whitish semitransparent, pale yellow, rhombohedral shaped, needle shaped crystals of Calcium-Barium Tartrate were obtained. Some of them were transparent diamond shaped, some are twined. Maximum sizes of the grown crystals are 5mm×3mm and thickness about 2to3mm. The crystals grown were characterized by Thermogravimetry (TGA), Differential thermal analysis (DTA) and Derivative thermogravity (DTG). The results of these observations are described and discussed.

Keywords: Gel technique, mixed tartrate crystals, TGA, DTA and DTG.

INTRODUCTION

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. A series of pure and mixed crystals

have been grown by several researchers with the aim of identifying new materials for practical and industrial purposes [1-5].Compounds of tartaric acid find several practical applications in science and technology because of their interesting physical properties such as dielectric, ferroelectric, piezoelectric and non-linear optical properties[6-10]. Most of the tartrate compounds are insoluble 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 of Calcium tartrate was reported [11]. A single crystal of Strontium tartrate was reported [12]. Thermal behaviour of Strontium tartrate was also reported [12]. Mixed crystals of tartrate have several applications in medicine, optics etc. And hence; it was thought worthwhile to undertake investigation on growth of crystals of mixed tartrate and their characterization by different methods.

The present work describes the growth of mixed Crystals of Calcium Barium tartrate grown in silica gel .These crystals are identified and characterized by Thermogravimetry (TGA) and Differential thermal analysis (DTA), Derivative thermogravity (DTG)

MATERIALS AND METHODS

Calcium Barium tartrate shows poor solubility in water hence it was thought worthwhile to grow such a kind of material by chemical reaction at controlled rate using gel method [13-14]. The crystallization apparatus for the growth of rare-earth tartrate crystals consist of borosilicate glass tube of length 20cm and diameter 2.5cm placed vertically on plastic stand. Silica gel was prepared by acidifying pure Sodium metasilicate (Na_2SiO_3) of specific gravity 1.04gm/cm3, with tartaric acid of a concentration in accordance with the requirement of a particular pH value. The tartaric acid solution was added slowly to Sodium metasilicate solution with continuous stirring to avoid any local ion concentration in which would otherwise cause premature local gelling and make the final solution inhomogeneous .Here, tartaric acid acted as a lower reactant. A fixed amount of gel solution with the desired value of pH was then transferred to several test tubes. The test tubes were sealed cotton to prevent fast evaporation and contamination of the exposed surface of the gel. The solution was then allow to set the gel setting time was found to be strongly dependent on pH, High pH value gel takes lower time to set than low pH value. After confirming the gel setting and aqueous solution of Calcium Chloride and Barium Chloride of the required concentration was then poured slowly along the sides of the tube, to avoid breaking the gel. Calcium Chloride and Barium Chloride solutions acted as upper reactants. Slow diffusion of the upper reactants ions through the narrow pores of the silica gel leads to reaction between these ions and the ions present in the gel as lower reactant.

The following reaction was expected inside the gel,

$$2C_4H_6O_6 + xCaCl_2 + (1-x)\,BaCl_2 \rightarrow Ca_XBa_{(1-x)}(C_4H_4O_6)_2.xH_2O + 4\,HCl$$

Mixed crystals of Calcium Barium tartrate are Whitish semitransparent, pale yellow, rhombohedral shaped, needle shaped crystals, some of them were transparent diamond shaped, and some are twined. Maximum sizes of the grown crystals are 5mm×3mm and thickness about 2to3mm.Are obtained.

RESULTS AND DISCUSSTION

Table- 1: Gives the various optimum conditions for Calcium Barium tartare crystals grown in silica gel.

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. Near the interface of gel-reactants, dendrites growth is observed due to fast growth rate. However as the reactants percolates through the gel, the controlled reaction occurs below the depth of about 3cm. Hence good quality, semi transparent, well developed faces crystals are observed. This result due to the decrease in concentration of reactants as the time passes.

Table -1: Optimum conditions for growth of Calcium Barium tartrate crystals

Conditions	**Calcium Barium tartrate**
Density of sodium metasilicate	1.04gm/cm^3
Concentration of tartaric acid	1M
Volume of tartaric acid	7ml
Volume of sodium meta silicate solution	16ml
pH of the gel	4.2
Concentration of $CaCl_2$	1M
Concentration of $BaCl_2$	1M
Temperature	Room temperature

Table-2: Summarizes the effects on the habits of single crystals. In the present work Figure-1, And Figure-2.shows optical photo graph of prismatic semitransparent crystals of Calcium Barium tartrate growing under different conditions.Figure-3. Illustrates different morphologies of pure Calcium Barium tartrate crystals grown under different conditions of growth. The crystals grown are Whitish, some are pale yellowish, semi transparent, rhombohedral shaped, at one end crystals are translucent were observed.

Table-2:.Effect of concentration of reactants of habit, quality and size of $Ca_x Ba_{(1-x)}(C_4H_4O_6)_2$

Conc. of reactant in gel	Conc. of reactant above gel	Habit	Quality	Size (mm)
$C_4H_6O_6$ 1.25M	$CaCl_2$:$BaCl_2$	Dendrite	Opaque	5×4 ×2
5 to7ml pH 4 .2	1M 15ml	semitransparent		
$C_4H_6O_6$ 1 M	$CaCl_2$:$BaCl_2$	prismatic	Good	5×3 ×3.
5 to7ml pH 4.2	1M 15ml			

s

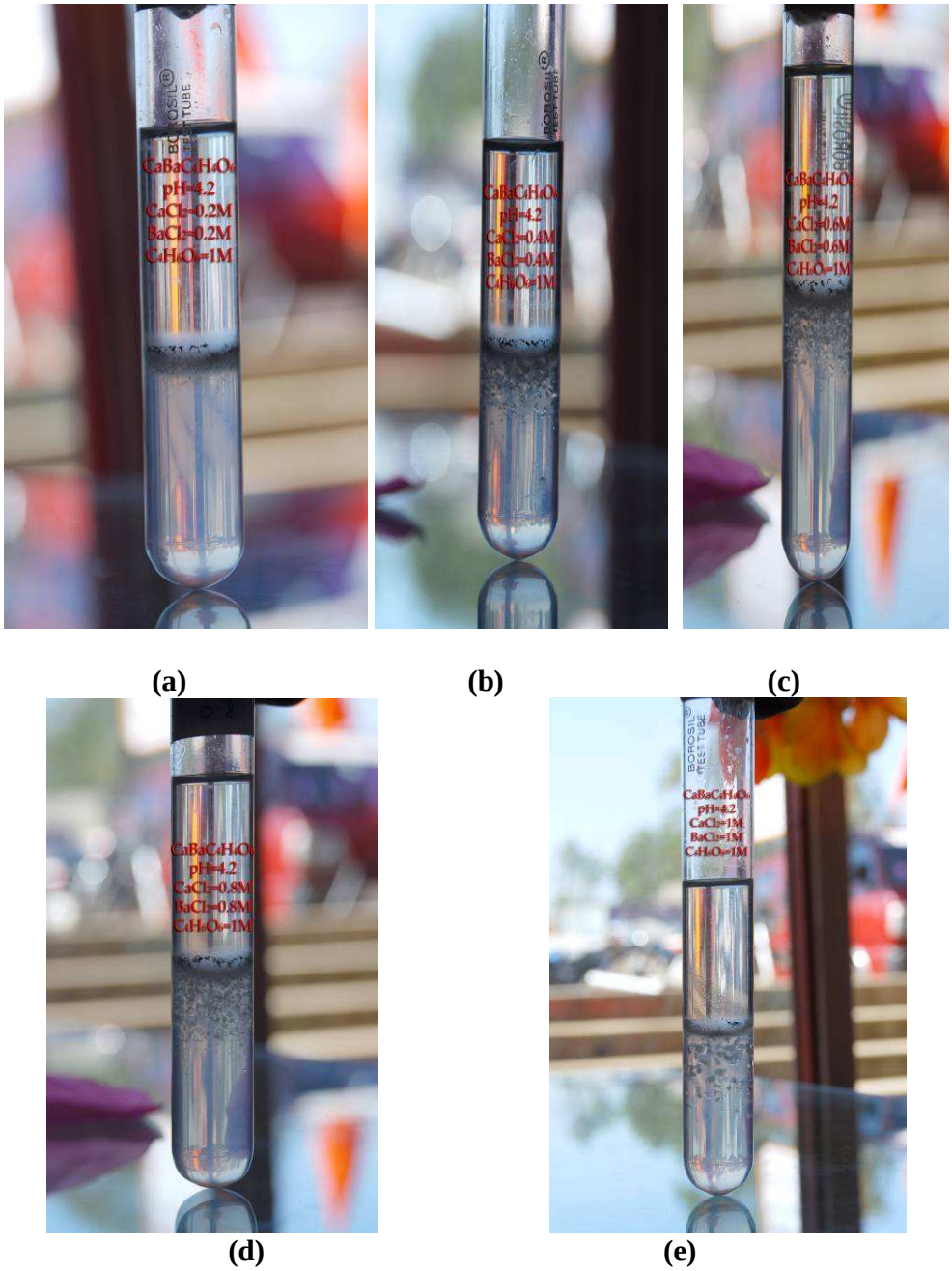
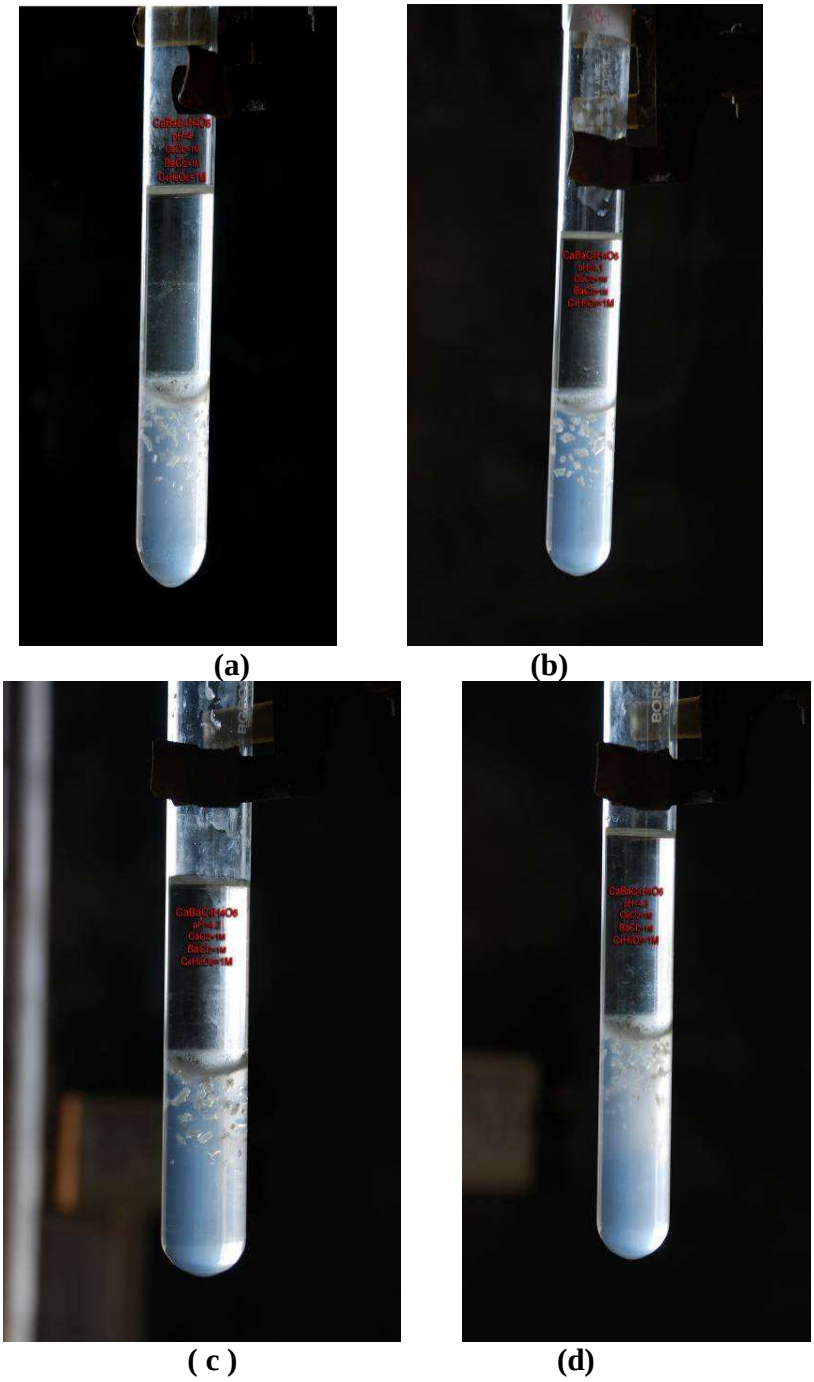


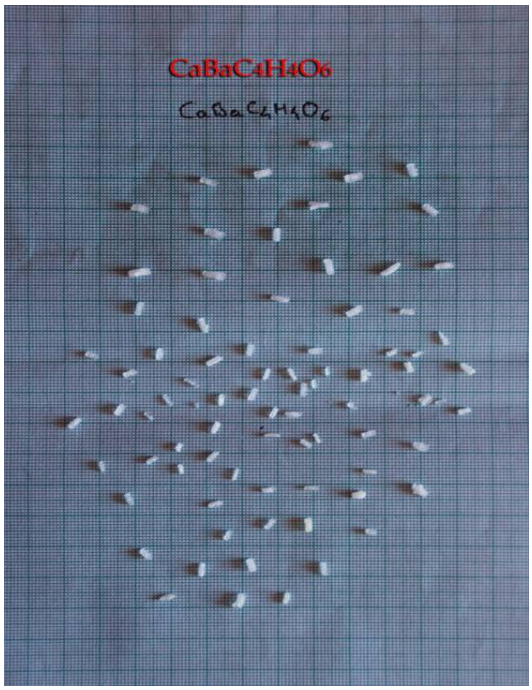
Figure-1:Optical photograph showing growth of Calcium Barium Tartrate crystals under variation of upper reactant concentration (a)0.2M(b)0.4M (c)0.6M(d)0.8M (e)1M.



(a) **(b)**

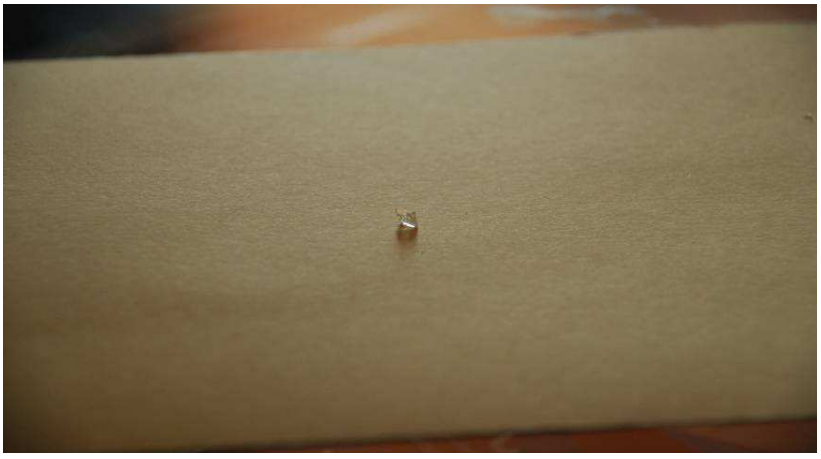
(c) **(d)**

Figure-2: Optical photograph of growth of Calcium Barium Tartrate under at different conditions (a) pH=4(b) pH= 4.1 (c) pH=4.2(d) pH=4.3



(a)

(b)



(c)

Figure-3: Optical photograph illustrating varied morphology of Calcium Barium tartrate crystals grown under different growth conditions.

Characterization

Thermal analysis: Thermogravimetric analysis (TGA), Differential thermal analysis (DTA), Derivative thermogravity (DTG), techniques are widely used for thermal studies of organic and inorganic compounds. Modern commercial thermo balances with variable heating rates, variable gaseous media, with vacuum or high- pressure facilities, and with continuous recording facilities eliminated satisfactorily the possible sources of errors in thermal studies of samples under study. As a result, numbers of possible analytical precipitates are mentioned in the literature. Thermal studies on tartrate crystals grow by gel method were reported by many investigators [15-18]. Thermal studies on pure and doped Calcium tartrates crystals grown by gel method using Calcium format mixed with formic acid as the supernatant solution was reported [19]. Thermal studies on pure gel grown Calcium tartrate crystal grown by gel method using Calcium Chloride as supernatant was reported [20]. The thermal decomposition study of Calcium Barium tartrate involves simultaneous TGA, DTA and DTG of the compound under ambient conditions.

- **TGA:**

TGA, DTA and DTG studies of Calcium Barium tartrate crystals were carried out at NCL, Pune. Figure 4(a), (b), (c) represent the TGA, DTA and DTG curves respectively.

The percentages of the weight loss in the different stages of decomposition of Calcium Barium tartrate are presented in the table -3

Calcium Barium tartrate is water coordinated compound. Therefore there is a possibility that this crystal may lose some of its water molecules while heating. TGA of Calcium Barium tartrate showed clearly four stages of decomposition as expected,

1) Dehydration 2) Calcium Barium tartrate to Calcium Barium Oxalate 3)Calcium Barium Oxalate to Calcium Carbonate and Barium Carbonate 4) Calcium Carbonate and Barium Carbonate to oxides of Calcium and Barium Similar observations are known from the literature on Rochelle salt and rare earth tartrates[16-18]. The TG curve did not show the appreciable weight change in the temp range 30-73^{0}C indicating that the Calcium Barium tartrate crystals are thermally stable in this range and no transformation took place. It was observed that the decomposition begins at 73^{0}C. And crystals are unstable beyond 73^{0}C.

It was observed that in the temperature range 73^{0}C to 291^{0}C in which weight loss of 31.649%, agrees very well with the calculated weight loss of 31.32%it is clear that Calcium Barium tartrate crystals are hydrated and the weight loss calculation clearly indicates that Calcium Barium tartrate crystals have twelve water molecules as water of crystallization.

A small plateau observed in the temperature range 73^{0}Cto 163^{0}C signals the loss of first 5H_2O molecule, plateau between 163^{0}C to 186^{0}C indicates the loss of 3H_2O molecule, and plateau between 163^{0}C to 291^{0}C indicates the formation of anhydrous Calcium Barium tartrate. In the temp range of 291^{0}C to350^0 C, the total weight loss of 18.05% is seen which is due to the loss of 4C & 4$H_2$0 this is in well agreement with calculated weight loss of 17.34%. Then an anhydrous Calcium Barium tartrate decomposes into Calcium Barium oxalate. Plateau between the temp 291^{0}C to 300^{0}C signals the loss of 4C molecule, 300^{0}C to 350^{0}Csignals the loss of 4H_2O

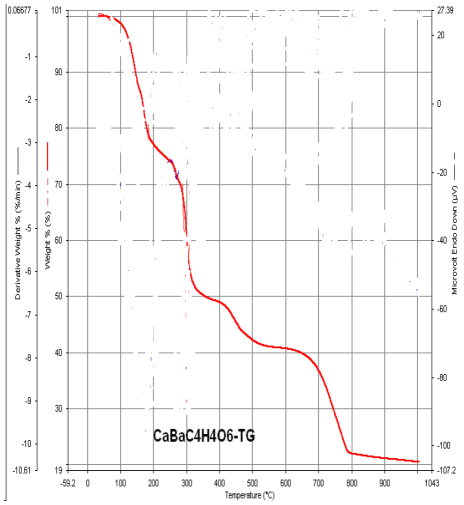
molecule. Plateau in the temperature range 350^0C to 400^0C is attributed to the stable Calcium - Barium oxalate.

In the third step of decomposition total weight loss 8.35% was observed in the temperature range 400^0C-510^0C which corresponds to the loss of 2CO. This weight loss aggress very well with the calculated weight loss 8.12%. Thus Calcium Barium oxalate further decomposes into calcium carbonate and Barium carbonate. Plateau in the temperature range 510^0C-659^0C is attributed to the stable Calcium Carbonate and Barium Carbonate.

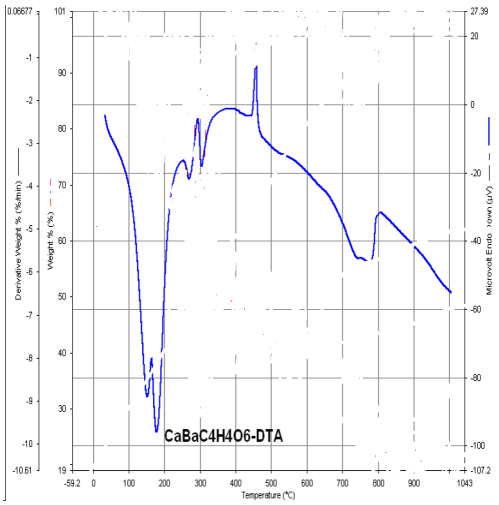
Finally in the temp range of 659^0C to 791^0C, total weight loss of 15% was obtained. This loss is attributed to the loss of $2CO_2$. This is in well agreement with the calculated weight loss of 16.54%. Thus the Calcium Carbonate and Barium Carbonate finally turns into Oxides of Calcium and Barium at 791^0C. Beyond 791^0C up to the end of analysis there is a stable CaO and BaO. DTA and DTG curve of the same compound shows its endothermic peaks at 150^0C, 181^0C, 281^0C, 304^0C,750^0C and an exothermic peaks at 295^0C,454^0C.

Stage	Temperature range 0^C	Observed % Weight loss	Calculated % Weight loss	Loss of molecule in stage
I	73-291	31.64	31.32	$12H_2O$
II	291-350	18.35	17.40	4C and $4H_2O$
III	400-510	8.35	8.12	2Co
IV	659-791	15	12.76	$2Co_2$

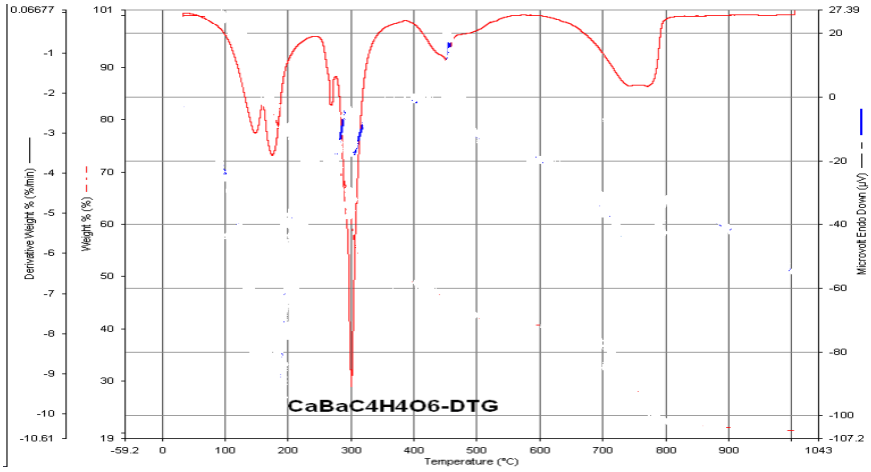
Table-3: TGA Data:



(a) TGA



(b) DTA



(c)DTG

Figure-4: TGA, DTA, DTG Curve of Calcium Barium tartrate

CONCLUSION

In view of the above observations, we may conclude the following;
(1) Gel grown system involving the use of Calcium Chloride. Barium Chloride as the super reactant and Sodium meta-silicate gel impregnates with tartaric acid leads to Crystallization of Calcium Barium tartrate.
(2) Different habits of Calcium Barium tartrate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants, concentration of impurities etc.
(3) It was found that well-developed single crystals of Calcium Barium tartrate are obtained at 1M concentration of feed solution in the pH range 4 to 4.5 of the gel
(4) The thermal behavior of the material reveals that decomposition takes place through many stages.
(5) The thermal behavior of the material reveals the presence of water molecules as water of crystallization. (6) From thermograms it was concluded that the grown crystals are thermally unstable beyond 73^0C and decompose into Calcium Oxide and Barium oxide through many stages of dehydration.
(7) The decomposition reactions show exothermic as well as endothermic peaks.

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