

Thermal and FTIR Studies of Gel-grown Calcium Tartrate Tetrahydrate Crystals

Vimal S. Joshi

Research Laboratory, Department of Physics, Shri R.K. Parikh Arts and Science College,
Petlad, Gujarat, India

ABSTRACT: As compounds of different tartrates found various applications in science and technology as well as in the field of medical and pharmaceutical sciences, they draw attention of many researchers. During last many years, various researchers have grown and characterized the pure and mixed tartrate crystals according to their choice and requirements. In the present study, calcium tartrate crystals were grown by the single diffusion reaction technique in silica gel at ambient conditions by using two different supernatant solutions. To grow calcium tartrate crystals, it is customary to prepare silica gel with tartaric acid and the aqueous solution of calcium chloride is allowed to diffuse in the set gel. However, in the present work two types supernatant solutions were allowed in the gel impregnated by tartaric acid, i.e., one is aqueous solution of calcium chloride and other is aqueous solution of calcium hydroxide. In both the cases, good quality crystals were grown in gel column. Powdered samples of the grown crystals were analysed by FTIR and TGA techniques. The results are discussed.

KEYWORDS: Gel, Crystal, Gel Growth, Crystal Growth, TGA, FTIR.

I. INTRODUCTION

There are many applications of pure and mixed tartrate compounds. Ferroelectric applications of sodium-potassium tartrate [1], antimony-barium tartrate in veterinary drugs [2], potassium-chromium tartrate in medicine [3] etc. Many researchers have studied different properties of various pure and mixed tartrate compounds such as pure and mixed iron- manganese levo-tartrate [4], effect of X-ray irradiation on the dielectric properties of calcium tartrate [5], IR and thermal studies of calcium tartrate [6], thermal behaviour of strontium tartrate [7], lattice variation and thermal parameters of pure and impurity-added calcium tartrate [8], spectroscopic studies of Ni^{2+} in calcium tartrate [9], thermal studies of cadmium tartrate [10], some properties of zinc tartrate [11] and strontium tartrate tetrahydrate [12] etc. In the present study, calcium tartrate crystals have been grown by single diffusion gel growth technique using aqueous solutions of calcium chloride (CaCl_2) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) as supernatant solutions, named as Solution A and Solution B, respectively. The grown crystals were characterized by FTIR for confirmation of proper formation of crystals. The thermal stability of the crystals was assessed by the thermo gravimetric analysis. Kinetic and thermodynamic parameters of dehydration process have been evaluated. Comparisons of results have been made for both the cases.

II. EXPERIMENTAL TECHNIQUES

Crystal Growth

In the present investigation, the calcium tartrate crystals were grown by gel method. The crystals were grown in glass test tubes of 2.5 cm diameter and 15 cm length. The gel was prepared by mixing sodium metasilicate solution of 1.03 specific gravity with one molar levo tartaric acid, so that pH 4.0 of the mixture was attained. After setting the gel in two different test tubes, two types of supernatant solutions were poured. Solution (A) was 1M aqueous solution of CaCl_2 while Solution (B) was 1M aqueous solution of $\text{Ca}(\text{OH})_2$. In both the cases, good quality platelet shaped crystals were grown. In the case of solution (A), transparent platelet type crystal was grown as shown in Fig.1, in the other case also transparent platelet, with more width, was grown as shown in Fig. 2.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016



Fig. 1 Platelet type crystal Grown by CaCl_2 (Solution A) Fig. 2 Platelet type crystal Grown by $\text{Ca}(\text{OH})_2$ (Solution B)

Thermogravimetric Study

Thermogravimetric study of powdered samples for both the crystals was carried out at Room Temperature to 800 °C with the heating rate of 15 °C/min in an atmosphere of Nitrogen using Al_2O_3 as a standard reference.

Fourier Transform Infrared Spectroscopic Study

The FTIR spectra of powdered samples of grown crystals were recorded on NICOLET MAGNA IR 500 series II FTIR spectrophotometer having DTGS-KBr detector and KBr beam splitter in the range of 400 cm^{-1} to 4000 cm^{-1} . Pellets of fine powder were prepared in KBr medium.

III. RESULTS AND DISCUSSION

The gel growth technique is particularly useful to grow different types of pure and mixed crystals of materials that are sparingly soluble in water or decompose before melting, at ambient temperatures [13,14]. The gel medium prevents turbulences, remains chemically inert and provides a three-dimensional structure, which permits the reactants to diffuse at a controlled rate.

In the present work, calcium tartrate crystals were grown using two types of supernatant solutions, viz., Solution A was 1M aqueous solution of CaCl_2 while Solution B was 1M aqueous solution of $\text{Ca}(\text{OH})_2$.

The uses of thermogravimetric data to evaluate kinetic parameters of solid-state reactions involving weight loss have been investigated by many workers [15]. The shape of the curve is determined by the kinetic parameters of calcium tartrate such as order of reaction, frequency factor and energy of activation.

Fig. 3 indicates the thermogram of calcium tartrate crystals grown by 1M aqueous solution of CaCl_2 ; while Fig. 4 indicates the thermogram of calcium tartrate crystals grown by 1M aqueous solution of $\text{Ca}(\text{OH})_2$. The TGA indicates that four water molecules were associated with the crystals and the crystals were not stable thermally.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

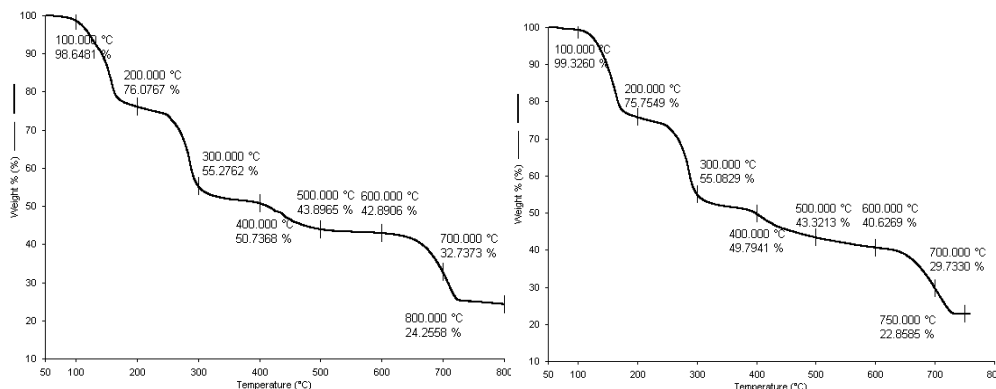


Fig. 3 Thermogram of crystal grown by CaCl₂ (Solution A) Fig.4 Thermogram of crystal grown by Ca(OH)₂ (Solution B)

The thermal behaviour of the crystals grown in the cases of supernatant solution A and supernatant solution B is studied and the decompositions observations are summarized in Table 1. The values of theoretical weight percentage and observed weight percentage at different stages were in consonance. The results are summarized in the Table 1 for both the crystals.

Sample	Temperature	Decomposition of Crystal	Theoretical Weight Loss%	Observed Weight Loss %
Solution A	50 °C	CaC ₄ H ₄ O ₆ .4H ₂ O	100	100
	258.42°C	CaC ₄ H ₄ O ₆	72.32	72.32
	412.18°C	CaC ₂ O ₄	49.25	49.98
	665.64°C	CaCO ₃	38.48	39.98
	812.40°C	CaO	21.56	24.08
Solution B	50°C	CaC ₄ H ₄ O ₆ .4H ₂ O	100	100
	256.79°C	CaC ₄ H ₄ O ₆	72.32	72.29
	405.08°C	CaC ₂ O ₄	49.25	49.24
	653.02°C	CaCO ₃	38.48	38.47
	730.15°C	CaO	21.56	22.96

Table 1 Thermal Decomposition of Crystals

From the thermograms, it was found that the calcium tartrate crystals were first dehydrated and then decomposed. At the end of first stage of the decomposition, crystals were converted into calcium oxalate. After further heating, they were converted into carbonate. Finally, in the last stage they were converted into calcium oxide and remain stable up to end of analysis.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

Kinetic and thermodynamic parameters can be evaluated from the thermograms. In the present investigation, the Coats-Redfern relation [16] was used to evaluate the kinetic parameters from the thermograms of Figure 3 and Figure 4. The Coats-Redfern relation is as follows:

$$\log_{10}[\{1-(1-\alpha)^{1-n}\}/\{T^2(1-n)\}] = \{\log_{10}[AR/aE][1-2RT/E]\} - \{E/2.3RT\}, \text{ (for } n=1)\dots\dots\dots(1)$$

- Where, α = fraction of the original substance decomposed at time t
- n = order of reaction
- A = frequency factor
- E = activation energy of the reaction
- R = gas constant
- a = heating rate in $^{\circ}\text{C}/\text{min}$

To determine the value of activation energy and order of reaction, a Coats-Redfern plot i.e. $-\log_{10}[\{1-(1-\alpha)^{1-n}\}/\{T^2(1-n)\}]$ versus $1/T$ is drawn for different values of n and the best linear plot gives the correct value of n. For the correct value of n, the best linear fitting for the Coats-Redfern plot yields the value of activation energy. Equation (1) cannot be used for n=1, therefore, it is modified as follows:

$$-\log_{10}[-\log_{10}(1-\alpha)/T^2] = \log_{10}[AR/aE][1-2RT/E] - [E/2.3RT], \text{ (for } n=1)\dots\dots\dots(2)$$

In the case of solution (A), the best linear fit was obtained for n = 3. Fig.5 shows the Coats-Redfern plot for n=3.

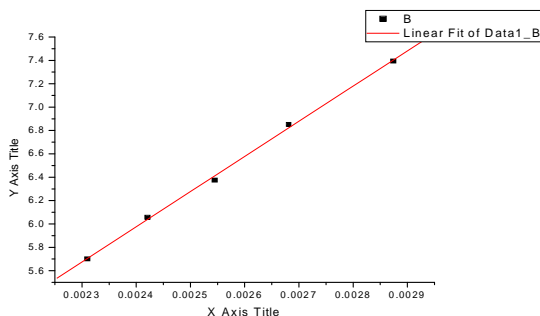


Fig.5 The Coats-Redfern plot for crystal Grown by CaCl₂ (Solution A)

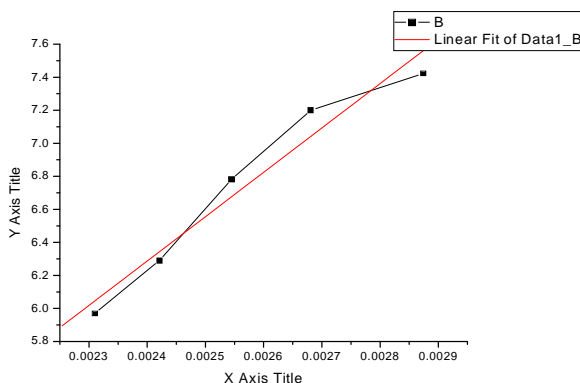


Fig.6 The Coats-Redfern plot for crystal Grown by Ca(OH)₂ (Solution B)

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

The values of activation energy and frequency factor are found to be $51.374 \text{ kJmol}^{-1}$ and 4.56×10^{18} respectively. The Coats-Redfern relation yields the frequency factor, which can be further used in the calculations of different thermodynamic parameters. The calculated parameters are entropy, enthalpy, Gibbs free energy and the standard change in internal energy, which are found to be $109.91 \text{ JK}^{-1}\text{mol}^{-1}$, $44.853 \text{ kJmol}^{-1}$, 1.752 kJmol^{-1} and $48.113 \text{ kJmol}^{-1}$ respectively. Whereas, in the case of solution B, the best linear fit was obtained for $n=0$. Fig. 6 shows the Coats-Redfern plot for $n=0$. The values of activation energy and frequency factor are found to be $57.570 \text{ kJmol}^{-1}$ and 1.24×10^{19} respectively.

No.	Parameters	Values	
		Grown using supernatant CaCl_2 (Solution A)	Grown using supernatant $\text{Ca}(\text{OH})_2$ (Solution B)
1	Activation Energy	$E = 51.374 \text{ kJmol}^{-1}$	$E = 57.570 \text{ kJmol}^{-1}$
2	Frequency Factor	$A = 4.56 \times 10^{18}$	$A = 1.24 \times 10^{19}$
3	Entropy	$\Delta^\circ S^\circ = 109.91 \text{ JK}^{-1}\text{mol}^{-1}$	$\Delta^\circ S^\circ = 118.32 \text{ JK}^{-1}\text{mol}^{-1}$
4	Enthalpy	$\Delta^\circ H^\circ = 44.853 \text{ kJmol}^{-1}$	$\Delta^\circ H^\circ = 51.036 \text{ kJmol}^{-1}$
5	Gibbs Free Energy	$\Delta^\circ G^\circ = 1.752 \text{ kJmol}^{-1}$	$\Delta^\circ G^\circ = 4.534 \text{ kJmol}^{-1}$
6	Standard change in Internal Energy	$\Delta^\circ U^\circ = 48.113 \text{ kJmol}^{-1}$	$\Delta^\circ U^\circ = 54.303 \text{ kJmol}^{-1}$

Table 2 Thermodynamic parameters

The values of entropy, enthalpy, Gibbs free energy and the standard change in internal energy are $118.32 \text{ JK}^{-1}\text{mol}^{-1}$, $51.036 \text{ kJmol}^{-1}$, 4.534 kJmol^{-1} and $54.303 \text{ kJmol}^{-1}$ respectively. All parameters are listed in Table 2 for both the cases.

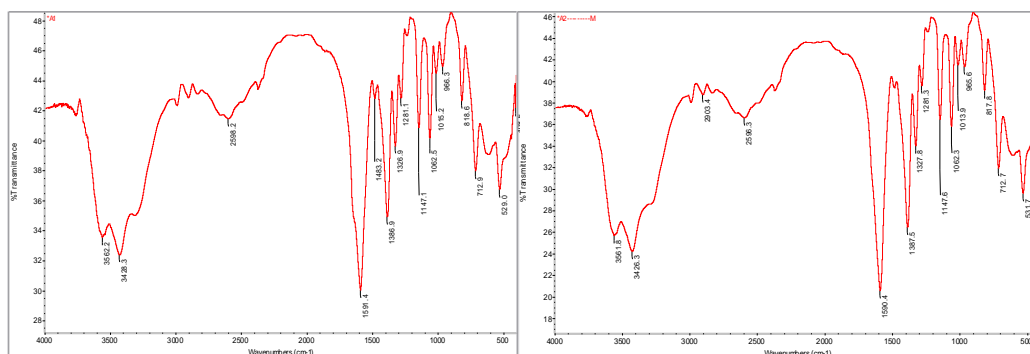


Fig.7 FT-IR spectrum for crystal grown by CaCl_2 (Solution A) Fig.8 FT-IR spectrum for crystal grown by $\text{Ca}(\text{OH})_2$ (Solution B)

Figure 7 shows FTIR spectrum of crystal grown with solution A. The absorption around 1591.4 cm^{-1} is due to carbonyl C=O group. The C-O stretching vibrations give rise to absorptions within 1386.9 cm^{-1} to 1281.1 cm^{-1} . The absorption at 1147.1 cm^{-1} is due to out of plane C-H stretching. The absorptions situated below 720 cm^{-1} are due to calcium–oxygen stretching vibrations. While, Fig. 8 shows FTIR spectrum of crystal grown by using solution B. The absorption around 1590.4 cm^{-1} is due to carbonyl C=O group. The C-O stretching vibrations give rise to absorptions within 1387.5 cm^{-1} to 1281.3 cm^{-1} . The absorption at 1147.6 cm^{-1} is due to out of plane C-H stretching. The absorptions situated below 817.8 cm^{-1} are due to calcium–oxygen stretching vibrations.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

Peak Assignments	Peak Positions in cm^{-1}	
	Grown by CaCl_2 (Solution A)	Grown by $\text{Ca}(\text{OH})_2$ (Solution B)
Symmetric and asymmetric stretching vibrations of O-H bond due to Water of Crystallization	3562,3428,2598	3561,3426,2903,2596
Carbonyl C=O group	1591	1590
C-O Stretching vibration	1386,1326,1281	1387,1327,1281
C-H Stretching vibration	1147	1147
O-H Stretching out of plane vibrations	1062,1015,966,818	1062,1013,965,817
Metal oxygen bond (Ca-O stretching)	712,529,408	712

Table 3 Peak assignments for FT-IR spectra

Peak assignments of FTIR spectra for both the cases are collectively summarized in Table 3.

IV. CONCLUSIONS

Calcium tartrate crystals were grown with the help of two aqueous solutions, viz., CaCl_2 and $\text{Ca}(\text{OH})_2$. The TGA indicates that four water molecules were associated with the crystals and the crystals were not stable thermally. From the thermograms, it is clear that, crystals loose water of hydration initially and converted into anhydrous form. After further heating, they were converted into calcium oxalate then after calcium carbonate, ultimately converted into calcium oxide, and remain stable up to the end of reaction. The values of kinetic and thermodynamic parameters were calculated. The FTIR spectra of both the crystals confirm the presence of C-H, $>\text{C}=\text{O}$ and $-\text{CH}=\text{CH}-$ bonds.

ACKNOWLEDGEMENTS

The author is thankful to Dr. M.J. Joshi, Physics Department, Saurashtra University, Rajkot for his guidance. The author is also thankful to Mrs. S.R.Vasant and Mr. Purvesh Vyas for fruitful discussion. The author is also thankful to Petlad Education Trust for encouragements.

REFERENCES

- [1] Valasek, J.; *Phys. Rev.*, 17 (1921) 475 "Piezo-Electric and Allied Phenomena in Rochelle Salt", *Phys. Rev.*, Vol.17, 475,1921
- [2] Joshi, V.S. and Mevada, K.C., "FT-IR, XRD and Thermal studies of gel-grown barium tartrate crystals", *Journal of Science*, Vol. 1, pp.68-71, 2010.
- [3] Veselaya, I.V. and Gordyski, V.I., *Voprosy onkologii (Vopr Onkol)*, Vol. 3, pp. 300, 1957.
- [4] Joshi, S.J., Parekh, B.B., Vohra, K.D. and Joshi, M.J., "Growth and characterization of gel grown pure and mixed iron-manganese levotartarate Crystals", *Bulletin of Materials Science*, Vol. 29, issue 3, pp. 307-312, 2006.
- [5] Gupta, S.K., Gon, H.B. and Rao, K.V.J. *Mater. Sci.Lett*, Vol. 6, issue. 1,1987.
- [6] Selvarajan,P., Das, B.N., Gon, H.B. and Rao, K.V., "Infrared spectroscopic and thermal studies of calcium tartrate single crystals grown by silica-gel technique", *Journal of Materials Science Letters*, Vol. 12, issue 15, pp. 1210-1211,1993.
- [7] Rahimkuty, M.H., Rajendra Babu, K.,Sreedharan Pillai, K., Sudarsana Kumar, M.R. and Nair, C.M.K., "Thermal behaviour of Strontium tartrate single crystals grown in gel", *Bulletin of Materials Science*, Vol.24, No.2, pp. 249-252, 2001.
- [8] Sahaya Shajan, X. and Mahadevan, C., "Lattice variation and thermal parameters of pure and impurity-added calcium tartrate tetrahydrate crystals", *Journal of Materials Science*, Vol. 39, pp. 4627-4629, 2004.
- [9] Reddy, P.P. and Reddy, Y.P., "Spectroscopic Studies of Ni^{2+} in Calcium Tartrate tetrahydrate", *Czechoslovak Journal of Physics B*, Vol.28, Issue. 9, pp. 1026-1030, 1978.
- [10] Dabhi, R. M. and Joshi, M.J., "Thermal studies of gel-grown cadmium tartrate crystals", *Indian Journal of Physics*, Vol. 77, pp. 481-485, 2003.
- [11] Dabhi, R. M. and Joshi, M. J., "Thermal Studies of Gel Grown Zinc Tartrate Spherulites," *Indian Journal of Physics*, Vol. 76A, No. 2, 2002, pp. 211-213."

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 5, May 2016

- [12] Arora, S.K., Patel, V., Amin, B. and Kothari, A., "Dielectricbehaviour of strontium tartrate single crystals", Bulletin of Materials Science, Vol. 27, No. 2, pp. 141-147, 2004.
- [13] Henisch, H.K., "Crystal Growth in Gels", University Park, Pennsylvania State University Press,1973.
- [14] Henisch, H.K., Dennis, J., Hanoka, H.I., "Crystal growth in gels", Physics and Chemistry of Solids, Vol. 26, issue 3, pp. 493-500, 1965.
- [15] Krevelen, D. W. van, Heerden, C. van, and Huntjens, F. J., "Physicochemical aspects of the pyrolysis of coal and related organic compounds, Fuel, Vol.30, pp. 253–258, 1951.
- [16] Coats, A.W. and Redfern, J. P., "Kinetic Parameters from Thermogravimetric Data", Nature, Vol.201, pp. 68-69, 1