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FT-IR, XRD and Thermal Studies of Gel-grown Barium Tartrate Crystals

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ABSTRACT

There are many applications of different tartrate compounds. Antimony barium tartrate is used for veterinary drugs. Barium tartrate crystals were grown by single diffusion gel growth technique in silica hydro-gel medium. White colour crystals of dendritic type were grown. Powdered XRD, FT-IR spectroscopic and thermal studies were carried out. By employing Thermogravimetric analysis (TGA), the thermal stability of crystals and the dehydration and decomposition nature was found. The Coats and Redfern relation was applied to evaluate the kinetic and thermodynamic parameters of dehydration. The powdered XRD and FT-IR spectroscopic study confirmed the formation of barium tartrate crystals.

Keywords: Gel growth, Barium Tartrate, TGA, kinetic parameters, Thermodynamic parameters, FT-IR.

INTRODUCTION

There are many applications of different tartrate compounds, for example, ferroelectric applications of sodium-potassium tartrate[1], potassium- chromium tartrate in medicine[2] and antimony-barium tartrate in veterinary drugs[3]. Many authors have studied different properties of various tartrate compounds such as thermal studies of cadmium tartrate[4], zinc tartrate[5] and calcium-strontium mixed levo tartrate[6]; dielectric properties of zinc tartrate[7] and strontium tetrahydrate[8] and magnetic properties of iron-manganese levo tartrate compounds[9]. In the present investigations author reports the growth of barium tartrate crystals by single diffusion gel growth technique. These crystals were characterized by FT-IR and powder XRD for the confirmation of proper formation of crystals. The thermal stability of the crystal was assessed by the TGA and the kinetic and thermodynamic parameters of dehydration process have been evaluated.

MATERIALS AND METHODS

In the present investigation the barium tartrate crystals were grown by the single diffusion gel growth technique. Glass test tubes of 25mm diameter and 140mm length were used as a crystallization apparatus. The AR grade chemicals were used to grow the crystals. As a one of the reactants, 1 M tartaric acid was mixed with sodium metasilicate solution of 1.03 specific gravity so that the pH of the mixture could be varying from 3.5 to 6.0. After setting gels, the supernatant solution of 1M barium chloride was poured very carefully without disturbing set gels. The test tubes were capped air tightly. The nucleation was observed within 24 hours. The best quality dendritic type crystals were grown for 5.5 pH, which are as shown in Figure-I.

Thermogravimetric analysis (TGA) for the present sample was carried out from temperature 35º C to 800º C at a heating rate of 15º C/min in an atmosphere of air using α-Al_2O_3 as a standard reference. Powdered sample was used for this study.

The FT-IR spectrum was recorded on BRUCKER IFS 66V FT-IR spectrometer in the range from 400-4000 cm^{-1}. Powdered sample in KBr medium was used. Powder XRD was conducted by using PHILIPS X'PERT MPD system by using Cu Ka radiation. The powder XRD patterns were analyzed by Basica software.

RESULTS AND DISCUSSION

The gel growth technique has attracted the attention of various workers because it has been proved to be the successful technique to grow crystals of sparingly soluble in water or decompose before melting, at ambient temperatures. This technique is also successfully employed to grow bio-materials crystals [10-13]. Figure-II shows FT-IR spectrum of barium tartrate. The absorption around 1599 cm^{-1} is due to carbonyl C=O group. The C-O stretching vibrations give rise to absorptions within 1388 cm^{-1} to 1218 cm^{-1}. The absorptions at 1137 cm^{-1} and 1079 cm^{-1} are due to out of plane C-H stretching. The absorptions situated below 920 cm^{-1} are due to barium – oxygen stretching vibrations Table-I shows the assignments of FT-IR spectrum. Figure-III shows the powder XRD patterns of barium tartrate crystals. The XRD data was analyzed basica software and the estimated values of cell parameters are as follows:

a = 8.1843 Å, b = 9.0491 Å, c = 8.3883 Å

which corresponds to the values available in the literature [14] as follows:

a = 8.1810 Å, b = 9.0360Å, c = 8.3920 Å

This confirms the growth of barium tartrate crystals. The use of thermo gravimetric data to evaluate kinetic parameters of solid state reactions involving weight loss has been investigated by many workers [15]. The shape of the curve is determined by the kinetic parameters of barium tartrate such as order of reaction, frequency factor and energy of activation. Figure-IV indicates the thermogram of barium tartrate crystals. The thermal behavior of barium tartrate crystal is as summarized in Table-II. The values of theoretical weight percentage and observed weight percentage at different stages were also mentioned in the table. From the thermogram, it was found that the barium tartrate crystals were first dehydrated and then decomposed. The first stage of the decomposition occurred at 360º C it was converted into barium carbonate. Finally, in the last stage it was converted into barium peroxide at 750º C. Kinetic and thermodynamic parameters can be evaluated from the thermogram. In the present investigation, the Coats-Redfern relation [16] was used to evaluate the kinetic parameters from the thermogram of Figure-IV.

The Coats-Redfern relation is as follows:

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

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 ºC/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:

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

In the present investigation the best linear fit was obtained for n = 12. Figure-V shows the Coats-Redfern plot for n = 12. The values of activation energy and frequency factor are found to be 305.12 $kJmol^{-1}$ and 3.52×10^{36} 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 448.43 $JK^{-1}mol^{-1}$, 294.55 $kJmol^{-1}$, 9.36 $kJmol^{-1}$ and 299.83 $kJmol^{-1}$ respectively as listed in Table-III.

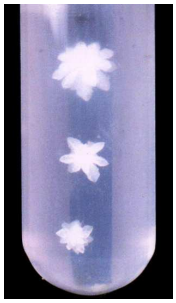

Figure-I: Dendritic type crystals grown for 5.5 pH and 1.03 specific gravity

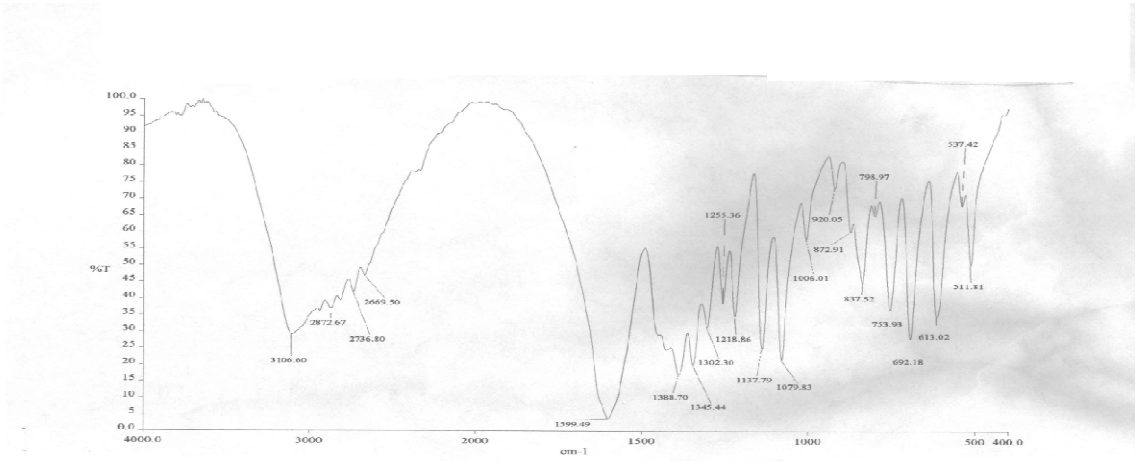

Figure-II: FT-IR spectrum of barium tartrate

Table-I: Peak assignment for FT-IR spectrum

Assignment of absorption peak	**Peak position in cm^{-1}**
O-H stretching vibrations	3106 and 2872
C=O stretching vibrations	1599
C-O stretching vibrations	1388,1345,1218
C-H stretching vibrations	1135 and 1079
Metal- Oxygen (Ba-O) stretching vibrations	920,837,753,692 and 613

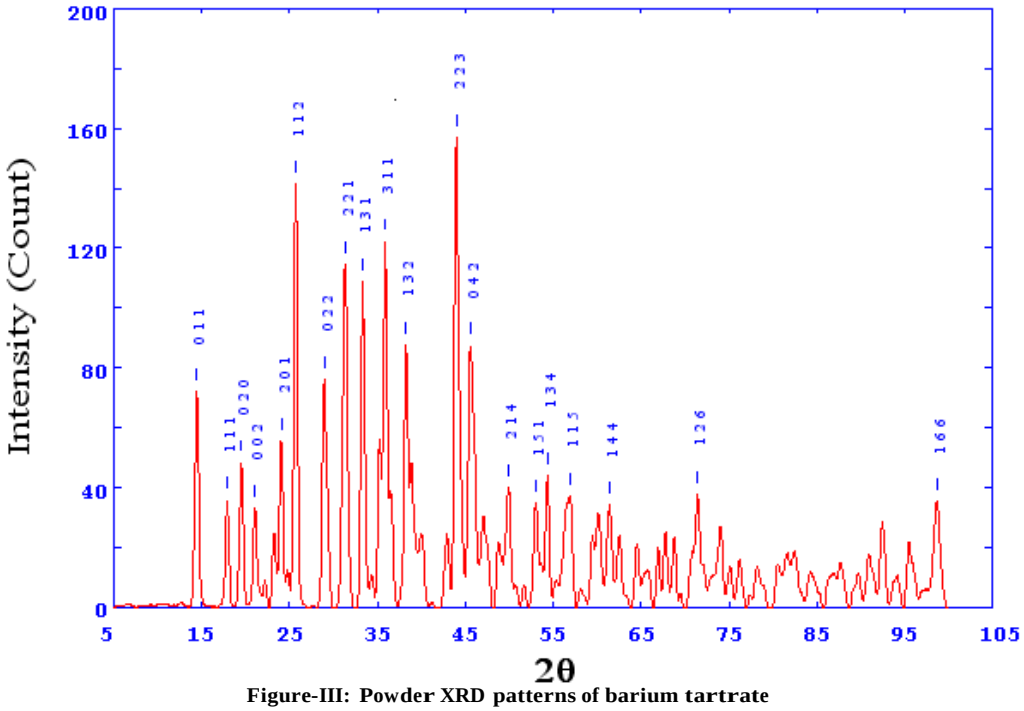

Figure-III: Powder XRD patterns of barium tartrate

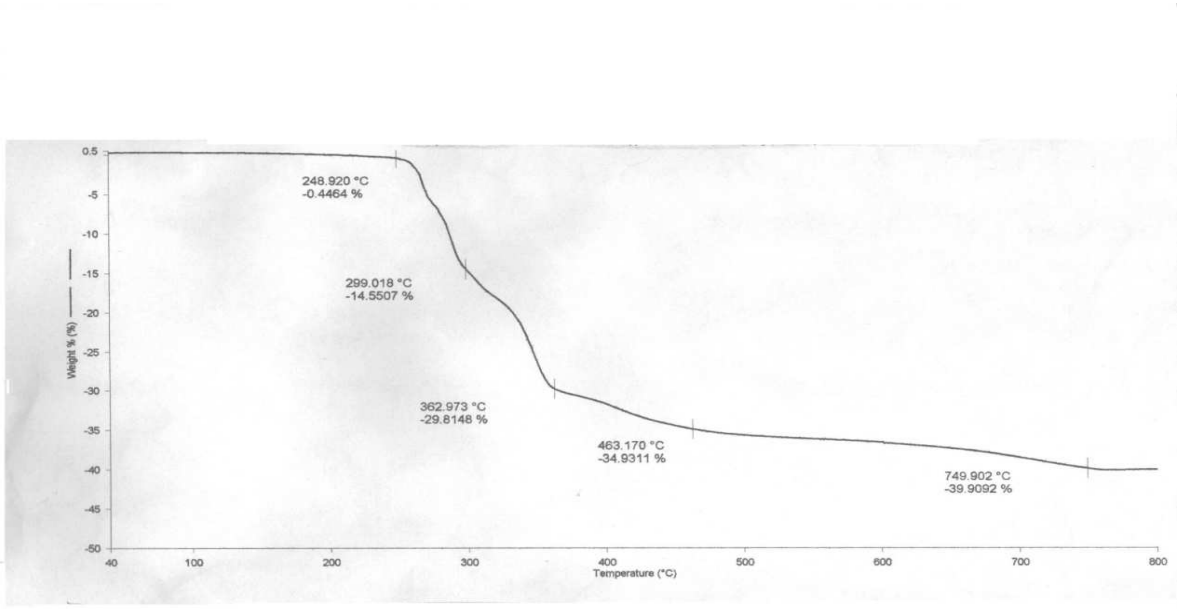

Figure-IV: The thermogram of barium tartrate

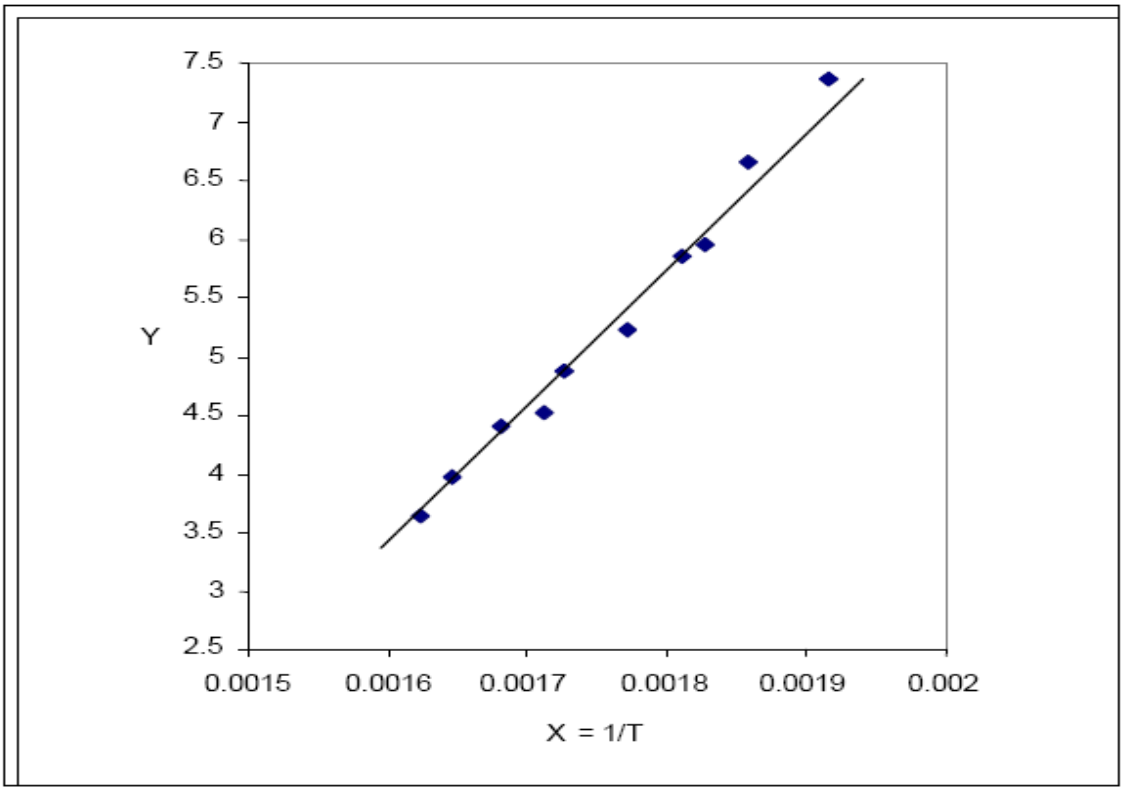

Figure-V: The Coats-Redfern plot for barium tartrate

Table-II: Decomposition table of barium tartrate crystals

Temperature °C	Decomposition of crystals	Theoretical weight in %	Observed weight in %
35	$BaC_4H_4O_6$	100	99.55
363	$BaCO_3$	69.14	70.18
750	BaO_2	59.33	60.09

Table-III: Thermodynamic parameters

No.	Quantity	Value
1	Activation energy	$E = 305.12\ kJmol^{-1}$
2	Frequency factor	$A = 3.52\times10^{36}$
3	Entropy	$\Delta^{\#}S = 448.43\ JK^{-1}mol^{-1}$
4	Enthalpy	$\Delta^{\#}H^{o} = 294.55\ kJmol^{-1}$
5	Gibbs free energy	$\Delta^{\#}G^{o} = 9.36\ kJmol^{-1}$
6	Standard change in internal energy	$\Delta^{\#}U^{o} = 299.83\ kJmol^{-1}$

CONCLUSION

Barium tartrate crystals were grown and the powder XRD confirms the unit cell parameter values with those available in the literature. The FT-IR spectrum confirms the presence of C-H, >C=O and –CH=CH- bonds[17,18]. The TGA indicates that the crystals are stable up to 250º C and decomposes into barium peroxide via intermediate stage of barium carbonate. The values of kinetic and thermodynamic parameters were evaluated.

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