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## Spectroscopic and thermal studies on lead tartrate crystals

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### ABSTRACT

Lead tartrate crystals were grown by using silica gel as the growth medium. Lead acetate was taken as the supernatant solution. The grown crystals were characterized by Fourier transform infrared spectroscopy. The FT-IR spectra of these crystals were recorded in the wavenumber range 400 – 4000  $\text{cm}^{-1}$ . The thermograms of the grown crystals were recorded in the temperature ranging from room temperature to 900 °C. FT-IR spectra reveals the presence of water molecules, O-H bond, C-O and carbonyl (C=O) bonds. The thermograms show that these crystals are thermally unstable and decompose through many stages. © 2011 Trade Science Inc. - INDIA

### KEYWORDS

Gel growth;  
Lead tartrate;  
FT-IR spectra;  
TGA.

### INTRODUCTION

Tartrate crystals and various compounds of tartaric acid find numerous applications in science and technology. These crystals are of considerable interest, particularly for basic study of some of their interesting physical properties<sup>[1-4]</sup>. Some crystals of this family are temperature sensitive and can be used to sense and measure temperature, some of them are ferroelectric, some of others are piezoelectric and quite a few of them have been used for controlling laser emission. As tartrates are sparingly soluble in water and decompose before melting, the gel method is found to be more promising than the high temperature crystal growth methods. The growth of single crystals of calcium tartrate was reported<sup>[5]</sup>. Thermal behavior of gel grown tartrates of yttrium and samarium was also reported<sup>[6]</sup>.

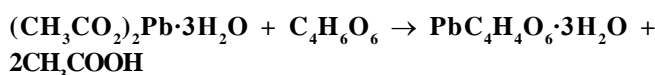
Lead tartrate is orthorhombic with lattice parameters  $a = 7.99$ ,  $b = 8.84$  and  $c = 8.35$ . In the present

study, we have grown lead tartrate crystals using lead acetate as the supernatant solution. The grown crystals have been characterized by FTIR and thermal studies.

### EXPERIMENTAL

The test tube diffusion method<sup>[7]</sup> was employed to grow lead tartrate crystals in the gel medium. 1 MAR grade sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) powder is used for preparation of the gel medium. To remove the impurities, 250 gm sodium metasilicate was dissolved in 1 liter of distilled water. On stirring it, dense milky solution of sodium metasilicate was formed. It was left for a couple of days, so that heavy insoluble impurities accumulate at the bottom of the beaker. The solution was filtered twice with Whatman (cat no 1001 125) filter paper of 12.5 cm diameter. Then the solution was centrifuged on MSE high speed centrifuge unit for about half an hour at 10000 revolutions per minute. As a re-

sult, all suspended impurities were got rid off and transparent golden colored solution of sodium metasilicate was obtained. This solution was titrated with 1 MAR grade tartaric acid to prepare the gel in such a way that the pH of mixture was maintained 5.0-5.2. The specific gravity of the gel was chosen 1.04. This gelling mixture was allowed to set in glass tubes of length 200 mm and diameter 25 mm. After a gel aging for 24 h, the supernatant solution was added over the set gel. The supernatant solution was 1 M lead acetate. The expected chemical reaction was



Small crystals appeared down the gel-solution interface in about 2 days and large crystals appeared down the gel column within a week. The crystals were harvested after a month. In the present investigation, the growth of lead tartrate crystals by gel method and its characterization by using FT-IR spectroscopic and thermal studies are reported.

## RESULT AND DISCUSSION

The grown crystals are characterized by various techniques, which are discussed here by.

### FT-IR study

Figure 1 shows the FT-IR spectrum of grown crystals. The spectrum was recorded in the wave number range 4000-400  $\text{cm}^{-1}$ .

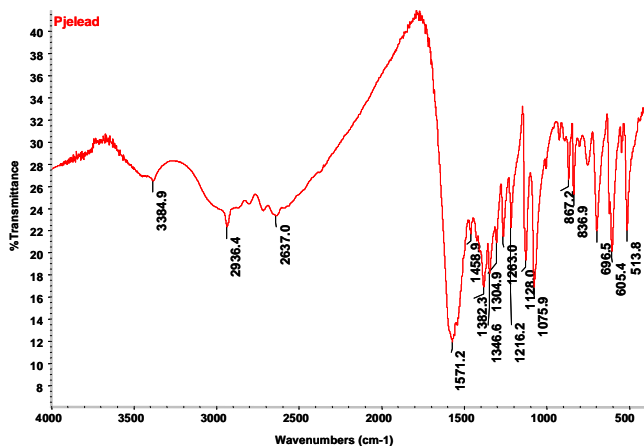


Figure 1

The OH stretching vibrations of alcoholic OH and OH (water) occur at 3384  $\text{cm}^{-1}$  and 2637  $\text{cm}^{-1}$ , respectively. The C-H stretching vibrations occur at 2936

$\text{cm}^{-1}$ , while C=O stretching vibrations of carbonyl group occur at 1711  $\text{cm}^{-1}$ . The peak at 1382  $\text{cm}^{-1}$  is assigned to bending mode of alkane. The C-O stretching vibrations of (-COO-) occur at 1128-1075  $\text{cm}^{-1}$ . The vibrations occurring between 900-513  $\text{cm}^{-1}$  may be due to formation of metal-oxygen bonding vibrations.

### TGA study

Figure 2 shows the thermo-gram of grown crystals.

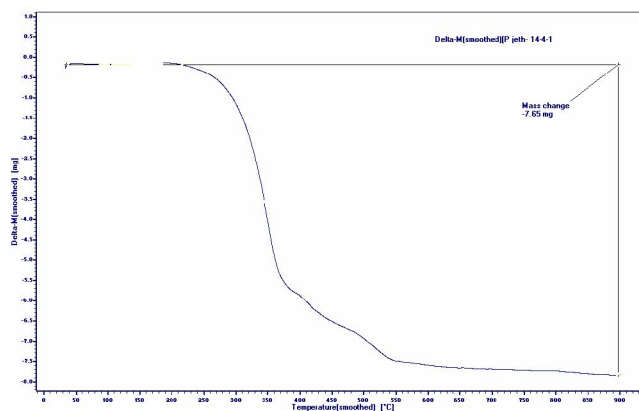


Figure 2

The graph shows that the sample is stable from room temperature to up to approximately 220  $^{\circ}\text{C}$ . Then a rapid decomposition starts up to 550  $^{\circ}\text{C}$ . After this temperature a very small loss of weight is noticed.

### Kinetic and thermodynamic study of dehydration

The use of thermo-gravimetric data to evaluate the kinetic parameters of solid state reactions involving weight loss has been investigated by many workers<sup>[8-11]</sup>. If the pyrolysis occurs through a many stepped mechanism, usually, the shape of the curve can be determined by the kinetic parameters of pyrolysis, such as order of reaction, frequency factor and energy of activation. Kotru et al<sup>[12]</sup>, reported the kinetics of solid state decomposition of neodymium tartrate. They also calculated various kinetic parameters and suggested that the decomposition process took place according to cylindrical kinetic model. Recently, the kinetics of dehydration of gypsum<sup>[13]</sup>, lithium sulphate monohydrate single crystals<sup>[14]</sup> as well as the kinetic and thermodynamic parameters of decomposition of chromate in different gas atmosphere<sup>[15]</sup> and L-arginine doped KDP crystals<sup>[16]</sup> has been evaluated.

Usually, the kinetic parameters can be evaluated from the TG curves by applying several equations<sup>[9-11,17]</sup>,

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which are proposed by different authors on the basis of different assumptions to the kinetics of the reaction and the Arrhenius law. These equations are (1) The Coats and Redfern Relation (2) The Horowitz and Metzger Relation and (3) The Freeman and Corroll Relation. However, in the present investigation, the Coats and Redfern relation is discussed in detail because it facilitates not only to evaluate the activation energy and order of reaction but also the frequency factor.

### Coats and redfern (C-R) relation

Coats and Redfern<sup>[8]</sup> derived the following equation to determine the values of activation energy and order of reaction.

$$\log_{10} \left( \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right) = \log_{10} \left( \frac{AR}{\alpha E} \right) \left( 1 - \frac{2RT}{E} \right) - \frac{E}{2.3RT}$$

In this equation, E is the activation energy of the reaction, A is the frequency factor,  $\alpha$  is the fraction of decomposed material at time t, n is the order of reaction and T is the absolute temperature. The plots of  $y =$

$-\log_{10} \left( \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right)$  versus  $x = 1/T$  were straight line

for different values of n, however, the best linear fit plot gives the correct value of n. The value of activation energy is obtained from the slope of the best linear fit plot. The activation energy can be calculated from the slope of the plot. The frequency factor can be calculated for a particular temperature using the above relation. The Coats and Redfern relation was solved for various values of n. The statistical regression analysis was applied to different values of n and the highest values of correlation co-efficient indicated the best linear fit curve. This was found for  $n = 3/4$ . Figure 3 shows the plot drawn for Coats and Redfern relation.

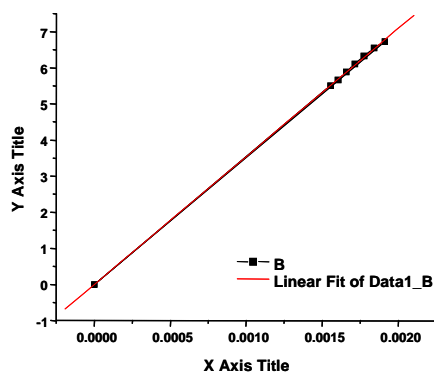


Figure 3

TABLE 1 summarizes the values of activation energy, frequency factor and the order of reaction.

TABLE 1 : The values of different kinetic parameters obtained from the coats and redfern relation

Order of Reaction (n)	Activation Energy (E) kJ Mol <sup>-1</sup>	Frequency Factor (A)
0.75	67.845	$3.631 \times 10^{17}$

### Thermodynamic parameters

Different thermodynamic parameters such as the standard entropy of activation ( $\Delta^\#S^\circ$ ), standard enthalpy ( $\Delta^\#H^\circ$ ), standard Gibbs free energy ( $\Delta^\#G^\circ$ ) and standard change in internal energy ( $\Delta^\#U^\circ$ ) were calculated by applying well known formula, as described in detail by Laidler<sup>[18]</sup>. The thermodynamic parameters for dehydration of gel grown iron (II) tartrate have been estimated by Joseph et al<sup>[19]</sup>. Dabhi and joshi<sup>[20,21]</sup> have reported the thermodynamic parameters for dehydration of various gel grown metal-tartrate crystals and Parikh et al<sup>[16]</sup>.

TABLE 2 summarizes the values of different thermodynamic parameters.

TABLE 2 : The values of different thermodynamic parameters

Standard Entropy ( $\Delta^\#S^\circ$ ) kJ Mol <sup>-1</sup>	Standard Enthalpy ( $\Delta^\#H^\circ$ ) kJ Mol <sup>-1</sup>	Standard Gibbs free energy ( $\Delta^\#G^\circ$ ) kJ Mol <sup>-1</sup>	Standard change in internal energy ( $\Delta^\#U^\circ$ ) kJ Mol <sup>-1</sup>
0.08569	58.4	10.2	63.16

From the TABLE 2 it can be noticed that standard entropy of activation  $\Delta^\#S^\circ$  and standard enthalpy of activation  $\Delta^\#H^\circ$  are positive and suggest that the process is spontaneous at high temperatures. Positive value of standard Gibbs free energy  $\Delta^\#G^\circ$  suggests that the samples are thermodynamically unstable.

## CONCLUSION

Lead tartrate crystals were grown in silica gel with lead acetate as supernatant solution. The grown crystals were characterized by FT-IR and TGA study. The FT-IR spectrum of grown crystals revealed the presence of O-H, C-O and C=O bonds. The presence of water molecules was detected. The thermo-gram of grown crystals revealed that the sample is stable from room temperature to up to approximately 220 °C. Then a rapid decomposition starts up to 550 °C. After this

temperature a very small loss of weight is noticed. Kinetic and thermodynamic parameters of the grown crystals revealed that the process is spontaneous at high temperature and the samples are thermally unstable.

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