



Investigations of various growth parameters, FTIR and thermal studies of gel grown pure and mixed levo-tartrates of calcium and strontium

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Abstract - Pure and mixed levo-tartrates of calcium and strontium have been grown by the single diffusion gel growth technique in silica hydro gel. The effects of growth parameters, such as pH of the gel solution and the type of supernatant solution, on the growth of crystals are reported. The grown crystals are characterized by the FTIR spectroscopy and thermogravimetry. Attempts are made to study the changes in the absorption bands of FTIR spectra in terms of the presence of strontium-oxygen or calcium-oxygen stretching vibrations. Thermograms clearly indicate the changes occurring due to increasing amount of calcium in the crystals. Two different states of calcium and strontium oxide are clearly visible in the thermograms of mixed crystals. The decomposition behaviors of the crystals are studied and further, the kinetic parameters for dehydration are deduced by using the Coats and Redfern relation from the pyrolysis curves of the crystals. The nature of the thermodynamic parameters suggests spontaneous type of process.

Keywords - Gel growth, FTIR, TGA, kinetic parameters, thermodynamic parameters, mixed calcium strontium crystals

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1 Introduction

The gel grown pure and mixed calcium and strontium tartrate crystals have attracted attention of large number of researchers [1-7]. Calcium tartrate crystals exhibit ferroelectrics and nonlinear optical properties [8-12]. Strontium tartrate is also ferroelectric material with device applications [13]. This has also been identified as an important material with some global business applications [14]. Recently, Arora *et al* [15] have reported dielectric behavior of strontium tartrate tetrahydrate single crystal. Moreover, the TGA (Thermogravimetric analysis) and DTA (Differential thermal analysis) studies reveal that the water molecules are locked up with different strength with the crystal lattice [13]. Also, strontium tartrate compounds are preferred in tracer compounds in ammunition units [16]. Suryanarayana *et al* [12] have reported optical and structural characteristics of strontium-doped calcium tartrate as well as Suryanarayana and Dharmaprakash [17] have reported the defect characterization of the same crystals. Later on, Joshi and Joshi [18] have reported the growth,

thermal and FTIR studies of calcium tartrate trihydrate crystals grown by the gel assistance in which the gel was impregnated by orthophosphoric acid, while calcium chloride and tartaric acid solutions were poured as supernatant solution.

Though large numbers of worker have widely studied calcium tartrate and strontium tartrate crystals in pure and mixed form, the present authors have attempted to use optically sensitive levo tartaric acid for the growth of pure and mixed levo tartrate crystals. The attempt is also made to study different parameters affecting the growth of pure and mixed calcium and strontium levo-tartrate crystals and the effects of their compositions on FTIR absorption bands, the dehydration and decomposition mechanisms and the kinetic as well as thermodynamic parameters.

2. Experimental technique

2.1 Crystal growth :

The crystallization apparatus employed were glass test

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tubes of 25 mm diameter and 140 mm in length. The gel was prepared by using sodium metasilicate solution, of specific gravity ranging from 1.02 to 1.08, which was acidified with levo tartaric acid so that pH could be set at 3.0, 3.2, 3.35, 3.6 and 3.8. However, the best crystals were grown at specific gravity of 1.06 and pH 3.8.

After setting the gel, the following solutions were poured without disturbing the gel in respective test tubes.

- (i) 10 ml 1M SrCl_2 + 00 ml 1M CaCl_2 (Solution-A)
- (ii) 08 ml 1M SrCl_2 + 02 ml 1M CaCl_2 (Solution-B)
- (iii) 06 ml 1M SrCl_2 + 04 ml 1M CaCl_2 (Solution-C)
- (iv) 04 ml 1M SrCl_2 + 06 ml 1M CaCl_2 (Solution-D)
- (v) 02 ml 1M SrCl_2 + 08 ml 1M CaCl_2 (Solution-E)
- (vi) 00 ml 1M SrCl_2 + 10 ml 1M CaCl_2 (Solution-F)

2.2 FTIR spectroscopic study

The FTIR spectroscopic study was carried out on powdered samples in KBr medium, using SPECORD IR 75, Carl Zeiss (Germany) spectrometer, in the range from 400 cm^{-1} to 4000 cm^{-1} with resolution of 1 to 5 cm^{-1} .

2.3 Thermogravimetry

The thermogravimetric analysis (TGA) was carried out from room temperature to 850°C, at a heating rate of 15°C/min, in an atmosphere of air. Powdered samples were used for the study. The analysis was performed on Perkin-Elmer TG2 setup having temperature range from room temp to 950°C and the heating rates available from ± 2 to $\pm 100^\circ\text{C}/\text{min}$.

3. Results and discussion

Hensch [1] has discussed the gel growth mechanisms in detail. The average crystal growth rate is greatest near the top of the diffusion column where the concentration gradients are high and smallest near the bottom, where the gradients are small, which may produce smaller but well defined crystals. It is also observed that the crystals which grow in the lower region of the system, are larger than those grow at gel-liquid interface [1]. This has been observed in the case of pure strontium tartrate and calcium tartrate crystals.

3.1 Growth observations

In case of pure strontium chloride containing supernatant solution, good quality and prismatic crystals are grown. Figure 1 shows photograph of growing strontium levo tartrate crystals in gel. In the case of mixed supernatant solutions, one finds the dendritic type of crystals at the



Figure 1 Photograph of growing strontium levo tartrate crystals in gel

gel-liquid interface, which are extended deep into the gel. However, some well-defined prismatic crystals were also found at the bottom of the test tubes. Figure 2 describes the growth of mixed crystals grown from 2 ml SrCl_2 and 8 ml CaCl_2 solutions. Once again, in the case of 10 ml CaCl_2 solution, large numbers of transparent, colorless, prismatic, crystals were grown in the gel medium.

3.2 The growth parameter study

The relationship between the pH of gel and the number of crystals grown in the gel has been studied for different supernatant solutions of strontium chloride and calcium chloride, which is shown in Figure 3. One can see that there is no peak observed in the plot of the number of crystals versus pH for 10 ml SrCl_2 solution and 2 ml SrCl_2 + 8 ml CaCl_2 solution at 3.2 pH, while all other solutions indicate a peak value at pH 3.2. It is also interesting to note that no crystal growth was observed at pH of 3.0 and 3.2 in case of 10 ml SrCl_2 solution.

Moreover, the relationship between the number of crystals grown in the gel and the amount of strontium chloride and calcium chloride solutions in the supernatant solution, at different pH values, has been studied, which are shown in plots of Figure 4. In the case of 3.0 pH, one

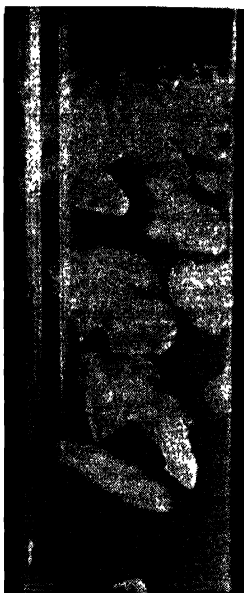


Figure 2. Photograph of mixed crystals grown from 2 ml SrCl₂ and 8 ml CaCl₂ supernatant solutions

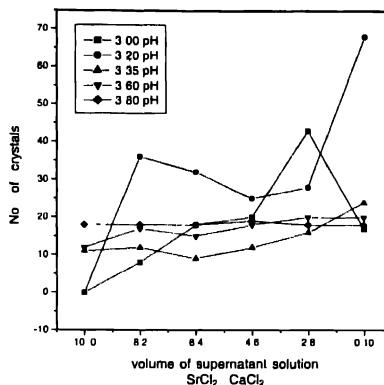


Figure 4. Plots of the number of crystals grown in the gel versus the amount of strontium chloride and calcium chloride solutions in the supernatant solution, at different pH values

remains constant. This also indicates why the best qualities of the crystals were grown at pH of 3.8 amongst all other pH values. This indicates that the pore size distribution is such that it facilitates the uniform diffusion of ions so that the number of crystals does not vary even with changing the composition of the supernatant solutions.

3.3. FTIR study :

Many authors have studied IR spectra of different tartrate compounds such as calcium tartrate [18], manganese tartrate [19], zinc tartrate [20] and iron tartrate [21]. These authors confirmed the presence of water of hydration, C=O bonds, C-O, O-H and metal-oxygen bonds by FTIR spectra Rajagopal *et al* [22] reported IR and polarized Raman spectra of SrC₄H₄O₆·3H₂O. As the divalent tartrate ion possesses lower symmetry in the crystal, splittings were observed for different vibrational modes. Separate band in the bending region of water suggested the existence of three crystallographically different water molecules in the crystal.

However, Sahaya Shajan and Mahadevan [23] reported FTIR spectra of strontium added calcium tartrate crystals, but could not identify the effect of strontium or calcium on absorption bands in FTIR spectra

The FTIR spectra of pure and mixed strontium and calcium levo tartrate crystals are displayed in Figures 5(a-e). One can find out that water of crystallization is associated with all crystals resulting into absorption taking place in 3600–3100 cm⁻¹ region. The carbonyl group C=O stretchings are occurring slightly below 1600 cm⁻¹; however, those are normally expected to occur in the

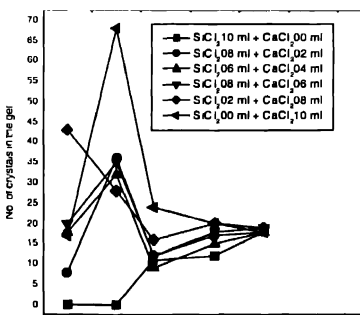


Figure 3. Plots of the pH of gel versus the number of crystals grown in the gel

maximum number of crystals is observed, whereas, in the other pH values, except for 3.8 pH, maxima and minima in number of grown crystals are observed. Interestingly, in the case of 3.8 pH value almost a straight line is observed. This means that in the case of 3.8 pH value, number of crystals grown in the gel containing different amounts of SrCl₂ and CaCl₂ in its supernatant solutions

range from 1625 cm^{-1} to 1675 cm^{-1} . The O-H deformation out of plane, in general, occurs below 995 cm^{-1} , but in the present study, those are found slightly above 1000 cm^{-1} . These variations may be due to the spatial geometry of molecules and/or the chemical mixing of different vibrational modes. It is of special interest to note that from observing Figures 5 (a-c), that an absorption at $963\text{--}964\text{ cm}^{-1}$, which develops in crystals of

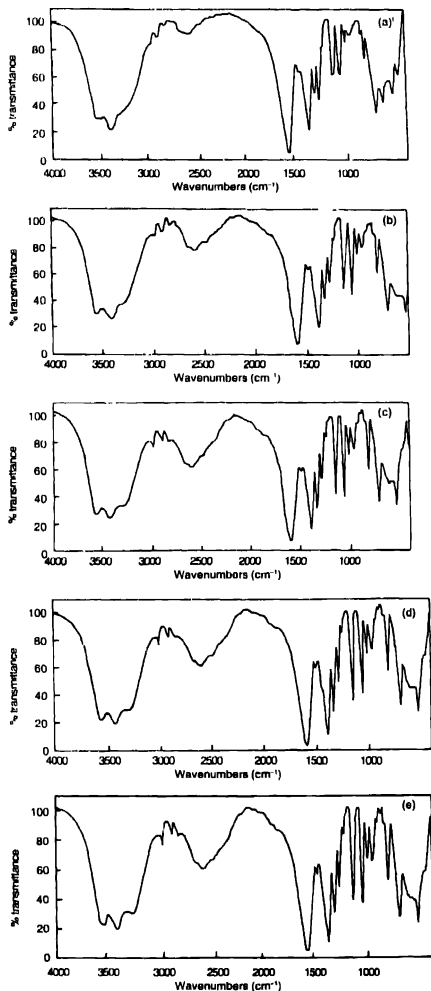


Figure 5(a-e). FTIR spectra of mixed strontium-calcium levo tartrate and pure calcium levo tartrate

$\text{Sr}_{0.4}\text{Ca}_{0.6}\text{C}_4\text{H}_4\text{O}_6\cdot 3\text{H}_2\text{O}$ and other crystals having higher contents of calcium, it becomes much stronger as the calcium content increases in the crystals. An absorption appears at 479.73 cm^{-1} in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{C}_4\text{H}_4\text{O}_6\cdot 3\text{H}_2\text{O}$ crystals, disappears in other crystals and an absorption occurs at 634.86 cm^{-1} in $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{C}_4\text{H}_4\text{O}_6\cdot 3\text{H}_2\text{O}$ becomes weak in other crystals of higher calcium content. It can be considered that absorption occurring at $663\text{--}664\text{ cm}^{-1}$ may be due to Ca-O stretching vibration as well as absorptions occurring at $410\text{--}479.73\text{ cm}^{-1}$ may be due to Sr-O stretching vibrations, which are missing on reducing strontium content in the crystals. Similarly, one can account for missing 634.86 cm^{-1} absorption as well as weak absorption at $605\text{--}606\text{ cm}^{-1}$, in high calcium containing crystals, with Sr-O stretching vibrations.

3.4 Thermogravimetric analysis

Many authors have reported TGA of various tartrate crystals. Joshi and Joshi [18] as well as Selvarajan *et al* [24] studied thermal properties of calcium tartrate crystals. By using thermogravimetry, Rethinam *et al* [25] reported the thermal study of nickel doped strontium tartrate tetrahydrate single crystal. Also, Kotru *et al* [26,27] reported the thermal studies of pure and mixed rare earth tartrate crystals.

Usually, water evolution is completed in two stage processes. The first reaction is the deceleratory diffusion controlled release of water from superficial zones of reactant crystals. The second reaction is a nucleation and growth process yielding the crystalline anhydrous salt. The gravimetric measurement for the first reaction is identified by three distinct dehydration processes. The first step is the rapid release of loosely bounded superficial water. The subsequent two deceleratory stages are characterized by diffusive loss of H_2O molecules from a crystal zone that is initially ordered in nature; but later on, becomes disordered due to the increase in water-site vacancies. Water loss during the first reaction of this crystalline hydrate gives a comprehensive layer of extensively hydrated material across all surfaces. Thereafter, in or under this water depleted layer, salt is recrystallized and dehydration continues a nucleation and growth reaction. Galwey *et al* [28,29] have given detailed analysis of dehydration mechanism of lithium potassium tartrate monohydrate. They have used thermogravimetry for dehydration and electron microscopy for surface observations. They conducted the study for single crystals as well as powdered samples.

The thermal study of gel-grown pure and mixed level tartrates crystals of strontium and calcium, has been

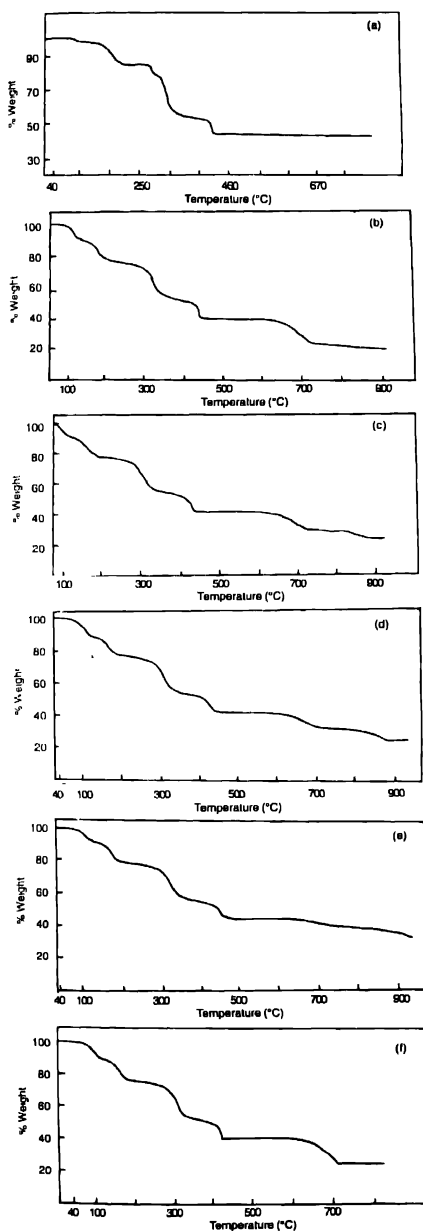


Figure 6(a-f). Thermograms of pure and mixed strontium and calcium tartrate crystals

carried out by using TGA. Figures 6 (a-f) shows the thermograms of pure and mixed calcium and strontium levo tartrate crystals. The $\text{SrC}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$ crystals decompose into anhydrous crystals at 175°C , further decompose into strontium carbonate at 278°C and finally, become SrO at 420°C and remain stable up to the end of analysis. This is exhibited in the thermogram of Figure 6(a). Two water molecules are associated with the crystals.

For $\text{Sr}_{0.8}\text{Ca}_{0.2}\text{C}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$ mixed crystals, the thermogram is displayed in Figure 6(b). The mixed crystal decomposes into anhydrous $\text{Sr}_{0.8}\text{Ca}_{0.2}\text{C}_4\text{H}_4\text{O}_6$ crystal through one stable state at 110°C . This further decomposes into $\text{Sr}_{0.8}\text{Ca}_{0.2}\text{CO}_3$ in a sharp transition at 454°C , finally, $\text{Sr}_{0.8}\text{Ca}_{0.2}\text{CO}_3$ turns into oxide of strontium and calcium in a smooth transition. Therefore, no sharp transition is observed above 720°C . Three water molecules are attached with the crystal as water of hydration as well as water of coordination.

In the case of $\text{Sr}_{0.6}\text{Ca}_{0.4}\text{C}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$ crystals, more-or-less, the same behavior is observed as it has been observed in the case of $\text{Sr}_{0.8}\text{Ca}_{0.2}\text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ crystals, which is shown in Figure 6(c). It is worth to note that a sharp transition at 433°C results into carbonate of strontium and calcium, which, further decomposes individually into their oxides by two clear steps at 698°C and 870°C temperatures. Also, three water molecules are found to be associated with these crystals.

The thermogram for $\text{Sr}_{0.4}\text{Ca}_{0.6}\text{C}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$ is exhibited in Figure 6(d). The decomposition behavior is similar to those of the previous two mixed crystals. Figure 6(e) also exhibits the thermogram for $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{C}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$ crystals. Once again, it has been observed that the carbonate $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{CO}_3$ decomposes into different oxides at two different temperatures, but this behavior is not as clear as in the other two mixed crystals. Three water molecules are associated with the crystals.

The thermogram of Figure 6(f) is for $\text{CaC}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$, which indicates that the dehydration behavior is, altogether, similar to the other crystals. The anhydrous crystal decomposes into oxalate at 336°C and then into carbonate at 427°C and finally into oxide at 718°C .

From the thermograms of Figures 6 (a-f), one can notice that the dehydration process is achieved in two steps. In the case of pure $\text{SrC}_4\text{H}_4\text{O}_6$ crystals, the transition from carbonate to oxide occurs at fairly low temperatures (at 420°C); on the other hand, for the mixed and pure calcium tartrate crystals this takes place at higher temperatures (above 698°C). In the mixed crystals, the two different decomposition steps were observed for carbonate

to oxide decomposition processes, which may be regarded due to the separate decomposition processes occurring for strontium and calcium at different temperatures.

It is interesting to note from Figures 6 (a-f) that the percentage weight loss for the ultimate product decreases as the substitution of calcium increases, for examples, the last product is 44.00% weight in pure strontium tartrate dihydrate crystals and 21.00% weight in pure calcium tartrate trihydrate crystals. This is due to the difference in the atomic weight of strontium and calcium. The atomic mass of strontium is 87.5 and calcium is 40.08. It has been also verified by using EDAX that within the experimental error the compositions of the mixed crystals correspond to the TGA results.

However, the present results of thermogram clearly indicate the changes occurring in the decomposition of mixed crystals upon increasing the content of calcium and also the effect of metallic ion mass.

3.5 Kinetic study of dehydration :

The shape of the thermogram is determined by kinetic parameters of pyrolysis, such as order of reaction, frequency factor and energy of activation. Several authors have reported kinetic studies of dehydration from thermograms for different crystals, for example, iron tartrate crystals [30], calcium tartrate crystals [18], cadmium tartrate crystals [31].

The present authors have attempted to derive several kinetic parameters from the thermograms of gel grown pure and mixed strontium and calcium levo tartrate crystals. The Coats and Redfern relation [32] has been applied to the first stage of dehydration in the crystals, which is represented by the following equation.

$$\log_{10} \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \log_{10} \left(\frac{AR}{aE} \right) - \frac{E}{2.303RT} \quad (1)$$

where α = fraction of the original substances decomposed at time t , n = order of the reaction, A = frequency factor, E = activation energy of the reaction, R = gas constant, a = heating rate in $\text{deg}\cdot\text{min}^{-1}$ ($15 \text{ deg}\cdot\text{C}/\text{min}$)

To determine the value of activation energy and order of reaction, the plot of $\log_{10} \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right]$ versus $1/T$ is drawn for different values of n and the best linear plot gives the correct value of n . This relation is valid for all values except for $n = 1$. Figure 7 is the plot of C-R relation for $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ crystal. The order of reaction for all the plots is found to be $n = 1/2$. The values of activation energy are calculated from the slope of the Coats and Redfern plots, using eq. (1)

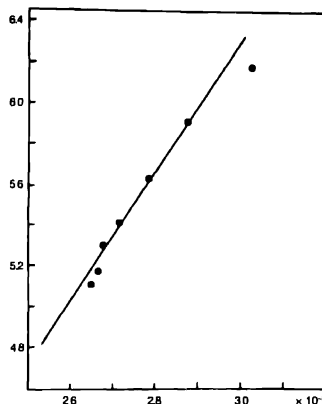


Figure 7. The plot of Coats and Redfern relation for $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ for $n = 1/2$

Table 1 compiles the values of different kinetic parameters such as, the activation energy, frequency factor and order of reaction. These values, initially increase with the content of calcium in the crystals and thereafter, from $\text{Sr}_{0.6}\text{Ca}_{0.4}\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ crystals they decrease on increasing the content of calcium. This further indicates that the dehydration mechanism is having same order of reaction but different values of activation energy and frequency factor. The dehydration curve varies from one crystal to another depending upon their compositions.

This study provides valuable information in terms of kinetic parameters of pyrolysis for dehydration process occurring in the crystals, which varies from one sample to another depending upon the compositions.

3.6. Thermodynamic parameters .

Many workers have reported the estimation of thermodynamic parameters of dehydration process from the pyrolysis curves of crystals such as, iron tartrate [30], calcium tartrate [18], cadmium tartrate [31] and zinc tartrate [33].

The standard entropy of activation, Δ^*S^\ddagger , could be calculated by using the following formula

$$\Delta^*S^\ddagger = 2.303 \times R \times \log_{10} [Ah/K_B] \quad (2)$$

where K_B = Boltzmann constant, h = Plank's constant, T_m = temperature, R = gas constant, A = frequency factor

The frequency factor can be estimated from equation (1). The standard enthalpy of activation, Δ^*H^\ddagger , was calculated by using following relation :

$$\Delta^{\circ}H^{\circ} = E - 2RT. \quad (3)$$

Also, the standard Gibbs energy of activation, $\Delta^{\circ}G^{\circ}$, is possible to estimate from the following equation.

$$\Delta^{\circ}G^{\circ} = \Delta^{\circ}H^{\circ} - T\Delta^{\circ}S^{\circ}. \quad (4)$$

The standard change in internal energy in passing from the initial to the activated state, $\Delta^{\circ}U^{\circ}$, can be represented as

$$E = RT + \Delta^{\circ}U^{\circ}. \quad (5)$$

Various thermodynamic parameters have been calculated using the eqs (1 to 5), which are discussed by various authors in detail [34,35]. The values of thermodynamic parameters are given in Table 2. The positive value of $\Delta^{\circ}S^{\circ}$ also suggests that the dehydration proceeds spontaneously from hydrated to dehydrated state. The negative value $\Delta^{\circ}G^{\circ}$ indicates that the dehydration proceeds spontaneously. From Table 2, it can be seen that as the calcium content increases, various thermodynamic parameters first increase and then decrease. This indicates that the water of hydration is involved in the lattice in the different manner, which supports the earlier results [13], and also the effect of compositions of crystals plays important role.

The FTIR spectra of pure and mixed crystals were analyzed by assigning absorption due to oxygen-calcium or strontium-oxygen vibration. The presence of water of hydration, C=O, C-O, O-H and metal-oxygen bonds were confirmed bonds by FTIR spectra. The thermogravimetry results clearly indicated the formation of mixed crystals and decomposition into their oxides occurred in two different distinct oxidation stages. The effect of difference in mass numbers of strontium and calcium was clearly observed from the thermograms. Thermodynamic and kinetic parameters for dehydration were calculated and the effect of composition of crystals was seen on the parameters. It could be conjectured that water is locked with the crystalline lattice in different manners in each crystal.

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Table 1 Kinetic parameters of dehydration of pure and mixed strontium and calcium levo tartrate crystals

Levo tartrate crystal	Order of reaction	Activation energy kJ mol ⁻¹	Frequency factor	Entropy JK ⁻¹ mol ⁻¹
SrC ₂ H ₂ O ₆ ·2H ₂ O	1/2	73.64	1.06 × 10 ¹⁹	115.56
Sr _{0.8} C _{0.8} C ₂ H ₂ O ₆ ·3H ₂ O	1/2	60.63	4.39 × 10 ¹⁹	129.29
Sr _{0.6} C _{0.6} C ₂ H ₂ O ₆ ·3H ₂ O	1/2	122.54	1.37 × 10 ²⁰	311.16
Sr _{0.4} C _{0.4} C ₂ H ₂ O ₆ ·3H ₂ O	1/2	114.88	1.54 × 10 ²⁰	293.06
Sr _{0.2} C _{0.2} C ₂ H ₂ O ₆ ·3H ₂ O	1/2	78.50	3.94 × 10 ¹⁹	185.86
CaC ₂ H ₂ O ₆ ·3H ₂ O	1/2	71.80	3.98 × 10 ¹⁹	166.67

Table 2. Thermodynamic parameters of pure and mixed strontium and calcium levo tartrate crystals

Levo tartrate crystal composition	$\Delta^{\circ}H^{\circ}$ KJ mol ⁻¹	$\Delta^{\circ}U^{\circ}$ KJ mol ⁻¹	$\Delta^{\circ}G^{\circ}$ KJ mol ⁻¹	$\Delta^{\circ}S^{\circ}$ JK ⁻¹ mol ⁻¹
SrC ₂ H ₂ O ₆ ·3H ₂ O	67.94	70.793	-39569.14	115.66
Sr _{0.8} C _{0.8} C ₂ H ₂ O ₆ ·3H ₂ O	54.9362	57.78	-44291.534	129.29
Sr _{0.6} C _{0.6} C ₂ H ₂ O ₆ ·3H ₂ O	116.84	119.69	-106611.04	311.16
Sr _{0.4} C _{0.4} C ₂ H ₂ O ₆ ·3H ₂ O	109.242	112.033	-100410.34	293.06
Sr _{0.2} C _{0.2} C ₂ H ₂ O ₆ ·3H ₂ O	72.8062	75.71	-63677.174	185.86
CaC ₂ H ₂ O ₆ ·3H ₂ O	66.1062	69.95	-57101.70	166.67

4. Conclusion

Pure strontium and calcium levo tartrate crystals were grown in a single crystalline form with well defined morphologies. The mixed strontium and calcium levo tartrate crystals were mainly of dendritic nature, only a few single crystals were observed at the bottom of the test tubes.

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