

Thermal behaviour of strontium tartrate single crystals grown in gel

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MS received 18 May 1999; revised 13 November 2000

Abstract. Thermal behaviour of strontium tartrate crystals grown with the aid of sodium metasilicate gel is investigated using thermogravimetry (TG) and differential thermal analysis (DTA). Effect of magnetic field and dopant (Pb)²⁺ on the crystal stability is also studied using thermal analysis. This study reveals that water molecules are locked up in the lattice with different strengths in the grown crystals.

Keywords. Strontium tartrate; dopant; effect of magnetic field; thermal behaviour.

1. Introduction

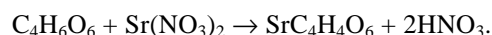
Strontium tartrate tetrahydrate (SrT) crystallizes in orthorhombic system in the space group $P_{2_12_12_1}$ containing four molecules per unit cell with unit cell dimensions $a = 0.948$, $b = 1.096$ and $c = 0.946$ nm (Bohandy and Murphy 1968). Most of the tartrate compounds are insoluble in water and decompose before melting. Hence, single crystals of such type of compounds cannot be grown by either slow evaporation or melt techniques. In this situation gel method is the appropriate one for their growth. The growth of single crystals of calcium tartrate was reported (Henisch *et al* 1965). Thermal behaviour of gel grown tartrates of yttrium and samarium was also reported recently (Jain *et al* 1997). In this paper we report the growth of strontium tartrate without any field, in the presence of magnetic field and in the presence of lead as dopant with the aid of sodium metasilicate gel.

2. Experimental

The chemicals used in this study were of BDH, AR grade. A test-tube diffusion method (Henisch 1973) was employed to grow strontium tartrate single crystals in a gel medium.

The growth experiments were carried out in test tubes using sodium metasilicate solution of density 1.03 and 1.035 g/cc. 1–2 M of tartaric acid solution was added to these solutions to form gels of pH values 5–10. Over the set gel an aqueous solution of strontium nitrate of varying strength (0.5–2 M) was gently poured.

The chemical reaction taking place in the gel medium was as follows



The crystallization apparatus used in the present study were test tubes of 20×200 mm, 15×150 mm and U tubes of 17×170 mm. The test tube was filled with gel of density 1.035 g/cc to a level of 100 mm. The pH of the gel was adjusted to 5 using 1 M of tartaric acid solution. The gel was kept undisturbed for a day. After setting the gel, the top solution of strontium nitrate (1 M) was gently poured over the gel surface. Strontium nitrate diffused through gel and a white thin film appeared just below the gel surface. Tiny crystallites were visible within a day. The size and number of isolated crystals increased in about a week. Orthorhombic crystals were obtained in all the experiments, their number depending on various factors like molarity, density, pH values and quantity of solution. The maximum size of the crystals grown was about $6.51 \times 4.80 \times 3.60$ mm³ (as shown in figure 1). As the crystals do not allow light nor reflect the same, the material need not be studied under transmitted or reflected petrological microscope. Hence the crystallinity is observed under a stereo binocular microscope (Carl Zeiss) and confirmed as single crystal.

In order to study the effect of dopants on the morphology and growth of strontium tartrate (SrT), 10% (W/V) solution of lead nitrate was also mixed with the top solution. Within two hours a white precipitate was observed at the gel solution interface of the lead doped samples at pH 8. After two days the length of the precipitate increased to a depth of 1.8 cm due to the diffusion of the top solution. After about a week the length of the precipitate increased to 4.3 cm and remained constant. There were few crystals

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in the lower part of the precipitate. The precipitate was transformed into dendrites which eventually yielded small crystals of lead doped strontium tartrate tetrahydrate (abbreviated as SrPbT). The diffraction patterns of grown crystals were analysed and the calculated '*d*' spacing, *hkl* and peak intensities were compared with those of strontium tartrate (for orthorhombic) reported in JCPDS files. The variation in the *d* values for the doped sample (SrPbT) can be attributed to the accommodation of the impurity ions in the crystal. Relative intensities of the reflections from the same *hkl* planes are found to vary in doped and undoped crystals. This is indicative of a change in conformation of the molecule due to doping, however small it be. The exact extent of change in conformation can be assessed only through single crystal XRD study which was not attempted in this work. Moreover to know whether Pb^{2+} occupy Sr sites or not, single crystal XRD study is necessary. Single crystals of strontium tartrate tetrahydrate were also grown by applying a magnetic field of 3×10^{-2} Tesla (abbreviated as SrTMF). The magnetic field is applied between the sides of the test tube. The magnetic field is formed by two magnets kept at a distance varying from 1.5–2.5 cm with 0.05–0.03 Tesla. The test tube is placed between the opposite poles of magnet.

When we apply a field perpendicular to the tube, path lengths of the diffusing ions increase which slow down the vertical displacement of the ions due to the increased resistance of the extra path which the ions have to travel. In effect this is equivalent to reducing the diffusion coefficient of the medium. The observed delay in the time of formation of the crystal in magnetic field is attributed to the decrease in the diffusivity of reaction ions. A later study of Higavshitani *et al* (1993) showed decreasing nucleation rate and increasing growth rate at values of (*B*) magnetic field above 3 Tesla. The uniformity of grown layers improves with increasing magnitude of the applied magnetic field (Qin *et al* 1995).

The thermal decomposition behaviour of the grown crystals was studied by thermogravimetry (TG) and diffe-

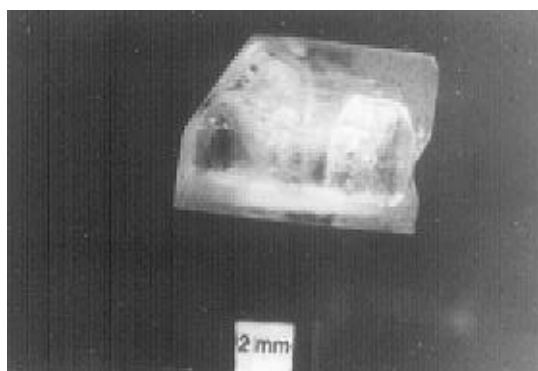


Figure 1. Optical micrograph of strontium tartrate tetrahydrate single crystals grown with 1.5 M solution in gel of density 1.035 g/cc at pH 6.

rential thermal analysis (DTA). Shimadzu TGA 50 H and DTA-50 H thermal analyser (Japan) was used for obtaining the TG and DTA curves. Experiments were carried out in static nitrogen atmosphere. The initial weight taken for recording the TG curves was 7.85 mg and heating rate was maintained at $10^\circ\text{C min}^{-1}$. The DTA curve was also recorded taking 14.4 mg of SrT, 16 mg of SrTMF and 16.4 mg of SrPbT of the sample. The heating rate was maintained at $15^\circ\text{C min}^{-1}$. The reference substance for DTA was $\alpha\text{-Al}_2\text{O}_3$.

3. Results and discussion

Perfect crystals of larger dimensions were obtained for pH values between 6 and 8 and the size of these crystals varied from 4–7 mm and were transparent with orthorhombic system. In the case of dopant added crystal growth experiment, the nucleation was delayed. As the concentration of the dopants was increased the number of days required for nucleation was also increased. Thus it was found from a series of experiments conducted that addition of Pb^{2+} increased the nucleation with a reduction in crystal size. With dopant (lead) a large number of crystals obtained were of lower transparency and non faceted. The field promoted growth of the crystals and increased the growth rate. This may be due to the accelerated diffusion (Desai and Shukla 1990) which might have been produced by the magnetic field, as happens when electric field was applied.

TG and DTA curves of $\text{SrC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ grown under different experimental conditions are shown in figures 2 and 3. It was observed that the onset of first decomposition begins slightly at different temperatures for each of

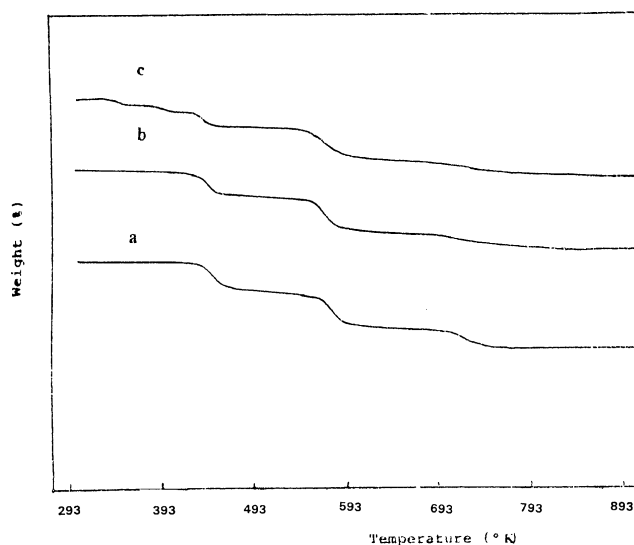


Figure 2. a. TG curve of strontium tartrate tetrahydrate (SrT), b. TG curve of strontium tartrate tetrahydrate crystals grown in presence of magnetic field (SrTMF) and c. TG curve of lead doped strontium tartrate tetrahydrate (SrPbT).

them indicating different degrees of thermal stability as discussed below.

3.1 Strontium tartrate ($\text{Sr}(\text{C}_4\text{H}_4\text{O}_6)4\text{H}_2\text{O}$)

In the thermogravimetric analysis, weight of the sample taken was 7.85 mg and the heating rate was maintained at $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Figure 2a shows the TG curve recorded for $\text{Sr}(\text{C}_4\text{H}_4\text{O}_6)4\text{H}_2\text{O}$. Here the decomposition process starts at 392.5°K . The first stage of decomposition continues up to 447.4°K , leading to the formation of strontium tartrate monohydrate which is stable up to 506.3°K . The second stage of decomposition starts at 506.3°K resulting in the formation of strontium oxalate monohydrate ($\text{SrC}_2\text{O}_4\cdot\text{H}_2\text{O}$) which remains stable up to 639.4°K . In the third stage between 639.4°K and 766.9°K strontium oxalate monohydrate eliminates water molecule and decomposes into strontium carbonate (SrCO_3). The energy required to dislodge water molecules depends upon how strongly they are locked up in the lattice. As water molecules are ejected from the lattice in two different stages, it appears that the water molecules are locked up in two different ways and thus required different amount of energy for their ejection from the lattice. This is in conformity with the IR spectral studies.

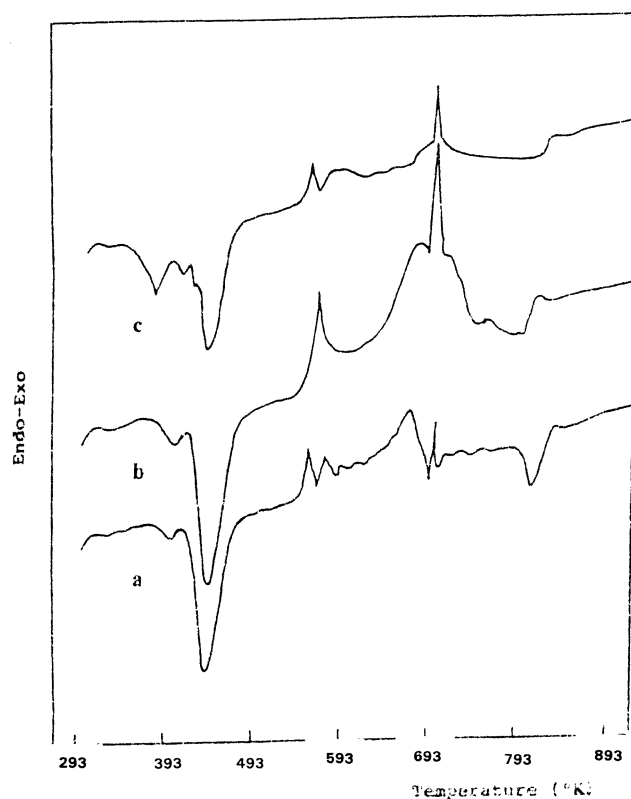


Figure 3. a. DTA curve of strontium tartrate tetrahydrate (SrT), b. DTA curve of strontium tartrate tetrahydrate crystals grown in presence of magnetic field (SrTMF) and c. DTA curve of lead doped strontium tartrate tetrahydrate (SrPbT).

Table 1 summarizes the decomposition steps and the expected and observed mass losses at different steps for $\text{Sr}(\text{C}_4\text{H}_4\text{O}_6)4\text{H}_2\text{O}$. Figure 3a illustrates DTA curve recorded for strontium tartrate tetrahydrate. The DTA curve was recorded taking 14.4 mg of SrT. The heating rate was maintained at $15^\circ\text{C min}^{-1}$ in nitrogen atmosphere. The DTA shows parallel peaks corresponding to weight losses in TG and the data are presented in table 1. The DTA curve shows an endothermic peak at 397.7°K corresponding to the elimination of the three water molecules. Thermal decomposition reactions are usually endothermic. However, some of the DTA peaks are exothermic. This is due to the concomitant oxidation reaction taking place along with decomposition. The results are quite similar to those for other rare earth tartrates reported (Kotru *et al* 1986a, b). Table 2 gives the summarized results of decomposition process of SrT, SrTMF and SrPbT.

3.2 $\text{Sr}(\text{C}_4\text{H}_4\text{O}_6)4\text{H}_2\text{O}$ grown in the presence of magnetic field SrT (MF)

Figure 2b shows the TG curve recorded for $\text{Sr}(\text{C}_4\text{H}_4\text{O}_6)4\text{H}_2\text{O}$ grown in the presence of magnetic field. Here the decomposition process starts at 389.1°K . The first stage of decomposition continues up to 448.2°K leading to the formation of strontium tartrate monohydrate which is stable up to 501.6°K . The second stage of decomposition starts at 501.6°K and is completed at 570.7°K resulting in the formation of strontium oxalate monohydrate which remains stable up to 661.7°K . In the third stage between 661.7°K and 842.6°K strontium oxalate monohydrate decomposes to strontium carbonate. Table 1 provides the summary of the decomposition steps and the expected and observed mass losses. Figure 3b illustrates DTA curve recorded for strontium tartrate tetrahydrate grown in the presence of magnetic field. The DTA curve shows parallel peaks corresponding to the weight losses in TG and the data are presented in table 1. The DTA curve shows an endothermic peak at 401.5°K corresponding to the elimination of three water molecules. Table 2 gives the summary of the results for SrT (MF).

3.3 Lead doped strontium tartrate (SrPbT)

Figure 2c shows the TG curve recorded for lead doped strontium tartrate tetrahydrate (SrPbT). TG curve reveals that decomposition starts at 360.9°K . The elimination of water molecules at a lower temperature for lead doped crystal shows that the water molecules are weakly locked up in the doped crystals. The first stage of decomposition continues up to 498.7°K , leading to the formation of strontium tartrate monohydrate. The second stage of decomposition starts at 498.7°K and is completed at 578°K resulting in the formation of strontium oxalate monohydrate which remains stable up to 636.1°K . The third

Table 1. TG results of decomposition process of SrT, SrT (MF) and SrPbT.

Stage	Samples	Temperature range (°K)	Mass loss (%)		Reactions
			Observed	Calculated	
I	SrT	392.5–506.3	16.85	17.55	SrC ₄ H ₄ O ₆ ·4H ₂ O–SrC ₄ H ₄ O ₆ ·H ₂ O
	SrTMF	381.1–501.6	16.82		
	SrPbT	360.9–498.7	18.19		
II	SrT	506.3–639.4	20.04	23.65	SrC ₄ H ₄ O ₆ ·H ₂ O–SrC ₂ O ₄ ·H ₂ O
	SrTMF	501.6–661.7	20.63		
	SrPbT	498.7–636.1	19.68		
III	SrT	639.4–766.9	10.75	9.32	SrC ₂ O ₄ ·H ₂ O–SrCO ₃
	SrTMF	661.7–842.6	10.02		
	SrPbT	636.1–857.2	11.09		

SrT, SrC₄H₄O₆·4H₂O pure crystal; SrTMF, SrC₄H₄O₆·4H₂O grown in presence of magnetic field; and SrPbT, SrC₄H₄O₆·4H₂O grown with dopant (lead).

Table 2. DTA data of SrT, SrT (MF) and SrPbT.

SrT Temperature range (°K)	SrT (MF) Temperature range (°K)	SrPbT Temperature range (°K)
397.7 endo	401.5 endo	380 endo
441.5 endo	441.2 endo	411.8 endo
586.6 exo	563.9 exo	439.3 endo
567.0 endo		559.2 exo
669.8 exo	687.3 endo	567.4 endo
692.3 endo		704.1 exo
700.1 exo	700.8 exo	
805.7 endo	789.2 endo	
	810.6 exo	831.9 exo

endo, endothermic reaction; exo, exothermic reaction; SrT, SrC₄H₄O₆·4H₂O pure crystal; SrTMF, SrC₄H₄O₆·4H₂O grown in presence of magnetic field; and SrPbT, SrC₄H₄O₆·4H₂O grown with dopant (lead).

stage starts at 636.1°K and is completed at 857.2°K corresponding to the conversion of strontium oxalate monohydrate into strontium carbonate. The thermo analytical data are given in table 2 for lead doped strontium tartrate (SrPbT). The DTA curve obtained is shown in figure 3c. DTA shows parallel peaks corresponding to the weight losses in TG and the data are presented in table 1. The DTA curve shows an endothermic peak at 380°K corresponding to the elimination of three water molecules.

4. Conclusions

Thermal study confirms that the crystals grown contains four water molecules in the unit cell. TG results were quite similar for SrT, SrTMF and SrPbT, as expected. This study also reveals that material is unstable even at

lower energies. The DTA curves show parallel peaks corresponding to weight losses in TG curves. The initial stage of decomposition corresponding to the elimination of three water molecules takes place at 392.5, 389.1, 360.9°K for the SrT, SrTMF and SrPbT. As water molecules are ejected from the lattice in two different stages, it appears that the water molecules are locked up in the lattice in two different ways. The thermal decomposition reactions are usually endothermic. However, some of the DTA peaks are exothermic. This is due to the concomitant oxidation reactions taking place along with decomposition reactions. The final solid products of thermal decompositions of those investigated are carbonates. Thermal study reveals that water molecules are locked up in the lattice with different strengths in the grown crystals. The bonding is strongest in SrT crystals. The locking of water molecules is weaker in SrPbT than SrT (MF).

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