Study of Strontium – Manganese Mixed Tartrate Crystals and Thermogravimetric Analysis

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Abstract:

There are a variety of crystals grown having numerous applications in science and technology. It is always of interest to study their physical and chemical properties. There are many other mixed crystals grown by different workers by the gel growth. Here we discuss about the growth and characterization of mixed Strontium-Manganese Levo-Tartrate crystals. In the supernatant solutions, the different amounts of $SrCl_2$ *and* $MnCl_2$ *solutions were added in such a way that the total volume of the supernatant solutions remained constant. Observations were noted two days after pouring supernatant solutions on set gel.*

Thermogravimetric analysis (TGA) is a very useful technique to assess the thermal stability of various substances; many workers have demonstrated its usefulness. Many authors have reported TGA for various tartrate crystals.

Keywords: *Crystal Growth, Sol-gel preparation, TGA*

1. Introduction

Compound of Tartaric acid find numerous application in science and technology. The growth of single crystals of Calcium and Strontium Tartrates and their solid solutions of various compositions has drawn considerable interest of various workers. Apart from Strontium-Calcium mixed crystals, There are many other mixed crystals grown by different workers by the gel growth; i.e. the mixed Rare Earth Tartrate crystals , The mixed crystals of $Cd_xBa_{1-x}CrO_4$ crystals, The mixed crystals of $LaxCux_3C_2O_4$, nH_2O , the mixed crystals of Iron-Nickel Tartrates as well as Iron-Cobalt Tartrates and also the mixed crystals of strontium – calcium Levo – tartrates and dextro-Tartrate. This chapter deals with the growth and characterization of mixed Strontium-Manganese Levo-Tartrate crystals.

2. Experimental Technique

2.1 Gel Preparation

In the present case AR grade sodium metasilicate powder is used for preparation of the gel medium. To remove the impurities 250g sodium metasilicate was dissolved in one liter of water taken in a beaker. On stirring it thoroughly, 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. This was decanted into another beaker and 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. Practically all suspended impurities were got rid off, and as a result transparent golden colored solution of sodium metasilicate was obtained. This could be preserved as a stock solution for quite a long period.

2.2 Crystal Growth

The crystallization apparatus employed for the present investigation consist of glass test tubes of 25mm diameter and 140mm length. The AR grade chemicals were used to grow the crystals. One of the reagents, 1 M levo tartaric acid, was mixed with sodium metasilicate solution to prepare the gel in such a way that the pH of mixture was maintained 4.5. The specific gravity of the gel was chosen 1.04. After setting the gel, the supernatant solutions containing various amounts of $SrCl_2$ and $MnCl_2$ having concentrations of 1M were gently poured without disturbing the gel surfaces, in respective test tubes. The growth of crystals was completed within the period of one month.

2.3 Crystal Growth Observation

In the supernatant solutions, the different amounts of $SrCl_2$ and $MnCl_2$ solutions were added in such a way that the total volume of the supernatant solutions remained constant.

The Following observations were noted two days after pouring supernatant solutions on set gel,
(1)For10 ml $SrCl_2$ supernatant solution:
There were many crystals found in gel and some very small crystals were found on the gel liquid interface. As going away from gel-liquid interface, into gel crystals shape changes from platelet to irregular shape. These crystals were transparent with yellowish tinge.
(2) For 8 ml $SrCl_2$ + 2 ml $MnCl_2$ supernatant solution: -
Crystals were small yellowish colored in the gel. No small crystals were grown on gel-liquid interface.
(3) For 6 ml $SrCl_2$ + 4 ml $MnCl_2$ supernatant solution: -
Crystals were not grown on the gel-liquid interface, but small yellowish colored crystals were grown in the gel.
(4) For 4 ml $SrCl_2$ + 6 ml $MnCl_2$ supernatant solution: -
There were large crystals found with yellowish color at the gel-liquid interface. Some large irregular shape crystals in the gel were also observed.
(5) For 2 ml $SrCl_2$ + 8 ml $MnCl_2$ supernatant solution: -
There were only two crystals found at the gel-liquid interface having large size. While one star shaped and completely transparent crystal was observed in gel.
(6) For 10 ml $MnCl_2$ supernatant solution: -

Only spongy precipitates were observed. No crystal found in the gel but many small crystals were found on the gel-liquid interface.
The chemical reaction which forms the crystals is as follows:

$$\begin{array}{lcl} SrCl_2\, mH_2O + MnCl_2.nH_2O & \longrightarrow & Sr\text{-}Mn\ C_4H_4O_6 + (m-n)\ H_2O + HCl \\ +H_2C_4H_4O_6 & & \qquad + 2nH_2O \end{array}$$

2.4 Characterization techniques

Thermogravimetric analysis (TGA) is a very useful technique to assess the thermal stability of various substances; many workers have demonstrated its usefulness. The sample weight drops slowly as pyrolysis begins, then drops precipitously over a narrow range of temperature and finally turn back to zero slope as the reactants are used up.

Thermogravimetric analysis for the present samples was carried out from room temperature to 950°C at a heating rate of 15 °C/ min in an atmosphere of air using α-Al_2O_3 as standard reference. Powdered samples were used for this study. The TGA was carried out at Sophisticated

Instrumentation Center for Applied Research and Testing (SICART), Vallabh Vidyanagar (Gujarat).

3. Results and Discussion

Many workers have reported the growth of Mn levo tartrate crystals as well as strontium tartrate. In present study mixed Mn-Sr levo tartrate crystals were grown and the growth observation suggested that as the concentration of $MnCl_2$ increased in the supernatant solution, the coloration changed gradually from light yellow to pinkish brown. It was also noted that from the supernatant solution (4) onwards the white spongy precipitates were observed. Various growth morphologies were observed such as prismatic, star shaped, rectangular shape, etc. Figure (A, B) shows the growing crystals in gel for $Sr_{0.6}Mn_{0.4}C_4H_4O_6$ $3H_2O$ supernatant solution.

Figure (1) to Figure (4) show the thermograms of mixed strontium and manganese tartrate crystals. From Figure (1) one can see that hydrated mixed tartrate crystals ($Sr_{0.8}Mn_{0.2}C_4H_4O_6$ nH_2O) decompose into anhydrous form at 175ºC, thereafter decompose into oxalate form at 343ºC, carbonate at 661ºC, and finally into oxide at 939ºC From fig (2) for $Sr_{0.6}Mn_{0.4}C_4H_4O_6$ nH_2O one can notice that this thermogram is similar to that of Figure (1). Fig. (3) is a thermogram of $Sr_{0.4}Mn_{0.6}C_4H_4O_6$ nH_2O, which shows that hydrated mixed tartrate crystals decompose into anhydrous form at 256ºC, thereafter decomposes into oxalate form at 349ºC, which is followed by a rapid decomposition into oxide at 760ºC. Here one observes that the oxalate stage has become minor, and the absence of carbonate stage. For $Sr_{0.2}Mn_{0.8}C_4H_4O_6$ nH2O, from fig (4) one can observe that crystals become anhydrous at 228ºC, which is followed by a rapid decomposition into oxide at 446ºC. In this case the carbonate and oxalate both stage are absent and direct decomposition into oxide occurs.

Figure A

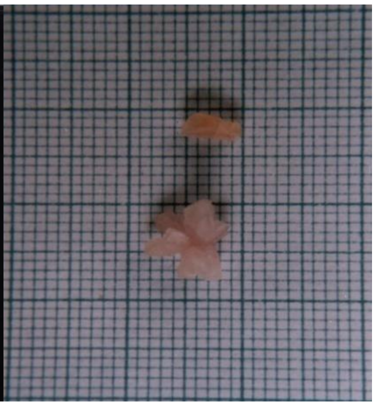

Figure B

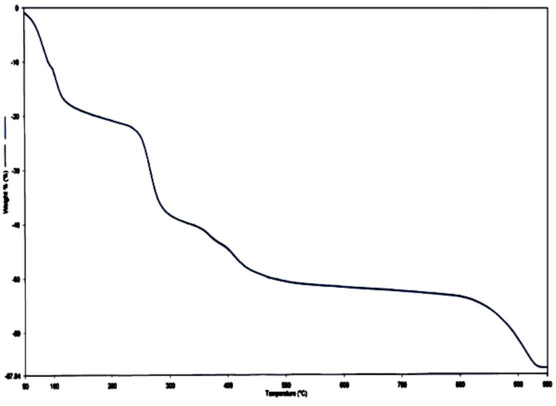

Figure (1)

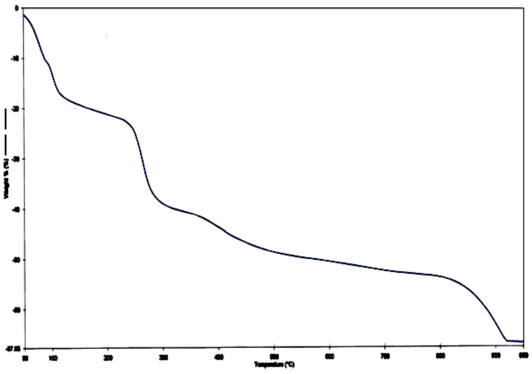

Figure (2)

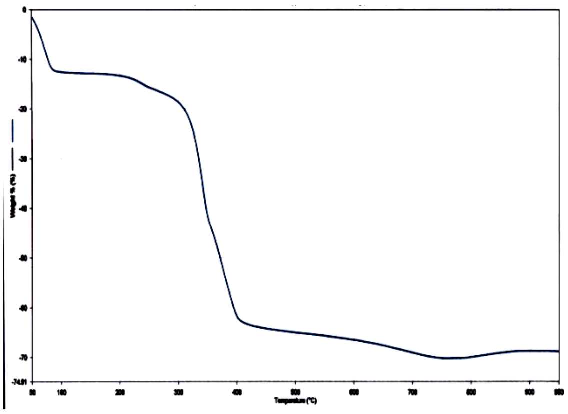

Figure (3)

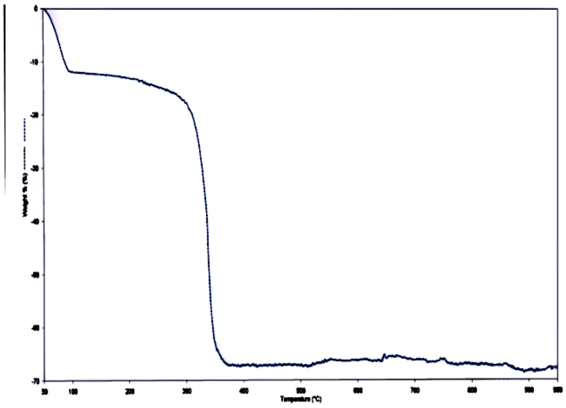

Figure (4)

Table 1

Temp (^{0}C)	Decomposition of Crystals	Theoretical Weight In %	Observed Weight In %
Room Temp.	$Sr_{0.8}Mn_{0.2}C_4H_4O_6$ $3H_2O$	100	100
175	$Sr_{0.8}Mn_{0.2}C_4H_4O_6$	80.9	80
343	$Sr_{0.8}Mn_{0.2}C_2O_4$	59.7	60
661	$Sr_{0.8}Mn_{0.2}CO_3$	49.8	50
939	$Sr_{0.8}Mn_{0.2}O$	34.3	33.66

Table 2

Temp (^{0}C)	Decomposition of Crystals	Theoretical Weight In %	Observed Weight In %
Room Temp.	$Sr_{0.6}Mn_{0.4}C_4H_4O_6$ $3H_2O$	100	100
160	$Sr_{0.6}Mn_{0.4}C_4H_4O_6$	80.48	80.0
332	$Sr_{0.6}Mn_{0.4}C_2O_4$	58.76	59.5
635	$Sr_{0.6}Mn_{0.4}CO_3$	48.64	48.0
936	$Sr_{0.6}Mn_{0.4}O$	32.72	33.5

Table 3

Temp (°C)	Decomposition of Crystals	Theoretical Weight In %	Observed Weight In %
Room Temp.	$Sr_{0.4}Mn_{0.6}C_4H_4O_6$ $2H_2O$	100	100
256	$Sr_{0.4}Mn_{0.6}C_4H_4O_6$	85.05	84.0
349	$Sr_{0.4}Mn_{0.6}C_2O_4$	60.4	59.5
760	$Sr_{0.4}Mn_{0.6}O$	33.05	30

Table 4

Temp (°C)	Decomposition of Crystals	Theoretical Weight In %	Observed Weight In %
Room Temp.	$Sr_{0.2}Mn_{0.8}C_4H_4O_6$ $2H_2O$	100	100
228	$Sr_{0.2}Mn_{0.8}C_4H_4O_6$	84.9	86
446	$Sr_{0.2}Mn_{0.8}O$	32.05	33

4. Conclusions

As the content of manganese increases in the crystals, the carbonate and oxalate stages gradually disappear and direct decomposition into oxide occurs. Table (1) to 4) indicates the decomposition process of Sample with theoretically calculated and experimentally obtained TG results

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