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Effect of Magnetic Field On The Structural And Thermal Properties Of Manganese Tartrate Dihydrate Crystal

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ABSTRACT:

The availability of suitable crystals is the boon for various technological developments . The growth of crystals from gel is well suited for the crystal growth of compounds, which are sparingly soluble and decompose fairly at low temperatures .In this work, manganese tartrate dihydrate crystals are grown by single diffusion gel method in the presence and in the absence of the magnetic field. The influence of magnetic field on crystal stability is studied from Thermo gravimetry analysis (TGA) and differential scanning calorimetry (DSC) analysis. The cell parameters are obtained from single crystal X-ray diffraction (XRD) analysis. The variation of 'd' spacing of the majority peak due to the application of magnetic field during the growth period is confirmed from powder XRD analysis.

KEYWORDS:manganese tartrate, magnetic field, gel method, XRD,TGA

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1. INTRODUCTION

In metal organic coordination complexes, the organic ligand plays a role for NLO effect. They contain metal and organic ligands linked by coordination bond. The structure of organometallic compound can be varied by changing the metal, coordination number , ligands etc. A non aromatic acid and an inorganic salt form the metal organic compound. To our knowledge there are only few literatures reporting the properties of manganese tartrate dihydrate crystals. There are reports on mixed iron manganese tartrate[1], iron manganese-cobalt tartrate crystal[2], ternary iron-manganese nickel tartrate crystal[3,4] and the thermal behavior of manganese tartrate[5]. The effect of concentration of reactants, pH of gel, ageing of gel and doping on the growth rate of tartrate crystals were also reported[6,7]. The influence of magnetic field on the thermal and optical properties of tartrate crystals are reported[8,9,10]. In this article the structural and thermal properties of manganese tartrate dihydrate crystals grown in the absence of magnetic field (MnTr) and in the presence of magnetic field (MnTrmf) are compared. Manganese tartrate crystals exhibit high efficiency of laser radiation conversion to the second harmonic [11].

2. EXPERIMENTAL WORK

Single diffusion gel method was employed to grow the crystals. The crystallization apparatus, borosilicate glass test tube of length 25 cm and diameter 2.5 cm was placed vertically on thermocole stand. Sodium metasilicate solution of 1.04 g/cm^3 was prepared. 1M tartaric acid of 9.5 ml quantity was added to 10ml of stock solution. Gel set was found after 24 hours. The set gel was left undisturbed for 15 hours. 1M manganese chloride solution of 10ml was added over the set gel along the walls of the test tube with the help of pipette in order to avoid any gel breakage. The manganese ions diffused through the narrow pores of the gel to react with tartrate ions which were present in the gel as inner reactant. The following chemical reaction took place

$$C_4H_6O_6 + MnCl_2 \rightarrow MnC_4H_4O_6 + 2HCl$$
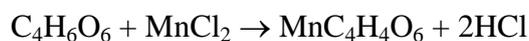
More number of crystals of small size were formed near the interface. Though the number of crystals formed was less, when we go deeper from the interface, the size of the crystals was found to be large. For growing the crystals under the influence of magnetic field, the set gel was subjected to the magnetic field of 182 Gauss, 5 hours before adding the outer reactant.

3. RESULTS AND DISCUSSION

3.1. Thermal analysis

3.1.1. Thermogravimetry Analysis

TGA was carried out in the nitrogen atmosphere of 20 ml/min using Perkin-Elmer make at the rate of 30 deg/min between the temperature range 35° C – 400° C. The TGA thermogram of MnTr and MnTrmf are shown in the Figure 1 and Figure 2 respectively. There is not much variation in the mass loss observed from TGA of MnTr and MnTrmf. The decomposition is observed in two stages. The first stage of decomposition is dehydration i.e. manganese tartrate dihydrate into anhydrous manganese tartrate. The second stage corresponds to the decomposition of anhydrous tartrate into manganese oxide. The observed mass loss is found to be the same as that of calculated values. The decomposition details are given in Table 1. The decomposition of manganese tartrate crystal grown under different environment yields Mn_2O_3 as the final product [12,13]. But in our case MnO is the final product.
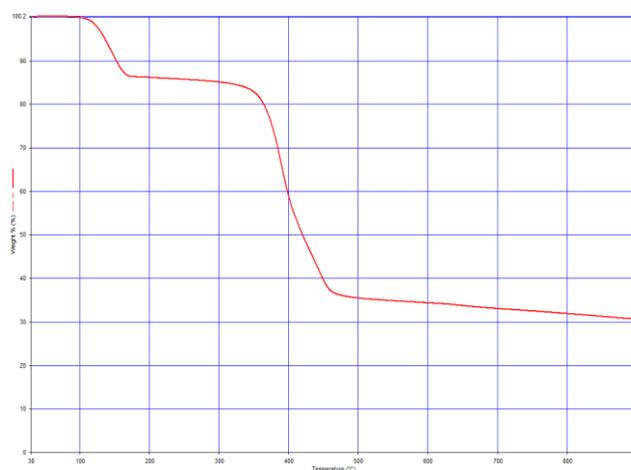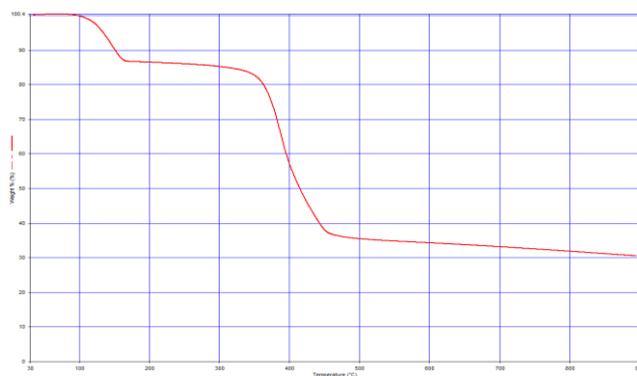

Figure 1 TGA of MnTr

Figure 2 TGA of MnTrmf

Table – 1 Thermal Decompostion Reactions of MnTr and MnTrmf

stage	Crystal	Temp range	Mass loss %		Reactions
			Observed	Calculated	
I	MnTr MnTrmf	100° C – 160° C	14 13	15.05	$MnC_4H_4O_6.2H_2O \rightarrow MnC_4H_4O_6$
II	MnTr MnTrmf	160° C – 900° C	55 57	57.17	$MnC_4H_4O_6 \rightarrow MnO + \frac{1}{2}O_2$

3.1.2. Differential Thermal Analysis (DTA)

Two endothermic sharp peaks are observed at 150° C and 390° C in DTA curve. The first peak is due to dehydration. The second peak is due to decomposition. There is no appreciable variation in the DTA of MnTr and MnTrmf crystals. The DTA curves are shown in Figure 3 and Figure 4
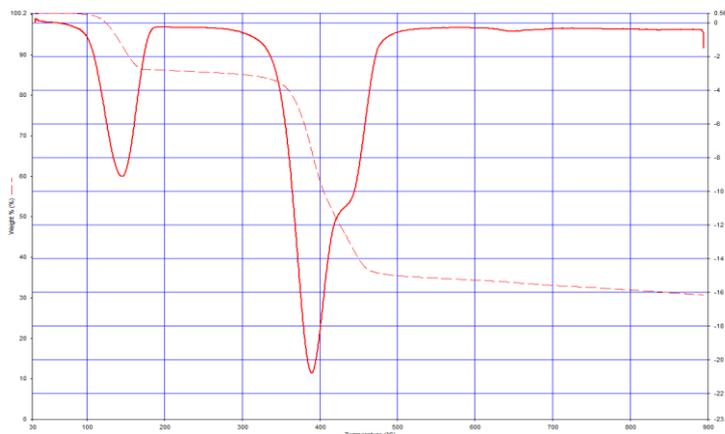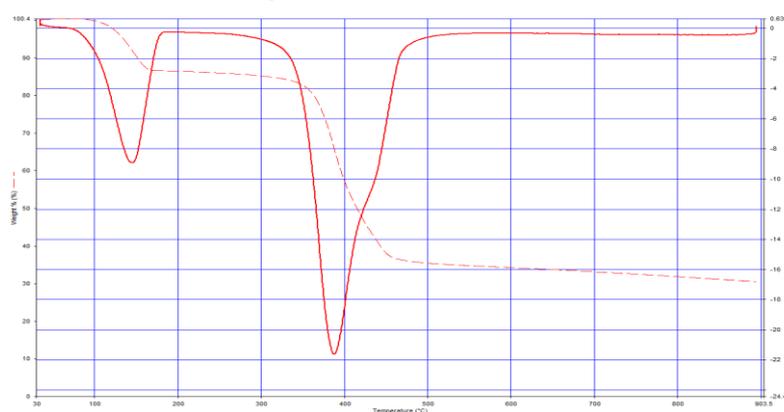

Figure 3 DTA of MnTr


Figure 4 DTA of MnTrmf

3.1.3. Differential Scanning Calorimetry (DSC) Analysis

DSC is carried out in the nitrogen atmosphere of 20 ml/min using Perkin-Elmer make at the rate of 30 deg/min between the temperature range 35° C – 400° C. DSC of MnTr shows two endothermic peaks at around 160° C and 385° C. DSC of MnTrmf shows two endothermic peaks at

around 170° C and 385° C. The peaks correspond to evaporation of water of crystallization and decomposition. The DSC curves are shown in Figure 9and Figure10. The heat flow at the temperature 160° C is 39 m/w for MnTr, but the heat flow at the temperature 170° C is 61 m/w for MnTrmf. For the endothermic peaks at higher temperatures, it is found that the heat flow for MnTr is around 34.5 m/w and MnTrmf is around 53 m/w.
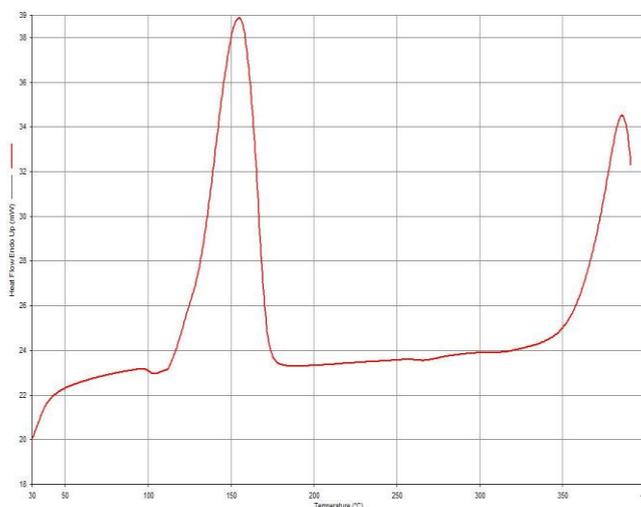
Figure 5 DSC of MnTr
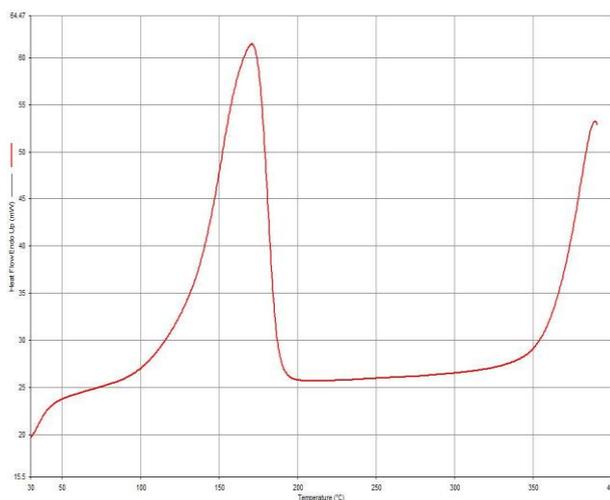
Figure 6 DSC of MnTrmf

3.2. Structural analysis

3.2.1. Single Crystal XRD Analysis

The crystal system and lattice parameters were identified from single crystal XRD analysis using Bruker Kappa APEX II diffract meter with Mo K_{α}(0.7107 Å) radiation as the source. The crystals belong to monoclinic system. There is small

variation in the volume of unit cell. The application of magnetic field increases the volume of unit cell by four units. The lattice parameters are found to be in coincidence with that reported [11]. The comparative crystallographic data is given in Table 2.

Table – 2: Comparative Crystallographic Data of MnTr and MnTrmf

Parameters	MnTr	MnTrmf
a Å	7.60	7.59
b Å	11.17	11.19
c Å	8.99	9.03
α	90°	90°
β	99°	99°44
γ	90°	90°
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
Volume ($Å^3$)	753	757

3.2.2. Powder XRD Analysis

The powder XRD was taken at room temperature using Rigaku Ultima 3 diffractometer. The diffraction pattern has sharp peaks. The XRD data was analyzed using Expo 2014 and chekcell software . The powder XRD pattern of the crystals MnTr and MnTrmf are given in Figure 7 and Figure 8 respectively.
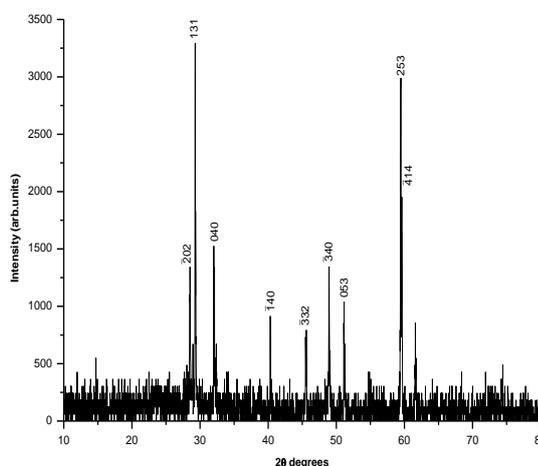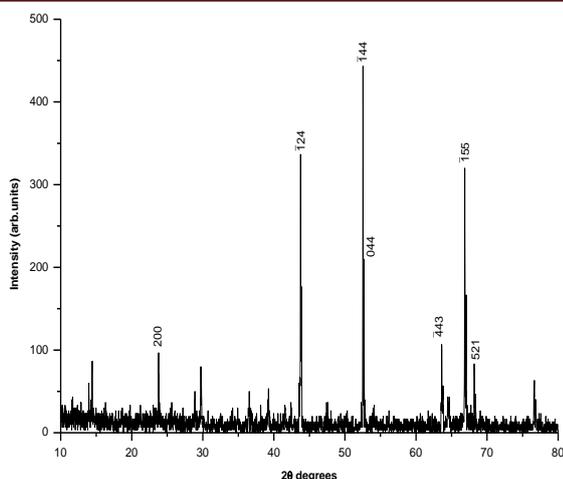

Figure 7 PXRD pattern of MnTr

Figure 8 PXRD pattern of MnTrmf

The d values corresponding to 2θ values are calculated. The indices of peaks observed in the spectra of the samples MnTr and MnTrmf are given in Table 3 and Table 4 respectively. The dominant habit faces of MnTr are (131), (253), $(\bar{4}14)$, (040), $(\bar{3}40)$, $\bar{2}02$ (053), $(\bar{1}04)$, $(\bar{3}32)$ and $\bar{5}11$ in the decreasing order of intensities. The dominant habit faces of MnTrmf are $(\bar{1}44)$, $(\bar{1}24)$, $(\bar{1}55)$, (044), (521), $(\bar{4}43)$ and (200) in the decreasing order of intensities.

There is decrease in the intensity of MnTrmf compared with that of MnTr. This signifies that the application of magnetic field of strength 182 Gauss during the growth of manganese tartrate crystals, resulted in the modification of the lattice. This modification would have resulted from the orientation of a considerable number of unit cells against thermal disordering, in a direction corresponding to the least value of magnetization energy. It is revealed from the Table 3 and Table 4 that the values of majority of the Bragg's diffraction peaks are in the increasing order of 'd' spacing for the crystals MnTr and MnTrmf. This indicates that the exposure to magnetic field during the growth period could result in the increase in the separation of the diffraction planes of manganese tartrate. The increase in the d spacing is in parallel agreement with the reported [14]. The cell parameters calculated from data are in good agreement with single crystal XRD data. There is change in cell dimensions and hence in the cell volume similar to reported literature[15]. Calculation of the cell parameters using software suggests that the crystal belongs to monoclinic system with $P2_1$ space group. The grain size is calculated as 1.96 nm for MnTr and 2.56 nm for MnTrmf.

Table – 3 hkl indexing of MnTr

2θ radians	d Å	Relative intensity	hkl index
61.60	1.5499	16	$\bar{5}$ 11
45.60	1.9878	24.07	$\bar{3}$ 32
40.31	2.2350	27.78	$\bar{1}$ 04
51.13	1.7847	31	053
28.52	3.1271	40	$\bar{2}$ 02
48.94	1.8596	40	$\bar{3}$ 40
32.02	2.7928	46	040
59.60	1.5043	59	$\bar{4}$ 14
59.48	1.5499	90.74	253
29.28	3.0475	100	131

Table – 4 hkl indexing of MnTrmf

2θ radians	d Å	Relative intensity	hkl index
23.78	3.7378	21	200
63.62	1.4613	24	$\bar{4}$ 43
67.06	1.3945	37	521
52.68	1.7360	47	044
66.86	1.3982	72	$\bar{1}$ 55
43.75	2.0670	75	$\bar{1}$ 24
52.54	1.7403	100	$\bar{1}$ 44

4. CONCLUSION

The title compound has been synthesized in the presence and in the absence of magnetic field. Structural and thermal characterizations were carried out. Thermal analysis shows the decomposition of manganese tartrate crystal in two stages. There is no major change observed in the thermogram of the grown crystals due to application of magnetic field during growth period. Due to the change in the favorable plane of growth, the grain size also differs by the application of magnetic field. From

single crystal XRD data, it is found that there is change in cell dimensions and hence the cell volume due to the application of magnetic field. The intensity of the powder XRD pattern of MnTr is higher than that of MnTrmf. From powder XRD pattern it is inferred that exposure to magnetic field during growth period resulted in change in the habit face of manganese tartrate crystal. This signifies that the application of 182 Gauss magnetic field during the growth of manganese tartrate crystals, resulted in a modification of the lattice planes. This modification would have resulted from the orientation of a considerable number of unit cells against thermal disordering, in a direction corresponding to the least value of magnetization energy.

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